



E-MRS 2005 Spring Meeting
May 31 – June 3, 2005

SYMPOSIUM I

**Advanced functional nanomaterials – from
nanoscale objects to nanostructured inorganic
and hybrid materials**

Symposium Organizers :

Markus Antonietti, MPI, Postdam, Germany

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Marc Drillon, IPCMS, Strasbourg, France

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Papers to be published in
Progress in Solid State Chemistry

E-MRS 2005 Spring Meeting

SYMPOSIUM I

Tuesday, May 31, 2005
Mardi 31 mai 2005

Morning
Matin

Session I : Nanoporous materials

Session chairs :

- I-I.01** 9:00 -Invited- DESIGN AND FUNCTIONALITY OF INORGANIC-ORGANIC COMPOSITE MICRO AND MESOPOROUS MOLECULAR SIEVES
Avelino Corma
- I-I.02** 9:45 -Invited- ASSEMBLING MOLECULAR SPECIES INTO 3D FRAMEWORKS: COMPUTATIONAL DESIGN AND STRUCTURE SOLUTION FOR ORGANIC-INORGANIC HYBRID MATERIALS
C. Mellot
- I-I.03** 10:15 HIERARCHICALLY ORGANIZED ARCHITECTURE IN MULTISCALES EMERGING FROM EXQUIEITE ASSOCAITION OF CRYSTALS, ORGANIC POLYMERS, AND DYES
Yuya Oaki and Hiroaki Imai, Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan
A novel type of hierarchically organized architecture emerged from an exquisite association of crystals, organic polymers, and dyes through simple biomimetic crystallization under ambient condition. The resultant potassium sulfate/poly(acrylic acid)/various organic dyes composite included six different tiers from nanoscopic to macroscopic (tiers 1 to 6). Furthermore, designing the superstructure and the properties in each scale was easily achieved by a change of polymer concentration. The macroscopically integrated composite (tier 1) was an assembly of the columnar architectures with various morphologies including tilted column, zigzag, and helical shapes (tier 2). The controlled assembly of the units (tier 3) induced the unique morphologies with an association of polymer. Interestingly, the two-tiered iso-oriented assembly (tiers 4 and 5) made up the units (tier 3) and formed the nanohybrid in the architecture. The incorporated dye molecules (tier 6) generated a nanoscopic tier and organized J-aggregate leading to strong emission in the nanohybrid. The multiple associations of the polymer played an important role for generation of the architecture in each scale. Moreover, we successfully advanced the architecture for a hierarchical host material and developed the approach to the formation of the similar architecture by using other materials. The approach would be widely applicable toward an innovational material by an appropriate conjugation of crystals, polymers, and functional molecules.
- 10:30 **BREAK**
- I-I.04** 11:00 -Invited- HIERARCHICALLY ORGANIZED MATERIALS
Nicola Hüsing
- I-I.05** 11:30 WATER INSERTION IN HYDROPHOBIC POROUS OXIDES
L. Coiffard(a), S. Sidis(b), V. Eroshenko(a), P. Barboux(b), (a)XTEC, Ecole Polytechnique, 91128 Palaiseau, France, (b)Physique Matière Condensée, UMR CNRS 7643, Ecole Polytechnique, 91128 Palaiseau, France
The original mechanical behavior of water- hydrophobic porous body mixtures can find interesting applications for mechanical energy storage and dissipation. We have studied the synthesis of porous hydrophobic systems made from mesoporous silica grafted with long-chain alkyl-chlorosilanes. The mechanism and density of grafting were studied by solid state MAS NMR and nitrogen adsorption isotherms. The penetration of water in these porous systems was studied by high pressure intrusion of water (water porosimetry between 0 and 50 MPa). A flat intrusion plateau was observed at the Laplace pressure and its reversibility was studied as a function of the pore size and the grafting density. The thermodynamic properties of water confined under pressure in these mesopores are strongly dominated by the interfacial interactions at the surface of these porous solids. They have been studied by calorimetry at the macroscopic level and through nuclear magnetic relaxation studies at the molecular level.

- I-I.06** 11:45 EFFECT OF THE ZEOLITE CRYSTAL SIZE ON THE STRUCTURE AND PROPERTIES OF CARBON REPLICAS MADE BY NANOCASTING PROCESS
 Fabrice Gaslain(a), Valentin P. Valtchev(a), Lubomira Tosheva(a), Julien Parmentier(a), Cathie Vix-Guterl(b), Joël Patarin(a), (a)Laboratoire de Matériaux à Porosité Contrôlée (LMPC), UMR CNRS 7016, ENSCMu, Université de Haute Alsace, Mulhouse Cedex, France, (b)Institut de Chimie des Surfaces et Interfaces (ICSI), UPR CNRS 9069, 15 rue Jean Starky, Mulhouse Cedex, France
 In recent years, novel microporous carbons have been synthesised from zeolite templates using the nanocasting technique. The carbons obtained in this way exhibit very high surface areas and show periodic ordering structures as the pores and walls of the zeolite become the walls and pores of the replicas, respectively. With such interesting physical properties, these materials have great potential in various applications, e.g., hydrogen storage or in super capacitors. However, during the process of making them, diffusion problems of the carbon precursors inside the zeolite microporous networks occur and lead to poor filling of the pores, which in turn results in inconsistent carbon replicas with random mesoporosity. Therefore, new approaches that decrease the diffusion limitations and allow faithful replication of the microporous templates are highly desired. Amongst different strategies, the reduction of the zeolite crystal size is the simplest but probably the most effective one. In this contribution, we compare the characteristics of different carbon replicas prepared from a zeolite template (either zeolite Beta or Y) with different crystallite sizes. The carbon replicas were prepared by either the impregnation of furfuryl alcohol followed by carbonisation or by vapour deposition (CVD) of propylene, or by consecutive application of these two methods. After removal of the inorganic template by an acidic treatment, the carbon materials obtained were characterised by XRD, N₂ and CO₂ adsorption and electron microscopy.
- I-I.07** 12:00 = **I/PIII.52**
- I-I.08** 12:15 MOLECULARLY ORDERED INORGANIC SOLIDS TEMPLATED BY SURFACTANTS
B.F. Chmelka, N. Hedin, S.C. Christiansen, Ryan Hayward, Dept. of Chemical Engineering, University of California, Santa Barbara CA 93106, USA; Robert Graf, Max-Planck-Institute für Polymerforschung, Postfach 3148, 55021 Mainz, Germany; Juergen Eckert, Los Alamos National Laboratory, NM 87545, USA; Christel Gervais, Laboratoire de Chimie de la Matière Condensée, Université Pierre et Marie Curie, CNRS Jussieu, 75252 Paris, France
 Surfactant-templated inorganic mesophases and nanocrystals are classes of hierarchically ordered inorganic solids that share several aspects in common. They often possess high extents of both molecular and mesoscopic ordering, though lack long-range three-dimensional (3D) atomic crystallinity. Such features have important influences on their macroscopic adsorption, mechanical, and optical properties and are desirable to control. However, their molecular structures have been notoriously difficult to characterize. Typically, long-range 3D atomic crystallinity is required for detailed analyses using wide-angle X-ray scattering on which structure determinations are frequently based. Multidimensional solid-state NMR, in combination with molecular modeling and X-ray diffraction, provide new means to establish and correlate the structures of hierarchically ordered inorganic solids, even in the absence of 3D crystallinity. Results will be presented on the synthesis and characterization of molecularly ordered layered silicate frameworks and InGaP nanocrystals that are formed in the presence of different surfactant template species.
- 12:30 **LUNCH**

Session II : Nanoobjects and self-assembling
Session chairs :

- I-II.01** 14:00 -Invited- ARCHITECTURE, SELF-ASSEMBLY AND MAGNETISM OF CLUSTERS AND MOLECULE MAGNETS ON SURFACES
J.P. Bucher, Institut de Physique et de Chimie des Matériaux de Strasbourg, UMR 7504, Université Louis Pasteur, 23 rue du Loess, 67034 Strasbourg, France
In the near future, progress in spin electronics and data storage will strongly rely on properties of nanostructures with characteristic sizes of only a few atoms. In this size range, it becomes utterly important that all entities are identical since properties such as magnetic anisotropy of metal clusters are sensitive to within one atom. In the last decade, coordination chemistry made it possible to synthesize small clusters with a well defined number of transition metal ions that behave like identical tiny magnets. Therefore, these so called single molecular magnets can be used as elementary units for data storage in the binary form with large implications for the design of a new generation of computers with a high level of integration. Exploiting recent developments in surface physics we show that atomic or supra-molecular clusters can self-organize on surfaces. A considerable advantage of this approach is that entities are then accessible to a detailed study by local probes such as STM. Before we focus on entities of a few atoms, we will present a revue of magnetic nanostructures, from the largest to the smallest. In lithographically patterned dots, the domain width is of the order of the linear distances of the dot while self-organized clusters of a few hundred atoms on surface reconstruction clearly behave as giant magnetic moments. Finally, single molecular magnets that contain only a few atoms are dominated by quantum effects and exhibit relaxation by quantum tunnelling.
- I-II.02** 14:45 -Invited- ORGANOMETALLIC SYNTHESIS OF IRON NANOPARTICLES : SIZE EFFECTS, SHAPE CONTROL AND ORGANIZATION
C. Amiens
- I-II.03** 15:15 MAGNETIC NANOPARTICLES WITH HYBRID SHAPES
D. Ung, G. Viau and F. Fiévet, ITODYS UMR 7086, Université Paris 7, case 7090, 2 place Jussieu 75251 Paris Cedex 05 France
By reduction of cobalt and nickel acetate salts in liquid polyols we have obtained recently CoNi metal particles with unusual shapes like nails, dumbbells or diabolos [1,2] that recall some hierarchical ZnO nanostructures or snow crystals. All these shapes are hybrid shapes between wire and platelet : the central part of the particles is a wire and the edges are hexagonal platelets. The diameter of the wires is about 10 nm and their length varies from a hundred to a few nanometers depending on the basicity of the solution. The diameter of the ending platelets is in the range 20-30 nm. Heterogeneous nucleation with ruthenium seeds was necessary to favour the formation of the hexagonal close-packed (hcp) phase that is the driving force for the anisotropic growth of the CoNi particles. The particle growth occurs in an heterogeneous medium : the CoII and NiII precursors are involved in an equilibrium between solution and an unreduced intermediate solid phase. The basicity of the medium controls the repartition of the precursors between solid phase and solution. Hybrid shapes are the result of a two-steps mechanism : a preferential growth first along and then perpendicular to the c axis. Magnetic measurements showed a ferromagnetic behaviour at room temperature with a coercivity in the range 1000-2000 Oe depending on the volume fraction of the wires and the platelets moieties within the hybrid particles.
[1] N. Chakroune et al., J. Mater. Chem., 13 (2003) 312. [2] D. Ung et al., Adv. Mater.,(2005) in press.

- I-II.04** 15:30 JANUS-HEAD TYPE GOLD NANOPARTICLES: SELF ORGANISATION AND OPTICAL EVIDENCIAS
A. Moores(a), F. Goettmann(b), P. Le Floch(a), C. Sanchez(b), (a)Laboratoire «Hétéroéléments et Coordination» UMR CNRS 7653 (DCPH), Département de Chimie, Ecole Polytechnique, 91128 Palaiseau cedex, France, (b)Laboratoire de Chimie de la Matière Condensée, UPMC-CNRS, 4 place Jussieu, 75005 Paris, France
 Janus-head type nanoparticles (NPs) are nanometrical-sized objects made out of an organic or and inorganic core which surface presents functionalities or objects spread in a bipolar fashion. Introduction of such a dissymmetry induces interesting physical properties (permanent dipolar moment, optical properties) and self-organization capabilities. Herein we present the first synthesis of mixed ligand shell NPs (ø 8 nm) stabilised by both a phosphinine ligand[1] and mercaptoundecanoic acid. We evidenced the formation of those Janus NPs by two techniques. First, the NPs self organised in a biphasic medium (water/organic). Vesicles or micelles were observed, by TEM, depending on the initial water concentration. These structures proved that the NPs act as giant amphiphiles. Then, the permanent character of this property in a monophasic medium was ascertained by UV-visible spectroscopy. Indeed, the plasmon band recorded for the Janus NPs (490 nm) was dramatically blue shifted compared to pure phosphinine (600 nm) or thiol (530 nm) substituted NPs. In fact, partially substituted NPs featuring no segregation would be expected to have a plasmon band intermediate between both the totally substituted ones. The strong blue shift was rationalised as due to the presence an intense electric field inside the nanoparticle induced by the ligand shell. This field alters the shape of the conduction electron cloud inside the NP and thus increases the spill-out of the latter. This physical phenomenon was thoroughly studied and provides an explanation of the NP-size dependency of the plasmon band.[2]
 [1] A. Moores, F. Goettmann, C. Sanchez, P. Le Floch, Chem. Comm. 2004, 2842.
 [2] A. Liebsch, Phys. Rev. B 1993, 48, 11317-11328.
- I-II.05** 15:45 REINFORCEMENT OF POLYSTYRENE BY COVALENTLY BONDED OXOTITANIUM CLUSTERS
L. Rozes, G. Fornasieri, C. Sanchez, Laboratoire Chimie et Propriétés de la Matière Condensée, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris cedex 05, France, C. Creton, Laboratoire Physico-Chimie des Polymers et des Milieux Dispersés, ESPCI, 10 rue Vauquelin, 75231 Paris cedex 05, France and S. Trabelsi, N.E. Zafeiropoulos, M. Stamm, Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, Dresden 01069, Germany
 Oxo-metallic clusters are employed as inorganic nano building blocks to obtain well defined organic-inorganic hybrid materials. The oxo-alcoxo cluster Ti16O16(OEt)32 presents a shell of labile ethoxy groups which can be selectively transalcoholysed with preservation of the titanium oxo-core. Both the kinetics and the number of substituted titanium atoms are strongly dependant on the nature of the alcohol and the transalcoholysis reactions lead to the elaboration of new oxo-alcoxo clusters Ti16O16(OEt)32-x(OR)x (R : alkyl, phenyl... groups). The number and the localization of the substituted titanium atoms are investigated by NMR measurements and single-crystal X-ray diffraction. Moreover, cluster modification by polymerizable alcohols allows though copolymerization reactions to obtain new hybrid nanocomposites with a perfect control of the cross-linking density. The study of the dispersion of the clusters in the organic matrix is performed by SAXS and AFM. The resulting nanocomposites exhibit an increase of the glass transition and the storage modulus with increasing cluster content. We demonstrate that the inorganic core, covalently linked to the polymer, acts as an effective nano-cross-linker.
- 16:00 **BREAK**
- I-II.06** 16:30 -Invited- NONAQUEOUS ROUTES TO CRYSTALLINE METAL OXIDE NANOPARTICLES: FORMATION MECHANISMS AND APPLICATIONS
M. Niederberger, G. Garnweitner, N. Pinna, J. Polleux, M. Antonietti, Max Planck Institute of Colloids and Interfaces, Colloid Chemistry, Research Campus Golm, 14424 Potsdam, Germany
 The unique characteristics of transition metal oxides make them the most diverse class of materials, with properties covering almost all aspects of materials science and solid state physics. The general trend to further miniaturization of functional devices in emerging technologies such as sensing, pigmentation, energy storage and conversion and electroceramics demands for the production of these materials with the highest possible purities, small crystallite sizes, well-defined particle morphologies and small particle size distributions.
 We developed novel reaction approaches using nonaqueous and halide-free procedures to synthesize a wide variety of different metal oxide nanoparticles including the binary metal oxides of group IV and V, SnO₂, In₂O₃ and perovskites such as BaTiO₃, SrTiO₃ and LiNbO₃. The routes involve the solvothermal reaction of metal oxide precursors such as metal alkoxides or metal acetylacetonates with oxygen supplying agents such as alcohols, aldehydes and ketones. The careful characterization of the organic species in the final reaction mixtures provides information about possible condensation mechanisms. In the case of BaTiO₃, the formation of the Ti-O-Ti bond most probably occurs via a novel mechanism involving a C-C bond formation between the isopropoxy ligand and the solvent benzyl alcohol. The use of oxidizing solvents instead of alcohols allows the preparation of lead-based metal oxides such as PZT. In this presentation, we will give an overview of the various nanoparticles synthesized via the nonaqueous sol-gel approach, the particle formation mechanisms found in these systems, and first examples of applications in gas sensing devices, catalysis and electroceramics.

- I-II.07** 17:00 PERIODIC METAL OXIDE NANOWIRE ARRAYS: TEMPLATE-DIRECTED FABRICATION AND PHYSICAL PROPERTIES
H.J. Fan, W. Lee, M. Alexe, K. Nielsch and M. Zacharias, Max Planck Institute of Microstructure Physics, Halle, Germany; A. Dadgar and A. Krost, Institute of Experimental Physics, Otto-von-Guericke-University Magdeburg, Germany
 We report the fabrication of large-scale periodic arrays of single-crystalline metal oxide (ZnO in current case) nanowires by combining substrate nanopatterning and catalyst-directed epitaxial growth. First, gold membranes of hexagonal-packed nanotubes were obtained from an electrochemical duplication process of perfect ordered porous alumina templates. Then, these metal membranes were used as shadow masks to deposit ordered Au nanodot arrays. Subsequent vapor-phase growth of ZnO results in vertically-aligned and hexagonal-arranged ZnO nanowires on GaN/Si substrates. The Au nanodots served as both catalyst and site-specific template for the nanowire growth. This technique also allows a variation of the wire diameter by choosing masks of different size. Our fabrication approach is in principle also applicable for other semiconductor nanowire arrays on the lattice-matched substrates.
 The electrical and piezoelectric properties of individual ZnO nanowires were studied using SEM-based manipulator and piezoresponse force microscopy (PFM), respectively. Results of the physical properties will be presented.
- I-II.08** 17:15 HIERARCHICALLY STRUCTURED CARBON AND METAL OXIDE MONOLITHS THROUGH NANOCASTING
Jan-Henrik Småt(a), An-Hui Lu(b), Stefan Backlund(a) and Mika Lindén(a), (a)Dept. Phys. Chem, Åbo Akademi University, 20500 Turku, Finland, (b)Max-Planck-Institut für Kohlenforschung, 45470 Mülheim an der Ruhr, Germany
 Monolithic silica exhibiting a three-modal, hierarchical pore structure has successfully been prepared via sol-gel-processing. Monolithic bodies with interconnected macropores in the μm range are a result of controlled phase separation and gelation kinetics, while textural mesopores in the 10-20 nm range originate from voids between particles. Furthermore, the particles exhibit internal mesoporosity with pore diameters in the 2-4 nm range originating from supramolecular templating. Nanocasted carbon monoliths exhibiting a three or four-modal porosity has been prepared by one-step impregnation, using silica monoliths containing a bi-modal porosity as hard templates. Combined volume and surface templating, together with controlled synthesis of the starting silica monoliths used as the scaffold, enables a flexible means of pore size control on several length scales simultaneously. The mesopore size can be tuned in the range of 2-20 nm, while the macropores are in the range of 0.5-30 μm . In a similar manner it is possible to prepare cobalt oxide replicas with a bimodal porosity, which has to our knowledge never been reported previously. Furthermore, it has been shown that the method can be generalized to other metal oxides as well. The different modes of porosity are arranged in a hierarchical structure-within-structure fashion, which is optimal for applications requiring a high surface area in combination with a low pressure drop over the material.
- I-II.09** 17:30 ELABORATION OF HYBRID NANOCLUSTER MATERIALS BY SOLUTION CHEMISTRY
S. Cordier, K. Kirakci, A. Perrin, C. Perrin, Institut de Chimie de Rennes, LCSIM, UMR 6511 CNRS-Université de Rennes 1, Avenue du Général Leclerc, 35042 Rennes cedex, France
 Metal "clusters" -finite group of metal atoms held together via metal-metal bonds- are encountered in reduced transition metal compounds synthesized by solid state routes. Octahedral clusters appear in nanosized face-capped $\text{M}_6\text{Li}_8\text{La}_6$ and edge-bridged $\text{M}_6\text{Li}_2\text{La}_6$ units that can be linked together or discrete within the solids. In the later case the compounds constitute relevant precursors for elaboration of hybrid organic/inorganic nanocluster materials by solution chemistry routes. Several examples of such hybrid materials will be presented. Indeed, $(n\text{-Bu}_4\text{N})_2\text{M}_6\text{X}_{14}$ and $[\text{Cp}^*(\text{dppe})\text{Fe-NCMe}]_2\text{M}_6\text{X}_{14}$ ($\text{M}=\text{Mo, Re; X}=\text{Br, I}$) were synthesized by cation exchange starting from $\text{Cs}_2\text{M}_6\text{X}_{14}$. Original building blocks for the design of low dimensional materials, for instance $\text{Nb}_6\text{Cl}_9\text{O}_3(\text{CN})_6$ or $\text{Nb}_6\text{Cl}_{12}(\text{SCN})_6$, were obtained by interaction of cluster compounds with KCN or KSCN solutions. The crystallization of $\text{Nb}_6\text{Cl}_9\text{O}_3(\text{CN})_6$ units with Mn cations led to $\text{Cs}_3\text{Mn}[\text{Nb}_6\text{Cl}_9\text{O}_3(\text{CN})_6]_3\text{H}_2\text{O}$ which exhibits a Prussian blue topology. The dimensionality of such compounds is controlled by a judicious complexation of transition ion with bidentate ligands as exemplified by various coordination compounds as $[\text{Ni}(\text{en})_2(\text{NH}_3)_2][\text{Ni}(\text{NH}_3)_4\text{Re}_6\text{Se}_8(\text{CN})_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ built from 1D chains. Original functionalized materials have been obtained after substitution of apical ligands of the cluster by functional phenate giving access to Mo_6 cluster-dendrimer assemblings with 18 silylferrocenic endings, useful for recognizing of biologic anions by electrochemistry.

17:45-19:00

POSTER SESSION I

POSTER SESSION I
Tuesday, May 31, 2005
17:45 – 19:00

- I/PL.01** NANOTUBE ON NANOFIBERS: A TOTAL GAS-PHASE ROUTE TO A STRUCTURED C-C NANOCOMPOSITES
Wei Xia, Jun Qian, Changhai Liang, Oliver F.-K. Schlüter, Martin Muhler, Laboratory of Industrial Chemistry, Ruhr University Bochum, 44780 Bochum, Germany
Commercial carbon nanofibers (Pyrograf III, 70-200 nm diameter, 50-100 µm length, Applied Science, USA) were used as support for the growth of carbon nanotubes. As-received nanofibers were treated by oxygen-plasma in a rotating barrel to introduce oxygen-containing functional groups, which act as anchoring points for foreign atoms. Iron oxide nanoparticles were synthesized on the treated nanofibers by chemical vapor deposition of ferrocene. Carbon nanotubes were subsequently grown by iron-catalysed pyrolysis of cyclohexane under mild conditions. With an iron loading of less than 1%, homogeneously distributed nanotubes (about 20 nm in diameter) were prepared and the morphology can be fine-tuned by growth time, temperature, gas composition and other process parameters. The BET surface area of the nanofibers was enhanced by one order of magnitude after nanotube growth. The C-C nanocomposites are of great potential as structured catalyst support or for reinforcement of polymers.
- I/PL.02** CARBON NANOTUBES REINFORCED POLY(VINYL ALCOHOL) COMPOSITE FILMS
Wei Chen, Xiaoming Tao, Pu Xue, Nanotechnology Center Institute of Textiles & Clothing The Hong Kong Polytechnic University Hung Hom, Kowloon, Hong Kong
Carbon nanotubes (CNTs) are molecular-scale tubes of graphitic carbon with outstanding properties. They are among the stiffest and strongest fibers known, with Young's modulus as high as 1 TPa and tensile strength of up to 63 GPa. There is currently great interest in exploiting these properties by incorporating CNTs in a wide range of polymer matrices. In this paper, we demonstrate the solution-based composite fabrication techniques which lead to free-standing poly(vinyl alcohol) (PVOH) composite films with very good nanotube dispersion at significant high loading level. Overall mechanical properties of the nanocomposite films were significantly improved as compared to the neat PVOH film. For PVOH-based materials at 9.1 wt% MWNTs loading, increases in Young's modulus, tensile strength, and toughness by factors of 4.5, 2.7, and 4.1 respectively, were achieved. The composite film also exhibits lower hysteresis and permanent set. Raman, SEM, and DSC techniques were used to evaluate the MWNTs/PVOH composite system. Acid treatment of the pristine MWNTs and the succeeding ultrasonication processing allowed good distribution of the nanotubes in the matrix, leading to better performance in mechanic. SEM shows apparent good wetting of the nanotubes by the PVOH matrix. These results are supportive of good interfacial bonding between the modified carbon nanotubes and the hosting polymer matrix.
- I/PL.03** COVALENT BONDED MULTI-WALLED CARBON TUBES COMBINED WITH DNA: SYNTHESIS AND CHARACTERIZATION
Weiwei Chen(a), Chi Hung Tzan(b), Jianxin Tang(a), Mengsu Yang(b), Shuit Tong Lee(a), (a)Center of Super-Diamond and Advanced Films (COSDAF) & Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, China, (b)Department of Biology and Chemistry, City University of Hong Kong, Hong Kong SAR, China
We have developed a multi-step method to covalently link functionalized multi-wall carbon nanotubes (MWNT) to deoxyribonucleic acid (DNA) oligonucleotides. X-ray photoelectron spectroscopy (XPS) was used to characterize the initial chemical modification to form amine-terminated MWNTs, which were then covalently combined with DNA. The morphology recorded by atomic force microscopy (AFM) gave direct and explicit imaging of the resulting DNA-MWNT adducts, showing that chemical functionalization occurred at the ends and sidewalls of MWNTs. The adopted methodology is an important first step in realizing a DNA-guided self-assembly process for carbon nanotubes
- I/PL.04** CR AND NI NANO ARRAYS EMBEDDED INTO BLOCK COPOLYMERS AND IMAGED WITH SPECTRO MICROSCOPY
O. Seifarth, Y. Burkov, D. Schmeißer, Brandenburg Technical University, Konrad Wachsmann Allee 17, 03046 Cottbus, Germany, A. Sydorenko, R. Kremek, M. Stamm Leibniz Institute for Polymer Research, Hohe Strasse 6, 01069 Dresden, Germany
The formation of metallic nano particles stored in thin films of block copolymers has been investigated by means of synchrotron radiation based photoemission spectroscopy (PES) and microscopy (PEEM). Empty channels in poly(styrene-block-4-vinylpyridine) copolymer with diameters of tens of nanometers filled with CrO₂, Cr₂O₃ and Ni provide ideal bases for performing electron spectroscopy with energy and lateral resolution on magnetic nano particles. We present UPS, XPS, NEXAFS spectra and PEEM images on and off the C 1s, Cr 2p, Ni 2p resonances and discuss the geometric and electronic structure of such compounds. In particular, we show that nano structured block copolymer formed by microphase separation allow storing of functional materials within this templates in different geometries. We identify characteristic features in the resonant photoemission data of Cr₂O₃ associated to formation of Cr₂O₃ nano particles in the templates and compare with results of Cr₂O₃ deposited simply on top of the block copolymer. In addition we present resonant photoemission on free standing Cr₂O₃ nano rods for the first time, formed with a preparation technique based also on microphase separation in block copolymers. Here the influence of the nano particle formation on the PES data will be also addressed. The synchrotron radiation was delivered from the U49/2 beamline at BESSY II and the growth modes of the metallic nano structures were monitored with AFM.

- I/PI.05** SILICON NANO-BEACON ARRAYS: SYNTHESIS, CHARACTERIZATION, AND SELF-ASSEMBLY
 Teng Qiu(a,b), Xinglong Wu(a) and Paul K. Chu(b), (a)National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China, (b)Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, China
 Unique structured Si nanowire arrays with light-emitting nanocaps as beacons were fabricated on SiO_xN_y -covered Si wafers via electroless metal deposition in ionic silver HF solution through selective chemical etching. The formation of these oriented nanostructures can be understood on the basis of the self-assembled localized microscopic electrochemical cell model and diffusion-limited aggregation process. The composite nanostructure exhibits enhanced blue emission. Emission and excitation spectral analyses suggest that the photoexcited carriers mainly take place in the quantum-confined Si nanowires, whereas radiative recombination occurs in the Si-N binding states of the SiO_xN_y nanocaps. Silver nanocaps formed in-situ could also be strong UV emitting source. The UV photoluminescence is considered to be due to the optical transition in the vacancy defect centers in the silver nanocaps on the Si nanowires. Their ordered nanostructures and light-emitting properties are promising characteristics for possible applications in future nanodevices such as nanowire UV photo detectors and optoelectronic devices.
- I/PI.06** CARBON NANOTUBE JUNCTIONS AND THEIR ELECTRONIC PROPERTIES
 Istvan Laszlo, Department of Theoretical Physics, Institute of Physics and Center for Applied Mathematics and Computational Physics, Budapest University of Technology and Economics, 1521 Budapest, Hungary
 Carbon nanotube junctions have emerged as good candidates for building blocks in nanosize networks. They are also interesting for their potential use in nanoscale transistor or amplifier applications. Single-wall carbon nanotubes can be either metallic or semi-conducting depending on both the diameter and chirality. Heterojunctions formed by a semi conducting and a metallic nanotube have rectifying properties. More sophisticated devices can be constructed by applying n-terminal junctions with $n > 2$. In this work an algorithm is presented for generating various junctions between nanotubes of different chirality and diameter. We shall study also the connection between the geometric structure of the junction and the corresponding electronic properties.
- I/PI.07** COLLOIDAL MOLECULAR SIEVES WITH FLUORESCENT PROPERTIES
 T. Doussineau(a), E. Gavilan(a), A. El Mansouri(a), M. Smaïhi(a), J.-O. Durand(b) and M. Granier(b), (a)IEM UMR 5635, CNRS, 1919 route de Mende, 34293 Montpellier Cedex 5, France, (b)CMOS UMR 5637 cc 007, UM2, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France
 Fluorescent colloidal zeolite nanoparticles have been prepared by adsorption of organic chromophores in the porous network of template-free zeolite beta nanoparticles. Two fluorescent dyes [3-hydroxyflavone (3OHF) and Rhodamine B (RhB)] have been studied. The structure of zeolite beta host was maintained during all steps of treatment. The dye entrapment is stable towards acidic treatments and extensive reflux processing. The colloidal properties of the particles are maintained after confinement of the dyes in the microporous cavities so that conventional optical transmission spectroscopic methods can be used to study the entrapped chromophores species within the zeolite.
 The emission spectra ($\lambda_{ex}=345$ nm) collected from 3-OHF loaded nanoparticles suspensions present one band peaked with a maximum around 450 nm, while in ethanol 3-OHF exhibit an intense band with a maximum at 550 nm. This modification in fluorescence emission is due to particular behavior of 3-OHF molecules which present an excited-state intramolecular proton transfer (ESIPT). The results are discussed in view of the ESIPT mechanism in the 3-OHF molecule. [...] The lifetime of the dye molecules in free and entrapped forms were measured at room temperature. In solution, the free-3OHF and free-RhB traces exhibit monoexponential behaviour of the decay with associated lifetimes of ~ 300 ps and ~ 1.6 ns respectively. For the zeolite entrapped dye, much longer lifetimes are measured. This denotes a more rigid environment for the dye molecule which prevents the free arrangement of the molecules and therefore accounts for the entrapment of the fluorescent molecules in the cages the inorganic host.
- I/PI.08** STRUCTURING OF NOT STOICHIOMETRICAL DISPERSIBLE FILLERS OF A INCLUSION PHASES IN THERMO STEADY POLYMERIC MATRIXES
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 At reception of polymeric composites filled the dispersed phase observes the various processes, resulting in to formation in a polymeric matrix statistical or ordered structures. These structures in many respects determine special properties of a composite.
 At reception of composites on the basis of powders of not stoichiometrical joints of titanium with carbon and nitrogen such as inclusion phases, and also various thermosetting binding us structuring dispersion particles of filler behind a threshold of passing was revealed. Depending on stoichiometry of filler, its nature and the grade binding formation of such structure occurs at filler content from 18-20 up to 30-45 % vol. The special morphology of such structure is developed by existence of bend on the graph of resistance of a material from composition. At a refabrication of a composite such structure disappears.
- I/PI.09** NEW SYNTHESIS OF NANOSTRUCTURED $\text{TiO}_2(\text{B})$ AND ITS ELECTROCHEMICAL BEHAVIOR
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 Nanostructured phase-pure $\text{TiO}_2(\text{B})$ with microfibrinous morphology was synthesized by newly developed protocol employing amorphous TiO_2 as a raw material. Compared to traditional syntheses from $\text{K}_2\text{Ti}_4\text{O}_9$, the new product exhibited better electrochemical performance and stability. Cyclic voltammetry of Li-insertion in the $\text{TiO}_2(\text{B})$ lattice revealed pseudocapacitive faradaic process of Li accommodation, basically different from lithium storage in anatase whose kinetics is controlled by solid-state diffusion of Li^+ . The presence of two pairs of peaks in cyclic voltammogram with formal potentials of ca. 1.5 and 1.6 V, a feature specific for $\text{TiO}_2(\text{B})$, enables to use cyclic voltammetry for identification of this phase in titania materials. $\text{TiO}_2(\text{B})$ was found to be present in a broad palette of TiO_2 materials of various origin.

I/PI.10**SELF-ASSEMBLY AND FUNCTIONALISATION OF HYBRID ORGANIC-INORGANIC SILICA**

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Nanostructured organic-inorganic hybrid materials have attracted much attention as they constitute a unique class of materials combining the properties of the organic moieties and the inorganic matrix. Starting from at least a bisilylated precursor $(RO)_3Si-R'-Si(OR)_3$, it is possible to obtain hybrid materials with a large variety of spacers R' including functionalized organic groups. These materials are generally considered as amorphous. However, it was shown by XRD that rigid organic moieties (R') induce a self-organization during the polycondensation with nanometer scale ordering.

Up to now, few examples of self-organization of polysilsesquioxanes with long-range structure have been reported, and the order was induced by hydrogen-bonding interactions. We found a method allowing to obtain hybrid organic-inorganic materials with long-range order (lamellar or 2D hexagonal structure) without structure directing agent, by hydrolysis and polycondensation of bridged organo-silica precursors $(MeO)_3Si-(CH_2)_n-Si(OMe)_3$ ($n = 12, 18, 30$) in aqueous solution, thanks to hydrophobic Van-Der-Waals type interactions. We show that the alkylene chain length controls the nanostructure. This new way was extended to the preparation of functionalised hybrid materials, which cannot be obtained by other routes.

I/PI.11**ELECTRON-HOLE EXCITATIONS IN METAL NANOCCLUSERS UNDER LOW-ENERGY ION SCATTERING**

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Size-dependent electronic properties of metal nanoclusters can be studied experimentally by screening response of cluster's electrons to sudden appearance of the uncompensated charge, resulting in many- and single-particle excitations, in particular creation of low-energy electron-hole (e-h) pairs near Fermi surface. Such excitations are known to lead to the asymmetry in the X-ray photoelectron spectra (XPS) of core-levels.

The creation of e-h pairs in metal nanoclusters is studied by low-energy ion scattering spectroscopy (LEIS). 1-10 nm size nanoclusters of Au, Co and Mo pulsed laser deposited on the surface of highly oriented pyrolytic graphite are investigated in situ by LEIS of He⁺ ions. The shape of the observed spectra (ions' energies $E_0=0.3-1.5$ keV) is found to be asymmetric, and can be well fitted by singular Doniach-Sunji  line-shape convoluted with Gaussian broadening of the initial ion flux. Anderson singularity index [1]; has been determined and found to increase with ions energy, that is attributed to the excitation of single-particle electron states. In contrast to XPS, LEIS spectra asymmetry is independent from the cluster size and has higher values for bulk metals, indicating the difference in the electronic states of surface (LEIS) and bulk (XPS) atoms. Experimental [2]; values allow to determine phase shifts of screening s-, p- and d-electrons and thus to analyze the band structure and electron-state density of nanoclusters.

I/PI.12**ELECTRON FIELD-EMISSION PROPERTIES OF PHOSPHOROUS DOPED SILICON NANOWIRE ARRAYS**

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Dense ensembles of silicon nanowires doped with phosphorous during growth were prepared by metal-catalyzed chemical vapor deposition on Si (001) in a gas-flow CVD-reactor at reduced pressure. Electron field-emission (FE) from these structures was studied at room temperatures in ultra-high vacuum ($10e-9$ Torr). Measurements were carried out with a Mo anode shaped as a rod of 1 mm diameter. The cathode-anode distance was varied from 25 to 200 μ m. It was found that voltage-current characteristics obey the Fowler-Nordheim law with an effective work function 3.2 eV, which differs substantially from the work function of silicon (4.3 eV). In addition, increasing the doping level from 8.1×10^{18} cm⁻³ to 3.1×10^{19} cm⁻³ leads to an increase of the emission current by about one order of magnitude. Observation of continuous operation of field emitters for 168 hours showed a decrease of emission current by two times and subsequent stabilization. To understand such a large decrease of effective work function we examined the structures using SEM and characterized them by SIMS, SNMS, and IR spectroscopy. Physical mechanisms responsible for the effects observed are discussed.

I/PI.13**CONVERSION CuO POWDERS TO NANOSTRUCTURES BY SOLUTION METHOD**

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Here we report a very simple method to convert conventional CuO powders to nanostructures by solution methods. CuO can be dissolve into ammonia aqueous, and the solution can be diluted by either deion water or alcohol and transferred onto a substrate. After annealing as low as 100C, the nanostructures with bunchy nanoparticles of Cu(OH)₂ can be formed. Using alcohol solution, nanoparticles are round and uniform with the size of about 50nm, while using deion water solution, nanoparticles in chain are not uniform. With annealing temperature about 200C, Cu(OH)₂ nanostructures can convert to CuO nanostructures.

- I/PI.14** SYNTHESIS AND CHARACTERIZATION OF SUPERPARAMAGNETIC NANOCOMPOSITES BY GRAFTING BIOCOMPATIBLE POLYMERS ONTO MAGHEMITE NANOPARTICLES
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 Hybrid organic-inorganic nanomaterials based on a magnetic core and a polymeric shell offer promising opportunities for therapeutic applications including MRI contrast agents, drug carriers and hyperthermia mediators. We focused on maghemite and poly(ϵ -caprolactone) to prepare materials combining the superparamagnetism and the innocuity of iron oxide nanoparticles with the polyester biocompatibility. Two grafting procedures have been developed. The first one consists in the immobilization of an amino-silane coupling agent at the surface of the maghemite, which will act as a co-initiator in the aluminum isopropoxide catalyzed ring opening polymerization of ϵ -caprolactone "from" the inorganic surface. The amount of grafted polymer was shown to depend on the monomer concentration and on the amine to aluminum ratio. Further experiments with poly(ethylene oxide) were also achieved, producing a water stable dispersion. An alternative technique consisted in a coupling reaction between silane-functionalized poly(ϵ -caprolactone) chains and the surface hydroxyls of maghemite providing well defined nanocomposites.
- I/PI.15** BN COVER ON THIN SiC WHISKERS
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 SiC whiskers of submicron 100-800 nm diameters and of ~ 20 aspect ratio covered by thin (~ 10 -30 nm) BN films were fabricated. The SiC whiskers were synthesized at the first stage by both a template method using carbon nanotubes and a carbothermal method. The whiskers were mixed in magnetic mixer with aqueous solution of boron acid and saccharose mixed with ethyl alcohol and surfactant. After drying and graduated heating up to 1100-1300 C during several hours a setting was cooled in nitrogen flow. Samples were characterized by SEM, TEM, IR, EPR, and Raman spectroscopy. TEM images of BN films show the onions, pure BN plates, graphene sheets, bamboo-like and straight nanotubes, as well as other inhomogeneities in their structure. After optimization of process parameters the entire compact thin cover have been obtained. Possible applications for nanodevices and nanocomposites are proposed.
- I/PI.16** OPTICAL THIN FILM PREPARATION USING WATER-BASED SILICA SOLS
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 Today, coatings used for high power laser optical component such as LIL or LMJ are prepared from sol-gel alcoholic solutions. Use of large-size dip-coating tank containing alcoholic media involve tricky constraints due to safety and environmental reasons.
 The aim of this work is to develop a coating solution suitable for optical thin film preparation which is non or slightly-flammable, time-stable and environmentally friendly.
 Ethanol-based colloidal sol is first prepared using the Stöber process. This chemical enable to prepare optical thin film having a very low refractive index ($n=1,22$) and a very high laser damage threshold. The choice of the co-solvent has been focused on water in order to develop water-based coating solutions so-called BLUESIL. The so-prepared sols are characterized using viscosity and size distribution measurements and show time-stability whatever the water content. Aqueous synthesis route is find to be an important factor determining both mechanical and optical properties.
 BLUESIL were then exposed to catalytic curing (ammonia-hardening). We show this procedure dramatically improve film scratch-resistance maintaining good optical properties such as high-transparency (99,8% transmission) and low refractive index. These macroscopic features are related to inter-particle bond formation involving siloxane bridging and hydrogen bonding.
 This proposed water-based silica sol thin film preparation gives rise to optical coating having high porosity ($\sim 50\%$) and nevertheless remarkable mechanical film properties (adhesion, scratch-resistance)
- I/PI.17** MESOPOROUS SILICE-TITANIA MIXED OXIDES OBTAINED FROM POLYETHYLENIMINE-CONTAINING HYBRID XEROGELS
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 The association of siloxane-titania mixed sols of different compositions with the macromolecules of Polyethylenimine (PEI) allows to prepare hybrid composites. After an exhaustive extraction of the organic polymer from the xerogel and the later elimination of residual organic material by calcination (550°C/2h) silice-titania mixed oxides with titania contents from 25 to 75% were obtained. The resulting materials were predominantly mesoporous with pore diameters of about 50 Å and high surface area, which decreases with the titania content (600 - 250 m²/g). It was found that the distribution of pore sizes is narrow and symmetrical in comparison with the obtained ones with other porogen agents with amino or amido groups such as chitosan or polyacrylamide based polymers. The narrow and symmetrical form of the pore size distribution curves observed in the mixed oxides indicates a wide and homogeneous distribution of the PEI domains in the precursor hybrid composite. This can be attributed to extensive interactions of the amino groups with the inorganic components through hydrogen bonding. By increasing the relative amount of PEI from PEI: (silice + titania) =1 to a value of 2 the area of the final oxides is increased approximately 15% in each case. So were achieved surface areas higher than 800 m²g⁻¹. The samples remain amorphous even after heating at 700°C/4h due to a high Si-O-Ti connectivity. XPS and 29-Si-RMN further confirmed this.
 Acknowledgments: To Conicyt, Project Fondap 1198-002

- I/PI.18** SYNTHESIS AND CHARACTERIZATION OF HIGHLY ORDERED BiFeO₃ MULTIFERROIC NANOWIRE ARRAYS
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 We report the synthesis and characterization of multiferroic FeBiO₃ nanotube arrays. The perovskite BFO nanotubes with diameters about 250 nm and lengths about 6-9.56 μm were fabricated by means of sol-gel method utilizing nanochannel alumina templates with post annealing at 700 °C. The microstructure of the BFO nanotubes were investigated by means of x-ray diffraction and transmission electron microscopy, and the ferroelectric characteristic of BFO nanotubes were demonstrated.
- I/PI.19** PREPARATION OF ADVANCED NANOCOMPOSITE CARBON/SILICA HYBRID AND NANOSTRUCTURED CARBON MATERIALS VIA CONTROLLED LIVING RADICAL POLYMERIZATION
 G.D. Fu, E.T. Kang, K.G. Neoh, Singapore
 Block copolymers of poly(dimethylsiloxane) (PDMS) and poly(acrylonitrile) (PAN) or PDMS-b-PAN copolymers, were synthesized by atom transfer radical polymerization (ATRP) from the PDMS macroinitiator. The chemical structure and composition of the PDMS-b-PAN copolymers were studied by nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared spectra (FTIR) and x-ray photoelectron spectroscopy (XPS). The nanocomposite carbon/silica hybrid (CSH) was obtained by the thermal crosslink of the PDMS and the carbonization of PAN of the PDMS-b-PAN copolymers. The subsequent remove of the silica part in the CSH by the HF treatment or carbon part by thermal treatment in air results in the formation of the porous carbon films or silica films. The porous structures of the resulting films were characterized by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM).
- I/PI.20** SOLID STATE SELF-ASSEMBLIES POLYPYRROLE-BASED WITH PORPHYRIN μ-OXO DIMER SPACERS
 Rodica-Mariana Ion, Dragos-Viorel Brezoi, Valahia University, Materials Science Department, Târgoviste, Romania
 Molecular aggregates composed of a iron oxide and a functional polymer (polypyrrole) with μ-oxo dimers of porphyrin spacers, can be prepared without employing complicated materials such as supramolecular and hybrid complexes. The ability of pyrrole to form higher order self-assembled ensembles and aggregates in the solid state is analyzed. Pyrroles represent a unique set of supramolecular "building blocks" that, depending on the nature and number of substituents, are capable of stabilizing a range of self-assembled ensembles in the solid state that form dimers and trimers. It has been found that relatively some changes in structure of assembly is obtained with μ-oxo dimers (spacers) which can lead to quite different products with dimeric structures. The μ-oxo dimeric form of iron(III) tetra(p-X-substituted) porphyrin, where X is phenyl (FeTPP) or sulphonato-phenyl (FeTSPP) or methoxy-phenyl (FeTMOPP), were investigated in this paper, too. On the other hand, the steric spatial dimensions of substituents are most likely to affect their aggregation tendencies, observing a tighter stacking of dimer/higher aggregates and slower formation/dissociation processes. The electron withdrawing effect of the substituents on the meso-phenyl rings of the porphyrin affect the structure by the possibility of generation of doubly bridged structures. The active species of tetravalent iron porphyrin are responsible for the electrical properties. The chemical and structural properties of the nanocomposite particles thus obtained are characterized by UV-Vis, FT-IR, X-ray diffraction and electron microscopy. The size of the Fe₂O₃-PPy with μ-oxo dimers porphyrins as spacers nanocomposite particles is in the range of 10-20 nm.
- I/PI.21** DEPENDENCE OF THE SILICON NANOWIRE DIAMETER ON DEPOSITION PARAMETERS
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 Si nanowires (NWs) were fabricated by a Nd:YAG pulsed laser with wavelengths of 325, 532 and 1064 nm using gold catalysts. Transmission electron microscopy and scanning electron microscopy images indicate that the products are crystalline silicon NWs. We report dependence of the Si NWs diameter on laser wavelength and ambient pressure in deposition process. The formation mechanism of the NWs is discussed.
- I/PI.22** PHOTOLUMINESCENCE PROPERTIES OF SnO₂ NANOWHISKERS GROWN BY THERMAL EVAPORATION
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 SnO₂ nanowhiskers were synthesized by thermal oxidation with (sample A) and without (sample B) a gold film as the catalyst. SEM images reveal wire-like nanowhiskers about several hundred micrometers in length and approximately 100 nm in diameter. The three Raman peaks at 474, 632, and 774 cm⁻¹ are indicative of the rutile phase of the as-synthesized SnO₂ nanorods and are consistent with data acquired by X-ray Diffraction. The photoluminescence properties between 10K and 300K are characterized in a spectral range of 340-800 nm using a He-Cd laser with a wavelength of 325 nm. The peaks corresponding to the excitation transitions from the conduction band to the valence band of the SnO₂ nanowhiskers are not observed. However, an ultraviolet (UV) emission at 3.13eV emerges and it can be assigned to the near band-edge emission in sample A. The intensity of the emission is observed to diminish rapidly with increasing temperature due to the thermal quenching effect. The peaks also shift to lower energy with increasing temperature, from 2.75eV to 2.12eV for sample A and 2.65eV to 2.25eV for sample B. The UV emission is related to oxygen vacancies in the SnO₂ nanowhiskers and others at lower energies can be correlated to the tin interstitials or dangling bonds.

I/PI.23AIBi₃C₅VI THIN FILMS AS NO SENSORS

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Nanostructured thin films of composite semiconductor materials AIBi₃C₅VI, where AI - Li, K, Rb; CVI - S, Se, are of particular interest for design of reliable chemical sensors, while aggressive impurities in the environmental air sufficiently effect the processes of oxidation of the film surface. As nitrogen oxide (NO) is one of the most ecologically harmful impurities in atmospheric air, the essential problem is to establish NO influence on the properties of the films in the range of concentrations up to 1 mg m⁻³. The investigated films were deposited onto the glass substrates in UHV system under T_{substrate} = 300 K and rate of deposition 1 - 5 Å s⁻¹. The thickness of the films was about 40 - 100 nm. Electron-microscopic investigations of the film surface revealed nanoscaled cluster-like relief with space density inhomogeneities. Studies of the film oxidation in air with NO concentration 1 mg m⁻³ showed the changes of the oxidation speed and composition of the sample. Investigation of oxygen desorption curves enabled us to estimate the concentration of adsorbate under different times of adsorption. Investigation of transmission spectra of the films before and after NO interaction made it possible to propose an active element for optical registration of aggressive impurities in the environmental air.

I/PI.24

A POTENTIAL TOOL FOR ANALYZING ALUMINOSILICATE MATERIALS: FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY

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Aluminosilicate compounds play a major role in material chemistry and in the industry. These nanosized structured materials have been intensively studied and characterized using vibrational spectroscopy (FTIR, Raman), NMR, electron microscopy (SEM and TEM), Atomic emission (ICP-AES), X-Ray Diffraction and Fluorescence. However none of these techniques give a global answer to the characterization problem: chemical and structural properties. Mass spectrometry could be a good and versatile tool to achieve these goals but only few studies are available on aluminosilicate materials.

We present a mass spectrometry method associated with a high-energy pulse laser beam called Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS). This method was applied to a series of aluminosilicates made by sol-gel. By using FT-ICR-MS, specific cluster charged families containing Si and/or Al atoms appear for all the samples in the negative ion mode. In the positive ion mode, an elementary composition is given systematically as single ions are detected. This work is promising for the analysis of aluminosilicates as FT-ICR-MS provides rapid insight concerning composition, synthesis method and stability. Moreover this analytical technique gives information related to the structure of the compounds and may contribute significantly to explore classes of hybrid (inorganic/organic).

I/PI.25

DEPOSITION OF 2-AMINO-1-PROPANOL ON Cu(110) SURFACE: CHEMISORPTION

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Chirality is a geometrical propriety of an object of existing in two mirror forms. Contemporary interest focuses on the possibilities of molecular-level engineering using chiral systems due to the increasing demand of producing molecular products of a single handedness, that is, enantioselective.

We are studying the possibility of transferring chiral information across an interface considering chiral molecules (2-amino-1-propanol) adsorbed on a metal surface Cu(110); this system represents an experimental model that works for molecular recognition in process such as enantiomeric separation of chiral compounds, enantiospecific sensors and heterogeneous asymmetric catalysis. Self-assembling of 2-amino-1-propanol on Cu(110) is performed in ultra high vacuum (UHV) and investigated via X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). We analysed the modifications of the core line of C 1s, O 1s, and N 1s and the LEED pattern as a function of the 2-amino-1-propanol coverage to understand growth morphology, molecule-substrate bonding formation and self-organization into long range ordered structures.

I/PI.26

NEW SPECIFIC SENSOR FOR VOLATILE ORGANIC CONTAMINATION USING MESO-POROUS SURFACES

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For the new nodes of 65 and 45 nm, the density and quality of layers are more sensitive to Volatile Organic Contaminants (VOC). The EUV and 193 nm lithography instruments and coatings also. The ITRS gives VOC values for different mass. VOC are also important in pharmaceutical and food industry. This paper will describe the principle of this new specific sensor of VOC based on Infra-Red 2 965 cm⁻¹ CH_x absorption bands with attenuated multiple reflection (MIR). A well chosen layer of meso-porous silica has been deposited on the silicon barr surfaces to enhance the sensitivity by a larger specific surface. The sensitivity is given for adsorbed CH_x at a level of a few E12 molecules per cm² and a response time of less than one minute in clean room environment. By heating the sensor at different temperatures, the mass separation can be operated between light and heavy CH and a reset operated. The optical lay-out, the sensitivity and results of tests will be presented. The comparison with other VOC analytical techniques will be given for advantages and limitations respectively, particularly the SAW sensors which are not specific. This new specific sensor can be used as a continuous alarm monitor, it can be integrated in tools, EFEM and carriers for VOC and used in analysis of mass.

I/PL.27

INTERACTIONS AND MULTILEVEL ORDERING IN SUPRAMOLECULAR ASSEMBLIES

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The process of self assembly at multiple lengthscales of bis-urea substituted toluene deposited on Au (111) by evaporation under high vacuum is studied by low temperature scanning tunnelling microscopy. Two dimensional organized supramolecular assemblies on areas higher than 100x100 nm² are obtained. Long oligomer chains (nx1) oriented by hydrogen bonds are obtained at the chemistry level in solution. Bringing these molecules to a surface leads to more complex structures (nxn) governed by other specific interactions at the endgroups of the molecule. This process of formation with different interactions types takes place at the early stages of organisation in which the substrate does not play a crucial role. Moreover, an interesting electronic behavior is evidenced by tunnel transparency at specific bias voltages. Correlation between hierarchical structures and electronic properties will be discussed from spectroscopic measurements of the LDOS. The orientation of the supramolecular layer with respect to the substrate will be discussed as a function of the organisation degree. This will evidence the competition of molecule-substrate and molecule-molecule interaction and their hierarchy on several lengthscales.

I/PL.28

CHEMICALLY SYNTHESIZED SEMICONDUCTOR NANOCRYSTALS EMITTING IN THE TELECOMMUNICATION WAVELENGTH RANGE

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The development of modern telecommunication networks requires the creation of efficient emitters at wavelength of 1.3 and 1.55 μm close to the low-loss windows of currently used optical fibers. Highly-efficient photoluminescence (PL) of colloidal prepared semiconductor nanocrystals (Ncs) and its size tunability make them very attractive for application in light-emitting devices. However, chemical synthesis of high-quality NCs is well-established only for wide-bandgap materials emitting in the visible.

Here, we report on a aqueous-based colloidal synthesis of HgTe Ncs with strong near-infrared PL, tunable in the wavelength range between 1.1 and 2.4 μm , using a variety of thiols as stabilizers. In contrast to previous reports on thioglycerol-capped HgTe NCs [1] we show the possibility to keep the PL quantum efficiency high during their growth. This is obtained by thermal annealing of Ncs emitting at 1.2 μm in aqueous solution, followed by a ligand exchange procedure, resulting in differently sized HgTe Ncs with PL peak positions up to 2.4 μm . By the choice of the capping thiol-molecules it is possible to provide different surface functionalities making Ncs soluble in variety of solvents. This opens great opportunities for the creation of the new functional materials via incorporation of HgTe Ncs into variety of matrixes. In particular, we have fabricated by layer-by-layer deposition techniques [2] highly luminescent thin film waveguides composed of hydrophilic HgTe Ncs and polyelectrolyte molecules, which can act as active materials in laser devices or in optical amplifiers.

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[2] G. Decher, Science 277, 1232 (1997).

I/PL.29

EXAMINING THE USE OF OXIDE PARTICLES TO ENHANCE THE SENSITIVITY OF POLYMER\CARBON BLACK NANOCOMPOSITE GAS SENSORS

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The versatility of polymer/carbon black composite materials is of special interest to the gas sensor industry where arrays of polymer/carbon black composites are used to identify gases and odours¹. These composite gas sensors operate at room temperature, which provides an advantage over thick film metal oxide gas sensors². They provide selectivity towards vapours based on the Flory-Huggins interaction parameter, which also make these materials ideal candidates for gas sensors³. The need to improve the response of existing gas sensing materials is always present. This study proposes the addition of SiO₂ particles to a polymer/carbon black composite to increase the sensitivity of polymer composites to Alcohol vapours. The sensors were prepared using 160mg polystyrene dissolved in 20ml THF. 40mg of carbon black was shear mixed into the solution along with 10mg of surfactant. Five polymer/CB suspensions were prepared in this manner with a different weight percentage of SiO₂ added to each suspension. A microlitre syringe was used to place a drop from each suspension onto interdigitated electrode patterns. Five sensors were tested with a homologous series of alcohols. The response of each sensor increased as the molecular weight of the Alcohol being tested increased. The response to each alcohol significantly increased as the weight percentage of SiO₂ in the sensor increased.

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2. Arshak K, et al., Sensor Review 2004.

3. Van Krevelen D. W., Properties of polymers, Elsevier.

I/PL.30NANOARCHITECTURES FROM WO₃, TiO₂ and CHITOSAN

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Novel nanocomposites formed from WO₃, TiO₂ and chitosan were prepared using the Layer-by-Layer (LBL) method. Characterization of the electrochemical and chromogenic properties of these materials have been examined, motivated by the stability, proton migration/diffusion process, colorless of chitosan and ability of complexation of chitosan with transition metal oxides, allowing the growth of nanocomposites. The quadratic logistic equation (QLE) was used to achieve the amount of electrochemical active sites (K) and molar absorption coefficient (ϵ) of WO₃ in LBL films, by fitting the absorbance changes (ΔA) resulting from the polaron hopping from W(V) to W(VI) sites. The number of electrochemical active sites for 4-bilayers of WO₃/chitosan before and after the deposition of TiO₂ nanoparticles were ca 15.5x10⁻⁹ mol cm⁻², 10.7x10⁻⁹ mol cm⁻², respectively. Different values of molar absorption coefficient were attributed to an enhanced polaron jump rate associated with ionic trapping effects, which was observed by electrochemical impedance spectroscopy. The association of these results with dissipation and feedback is discussed.

I/PL.31

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I/PL.32

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I/PL.33**PROBING THE MICROPOROUS NATURE OF HIERARCHICALLY TEMPLATED MESOPOROUS SILICA VIA POSITRON ANNIHILATION SPECTROSCOPY**

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Mesoporous silicas templated with amphiphilic block copolymers, either by true liquid crystal templating or those templated via cooperative processes have recently been shown to be hierarchically templated. The supramolecular template contributes to the overall mesopore, which is easily characterised via standard techniques, while the hydrated poly ethylene oxide in the amphiphilic block copolymer gives rise to the much smaller microporosity, the size of which has been relatively difficult to characterise.

In this study we report on the use of positron annihilation lifetime spectroscopy (PALS) to probe the micropores in silica materials templated from amphiphilic block copolymers in a cooperative process (SBA-15) and silica materials templated from amphiphilic block copolymer and trimethylbenzene microemulsions (mesocellular foam, MCF). The technique is seen to be powerful in detecting a decrease in the micropore size as the synthesis temperature is increased, which follows the trend seen in the micropore volumes determined from nitrogen adsorption t-plot analysis. For SBA-15, the micropore size determined compares well to a previously reported value estimated from argon adsorption t-plot analysis, while for MCF we provide the first reported investigation of its microporosity. We also examine the changes seen in the micropore size after the formation of hybrid (3-aminopropyl)triethoxysilane coated mesoporous silica, formed via post synthesis functionalisation. For the hybrid material, the BET surface area is significantly reduced, while the pore size remains essentially unchanged, possibly indicating that blocking or partial blocking of the micropores is occurring. This result is confirmed via PALS, where a reduction in the size of the micropores is seen.

I/PL.34**ASSEMBLY OF PREFORMED CRYSTALLINE NANOBUILDING BLOCKS INTO MESOPOROUS METAL OXIDES**

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Mesoporous metal oxides are attractive materials for diverse applications such as gas sensing, catalysis, optics, or electrochemistry. The evaporation induced self-assembly (EISA) of preformed crystalline nanobuilding blocks (NBB) combined with block copolymer templating techniques provides a versatile route to mesoporous metal oxides. The use of preformed nanoparticles is a particularly advantageous approach, because on one hand there is a large toolbox of readily available nanoparticles covering a wide range of compositions, sizes and shapes and on the other hand the reproducibility is generally enhanced, because control over hydrolysis and condensation of the molecular precursors as well as over the crystallization process during calcination can be avoided. The shrinkage of the metal oxide framework is negligible during the removal of the organic template by calcination and the pore accessibility may be enhanced because of particle-particle interstices. Finally, and most important, the nanoparticle approach offers the possibility to mix several different metal oxide nanoparticles in order to obtain mesoporous materials with highly complex compositions, which cannot be realized by molecular precursor approach.

We will present the synthesis of various crystalline mesoporous metal oxides prepared by the NBB approach based on the polymer-directed assembly of preformed metal oxide nanoparticle sols. As starting material we use single component metal oxide nanoparticles as well as mixtures of various metal oxide nanoparticles dispersed in water as well as in tetrahydrofuran. We will present the experimental procedures together with a detailed structural characterization of the final porous material.

I/PL.35**SYNTHESIS AND CHARACTERISTICS OF SEMICONDUCTOR AND METAL NANOPARTICLES BY A MICROCHANNEL REACTOR**

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Semiconductor and metal nanoparticles are synthesized in continuous flow by microchannel reactor. The microchannel reactor was used due to its possibility of continuous process in nanoparticle synthesis. The synthesis was carried out in microchannel (several hundreds mm diameter) made from stainless steel or PTFE. The relationship between particle size and experimental variables including reaction temperature, time and concentration of precursor solution were investigated. Their size, morphologies and phase are analyzed with high-resolution transmission electron microscope, X-ray diffraction and photo-luminescence. Nanosized particles of semiconductor and metal were successfully prepared by this method. Detailed properties of nanoparticles and their possible applications will be discussed.

I/PL.36**LIGHT-EMITTING DIODES FROM SELF-ORGANIZED CONJUGATED POLYMER/SILICA MESOSTRUCTURES**

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The photophysics of conjugated polymers are determined by intrachain excitations. However, it has been well established that the optical and electrical processes in semiconducting polymer devices are dramatically affected by solid-state effects such as polymer crystallinity, aggregation, interchain interactions and stacking. Therefore, attaining control over the morphology and hierarchical structure in the polymer film is expected to enhance device performance and provide an entry to the design and fabrication of new types of devices. In this study conjugated polymers are confined into the ordered pores of a mesoporous silica scaffold to avoid aggregation and control orientation of individual polymer chains. The mesoscopically ordered conjugated polymer/silica nanocomposite thin films are prepared using the evaporation-induced self-assembly technique from a homogenous sol containing surfactant and pre-polymerized polymers on a variety of substrates. The hierarchical structure is studied with XRD and TEM. A red-shift in the absorption and emission spectra of the confined polymer compared to those of a pristine polymer film, and the absence of a Stokes shift, are indicative of an extended planar intrachain arrangement with no interchain interaction. Light-emitting diodes were prepared by sandwiching (PPV)silica and (polyfluorene)silica composite films between an ITO anode and a metallic cathode. The observed electroluminescence is due to intrachain electronic processes including transport, exciton formation and radiative recombination. Hence, these nanocomposites and diodes provide a unique system to study opto-electronic processes on single polymer chains.

- I/PL37** ELECTROCHEMICAL STUDY ON OVER-GRAFTED PLATINUM NANOPARTICLES LANGMUIR-BLODGETT FILMS
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 We report on Pt nanoparticles functionalized with 4-mercaptoaniline [1] over-grafted with 2-thiophenecarbonyl chloride. We built up stable Langmuir-Blodgett (LB) films from these particles mixed with a fatty acid. Such ultra-thin films were transferred on various substrates, which allowed characterization by CV, and physical techniques as IR, XPS, TEM and XRD.
 The electrochemical activity of such nanoparticles towards O₂ reduction was investigated in acidic medium [2]. It revealed a direct activity without any previous activation treatment in spite of the presence of the organic crown at the particles surface. Furthermore, XPS evidenced that this organic shell was not modified upon prolonged cycling. We present here the study on the influence of the number of LB layers on the electroactivity towards O₂ reduction. By increasing the number of layers, the peak potential shifts towards a positive limit and the current density increases to reach a plateau. This last current saturation suggests that only the external part of the multilayer is electroactive. Thus the buried layers work only as an electrons transmitter. To confirm this particular configuration, we used a reversible and monoelectronic system such as [Fe(CN)₆]^{3-/4-} as electrochemical probe. By increasing the number of layers the two peaks potentials got slightly closer and the current densities grew up until a plateau as in the case of O₂ reduction. We also performed an XPS characterization of the samples bearing an increasing number of layers, which showed the layered structure of the films.
 [1] H. Perez, J-P. Pradeau, P-A. Albouy, J. Perez-Omil, Chem. Mater., 1999, 11, 3460.
 [2] S. Cavaliere, F. Raynal, A. Etcheberry, M. Herlem, H. Perez, Electrochemical and Solid State Letters 2004, 7, A358.
- I/PL38** MICROSTRUCTURE OF BRACHIOPOD SHELL CALCITE - A WELL OPTIMIZED HYBRID FIBRE COMPOSITE MATERIAL
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 The calciumcarbonate armors of shell-forming invertebrates are excellent prototypes for optimized micro- and nanostructured hybrid materials. We investigated the ultrastructure of the calcite shell of three terebratulide brachiopod species with SEM and electron beam backscattering diffraction. The primary layer is nanocrystalline and displays strongly enhanced Vickers hardness. The material of the secondary layer is an inorganic/organic fibre composite optimized for fracture toughness. The morphological fibre axes of the single crystal fibres with typical dimensions of 150 microns x 15 microns x 8 microns are almost parallel to the shell surface. The fibrous growth occurs in arbitrary directions perpendicular to the <0001> triad symmetry direction of calcite. Accordingly, the fibres form a cylindrical <0001> "fibre" texture, with the texture axis perpendicular to the shell surface. A curvature of the fibres is caused by lateral displacements or rearrangements of the secreting cell array during growth. The Vickers hardness of the fibrous layer decreases from the outside to the inside surface of the shell.
- I/PL39** Withdraw
- I/PL40** STAR GEL HYBRID MATERIALS WITH MEDICAL APPLICATIONS
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 Star Gels are a type of organic-inorganic hybrids that present a singular structure of an organic core surrounded by flexible arms which are terminated in alkoxy silane groups. These groups would form a silica-like network through the sol-gel process. This characteristic structure allows to have precursors with flexibility at a molecular level, which is an important feature when used as implant materials.
 The synthesis of star gel monoliths requires long time of drying, and the formed network presents mechanical characteristics between conventional glasses and highly cross-linked rubbers. In the present work, the star gels are synthesised through the sol-gel process using an acid catalysed route. Thus, the presence of silanol groups together with the possibility of introduction of Calcium brings the possibility of having a bioactive behaviour. This feature together with the particular mechanical properties of the material, make these hybrids as a good candidates to use as implant materials. The hybrids have been prepared with the appropriated precursors and calcium alkoxides as the calcium source as starting materials and subsequently soaked into a simulated body fluid (SBF) for different periods of time and the bioactivity of hybrids was determined by examining the apatite formation on the surface of the monoliths by Fourier Transform Infra-Red (FT-IR) spectroscopy, X-Ray and Scanning Electron Microscopy (SEM).
- I/PL41** TAILORING THE MORPHOLOGY OF OXIDE NANO-ISLANDS THROUGH THE SUBSTRATE MISCUT ANGLE
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 The control of the microstructure at a nanometer scale of advanced materials is a crucial issue in the continuous scaling of opto- and micro-electronic devices to ever smaller dimensions. In particular oxide materials are subject of intense research although few is known about their ability to spontaneously form self-assembled or self-organized nanostructures, as compared to III-V or IV-IV semiconducting materials.
 In this communication we focus on the effects of the surface energy of the substrate on the morphology of the epitaxial yttria-stabilized-zirconia (YSZ) nano-islands. YSZ thin films have been grown onto (0001) sapphire substrates by sol-gel dip-coating. The microstructural characterizations have been carried out by atomic force microscopy and high-resolution X-ray diffraction with the reciprocal space mapping technique. In agreement with previous works, it is shown that YSZ thin films break up into epitaxial nano-islands after high temperature post-deposition thermal annealing. Two different island morphologies are encountered: flat-top islands and rounded islands each having a characteristic orientation to the substrate, and thus different interface energies. A modification of the substrate surface energy via the miscut angle allowed to change the relative amount of those two types of islands. The modification of the miscut angle appears as an attractive and simple method to control the morphology of epitaxial nano-islands.

I/PI.42**SYNTHESIS, SELF-ASSEMBLY AND ELECTRICAL PROPERTIES OF OLIGOTHIOPHENES 'FREE' OR GRAFTED TO ALIPHATIC RIGID SCAFFOLDS**

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The ability of oligothiophenes to hierarchically self-assemble in thin films upon melt-quenching or vacuum evaporation processes has been recently demonstrated.[1,2]

However, more systematic studies are required in order to synthesize molecular structures capable to achieve high molecular ordering - hence good electrical performance - by spontaneous self-assembly, for example by casting from solution. Our strategy to tackle this problem consists in imposing well defined chemical spatial constraints to the spontaneous tendency of thiophene oligomers to self-organize. In this communication we report the synthesis and characterization of several quater- and quinquethiophenes with p or n semiconductor properties and characterized by liquid-crystalline behaviour. The oligomers were then grafted to rigid scaffolds of different shapes and the characteristics of the films obtained by solution casting of these superstructures were analyzed with a variety of techniques. The relationship between the structure of the films and the electrical characteristics will be discussed.

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[2]P. Viville, R. Lazzaroni, J. L. Brédas, P. Moretti, P. Samori, and F. Biscarini. Adv. Mater. 1998, 10, 57-60.

I/PI.43**DEPOSITION OF 2-AMINO-1-PROPANOL ON Cu(110) SURFACE: CHEMISORPTION**

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Chirality is a geometrical property of an object of existing in two mirror forms. Contemporary interest focuses on the possibilities of molecular-level engineering using chiral systems due to the increasing demand of producing molecular products of a single handedness, that is, enantioselective.

We are studying the possibility of transferring chiral information across an interface considering chiral molecules (2-amino-1-propanol) adsorbed on a metal surface Cu(110); this system represents an experimental model that works for molecular recognition in processes such as enantiomeric separations of chiral compounds, enantiospecific recognitions in sensors and heterogeneous asymmetric catalysis. Self-assembling of 2-amino-1-propanol on Cu(110) is performed in ultra high vacuum (UHV) and investigated via X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). We analysed the modifications of the core line of C 1s, O 1s, and N 1s and the LEED pattern as a function of the 2-amino-1-propanol coverage to understand growth morphology, molecule-substrate bonding formation and self-organization into long range ordered structures.

I/PI.44**HIGH TEMPERATURE NANOSTRUCTURED HYBRID MEMBRANES FOR FUEL CELLS**

Ioan Stamatin(a), Adina Morozan(a), Keith Scott(b), Anca Dumitru(a), Victor Ciupina(c), G. Prodan(c), (a)University of Bucharest, Faculty of Physics, 3Nano-SAE Reserch. Centre, P.O. Box MG-11, 077125, Bucharest-Magurele, Romania, (b)School of Chemical Engineering and Advanced Materials, University of Newcastle upon Tyne, NE1 7RU, U.K., (c)Ovidius University of Constanta, Bd. Mamaia 124, Constanta, Romania To reach higher working temperatures for polymer electrolyte fuel cells (PEMFC), a great deal of effort is required to develop new polymers and hybrid organic/inorganic compounds. These materials must have high thermal stability improved ionic conductivity, CO-tolerance,etc. In fuel cells design there are two extremes: SOFCs (high operating temperature places severe constraints on materials) and PEMFCs (low temperature but with the inconveniences of polymer membranes). To combine the two materials technology advantageously requires materials organized at the nanoscale by functionalizing or mixing their properties. The aim of this paper is to combine a new membrane of polyacrylonitrile (PAN), in different stages of thermo-oxidation, with nanometric yttria stabilized zirconia (YSZ), over the percolation threshold, to achieve thermal stability up to 400 0C, whilst maintaining the same ionic conductivity as in the SOFC. By a proprietary method, of thermo-oxidation of the PAN in a thermo-centrifugal field, ladder polypyridine derivative films with embedded nanometric YSZ particles were obtained, and used as high temperature nanostructured hybrid membranes. The characterization was achieved with FT-IR, XRD and TEM. Ionic conductivity and permeability were evaluated in a special fuel cell setup. When the nanometric YSZ is used in a matrix with high thermal stability, the performance is close to that of Nafion membranes, but in a larger range of temperature, up to 400°C.

I/PI.45**PREPARATION OF NANOGEL-CALCIUM PHOSPHATE HYBRID NANOPARTICLES**

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Organic-inorganic hybrid nanoparticles of polymer nanogels and calcium phosphate were synthesized by controlled precipitation from aqueous solution. Nanogels of cholesterol-bearing pullulans (CHPs) were employed as templates for calcium phosphate formation. CHPs form stable hydrogel nanoparticles 20-30 nm in size in aqueous solution by the self-assembly of hydrophobic cholesterol moieties of CHP.[1] Calcium phosphate was precipitated from aqueous solution in the presence of CHP nanogels at room temperature. Transmission electron microscopy, atomic force microscopy, and infrared spectra analysis revealed that the precipitates obtained were hybrid nanoparticles less than 100 nm in size consisting of CHPs and amorphous calcium phosphate. These new hybrid materials have potential applications in the fields of regenerative medicine and drug delivery systems.

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I/PI.46**POLY(FERROCENYLSILAZANES) PRECURSORS FOR ADVANCED NANOSTRUCTURED CERAMICS**

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Polymer-derived ceramics (PDCs) is a relatively young research area, thus new types of ceramic materials for high-temperature applications can be processed at relatively low temperatures compared to traditional ceramic fabrication methods. Specifically, this development enables the production of non-oxide containing ceramic materials via pyrolysis-sintering of organometallic polymers

This work proposes a plasm-chemical route for copolymer precursor's synthesis as sources of advanced nanostructured multicomponent ceramics, with predictable properties such as high thermal stability and magnetic properties. The contribution concerns with advantages offered by plasma polymerization of poly(ferrocenylsilazane) copolymers from precursors silazanes and ferrocene. This method is more suitable for precursors in nanostructured ceramics as ready for sintering. Plasma polymerization has been done in a large volume RF-reactor, inductive coupled and collected powder was converted in a ceramic by thermal treatment at 1500 °C. XRD, SEM, TEM, dielectric and magnetic properties are taken in account to evaluate the performances of these materials. The composition and architecture of the cross-linked copolymer material and correspondingly, the resultant ceramic can be tailored through variations of synthesis parameters (flow, pressure, power discharge, temperature, time, monomer dosage and atmosphere), and respectively pyrolysis conditions.

I/PI.47**HIERARCHICAL ASSEMBLY OF SURFACTANT MICELLES THROUGH COORDINATION CHEMISTRY**

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A novel approach to the fabrication of supracolloidal structure where specific coupling agents drive the assembly of spherical and cylindrical surfactant micelles is described. The coupling agents used bear chelating functions inducing a metal-ligand complex as linkage between the micelles. The supracolloidal built structure is dictated by both the interactions types used, related to the nature of the coupling agent, and also by an adjustable degree of connectivity.

The challenge is to tune the amplitude and range of the induced attractive potential between surfactant micelles allowing the assembly of the surfactant micelle in order to obtain stable supracolloidal suspensions. Several types of coupling agent (functionalized surfactant and double hydrophilic block copolymer) were developed with various chelating groups (phosphoryl, carbonyl and glycol) and different anchoring groups. The influence of nature of the metal (Al, La, Ni...) on the supracolloidal structure was also investigated. Supracolloidal structures from spherical micelles were characterized by scattering techniques (SANS, DLS) while those obtained from giant cylindrical micelles were characterized by rheology.

I/PI.48**STRUCTURE AND COAGULATION OF TiO₂ HYDROSOLS OF DIFFERENT DISPERSITY**

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Nanocrystalline TiO₂ hydrosols are used for the preparation of highly ordered nanostructures. For the formation of these structures it is necessary to have uniform TiO₂ nanocrystals and to know features of their coagulation in water media. In this work we isolated some narrow fractions of TiO₂ nanocrystals from the initial stable hydrosol, prepared from them a series of uniform hydrosols stabilized by acid with a mean hydrodynamic particle radius R ranged from 5 to 15 nm, studied the peculiarities of coagulation of these sols by HCl and KCl, and regarded the structure of some concentrated sols and gels.

XRD in small and wide angles of scattering revealed that the TiO₂ fractions studied consist of anatase nanocrystals of a plate-like shape, the plate thickness amounting 2-3 nm. The concentrated sols and gels with the reduced concentration of electrolytes were found to have the nanometer periodicity. Investigation of the coagulation using turbidimetry, QELS, and SAXS elicited the rapid and slow processes. The reversibility of the both processes was studied. Dependencies of the rapid coagulation threshold and of the slow coagulation rate on R, pH, and electrolyte composition were regarded. It was shown, in particular, that the coagulation threshold increases essentially on decreasing the nanocrystals size and the slow coagulation rate has a minimum on changing pH. The coagulation dependencies studied permit to optimize the fractionation of TiO₂ hydrosols and the formation of colloid crystals procedures.

I/PI.49**HIERARCHICAL POROUS MATERIALS WITH A MULTIMODAL PORE SYSTEM AND THIN FILMS OF METAL OXIDES**

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Hierarchical porous materials are of great interest owing to their important role in the systematic study of structure-property relationship and sol-gel templating.

In this study porous materials (silica and titania) exhibiting a hierarchically ordered multimodal pore system with a well-defined reverse opal microstructure and bimodal mesoporosity in the walls were fabricated using mixtures of polymer colloids and specifically designed surfactant templates in a sol-gel templating process. In order to create mesopores of ca. 13 nm in size, so-called "KLEs" (poly(w-hydroxypoly(ethylene-co-butylene)-co-poly(ethylene oxide)), and for the smaller ones an ionic liquid (IL) template (1-hexadecyl-3-methylimidazolium-chloride) were used. Additional macroporosity was created by the presence of colloids of tunable size (50-500 nm). These silica materials, besides having smaller macropores down to 70 nm, represent a significant progress compared with previously reported bi- or trimodal porous systems. The pores are well defined in size and shape on all two or three length scales and no phase separation is observed between two surfactant templates. Our results exclude the formation of mixed micelles of KLE with the IL that is attributed to the strong self-aggregation tendency of the IL. Another peculiarity of these materials is high BET surface area and mesoporosity. Mesoporous-macroporous highly crystalline titania was also prepared with the same approach by addition of an amorphous mortar such as P2O₅. The addition of P2O₅ prevents mesostructural collapse and increases the temperature stability of the materials. This approach is also applicable to fabricate corresponding thin films of metal oxides with hierarchical porosity.

I/PI.50**SOL GEL DERIVED ZnO/SiO₂ NANOSTRUCTURES FOR SECOND HARMONIC GENERATION**

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In the recent years there has been intense interest in the development of new non linear optical materials. In that context, zinc oxide (ZnO) has been recently re-discovered as a promising material for efficient second-harmonic generation (SHG). In particular significant enhancement of the 2nd order non-linear susceptibility occurs when the ZnO crystallites size is reduced to a few nanometers. In this communication attention is focused on ZnO/SiO₂ nanostructures produced by sol-gel processing. Zinc nitrate and tetraethylorthosilicate were used as precursors for ZnO and SiO₂. We recently developed a specific gelation and drying procedure that allows to produce large samples of bulk xerogel. Subsequent thermal treatment at 600°C induces the appearance of zinc oxide nanoparticles (~10 nm) dispersed in a transparent silica glass matrix. The crystallization and growth behavior of those particles have been investigated using small angle x-ray scattering (SAXS), transmission electron microscopy (TEM) and high resolution x-ray diffraction (XRD). The SHG properties have been investigated using the 1064 nm output of a Nd-YAG laser. SHG have been observed in these materials and we investigated the dependence of the SHG signal on the microstructure of the samples. Detailed results will be given at the conference.

I/PI.51**KNbO₃ EPITAXIAL THIN FILMS GROWN BY POLYMERIC PRECURSOR METHOD**

I.T. Weber, A. Rousseau, V. Bouquet, M. Guilloux-Viry, A. Perrin, Institut de Chimie de Rennes, LCSIM-UMR 6511 CNRS, Université de Rennes 1, 35042 Rennes Cedex, France

KNbO₃ is a ferroelectric material well known for its potential application in different areas. Nowadays, microwaves devices appear as a large field of application and give to KNbO₃ and its solid solution KNb_xTa_{1-x}O₃ a specific interest as a low loss material with the possibility to tune the Curie temperature via "x" values. For these applications high quality materials fitting integration criteria are required. In this context, KNbO₃ thin films were prepared by the aqueous chemical solution route based on Pechini process, which is a quite simple method requiring low cost equipments. Thin films were grown onto different single crystal substrates (LaAlO₃, SrTiO₃ and MgO). Well crystallized single-phased films were obtained for samples annealed at temperatures above 550°C, provided that synthesis and coating conditions were optimized. In particular, no K deficient neither K enriched phases were detected up to 750°C. Epitaxial growth was evidenced in the case of LaAlO₃ and SrTiO₃ by electron channeling patterns (ECP) and 4-circles X ray diffraction patterns. Depending on the films, (110) and (001) orientations were promoted. Scanning electronic microscopy (SEM) observations showed that the films microstructure is homogenous, continuous, crack-free and quite dense, presenting good adhesion and thickness of approximately 100 nm per layer.

I/PI.52**MOLECULAR DYNAMICS OF CONFINED GLUCOSE SOLUTIONS**

G. Lelong, CRMD, 1B Rue de la Férollerie, 45071 Orléans Cedex 2, France, D.L. Price, HFIR/Center for Neutron Science, Oak Ridge National Lab., Oak Ridge TN, USA, A. Douy, CRMHT, 1D avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France, S. Kline, NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg MD, USA, J.W. Brady, Dept of Food Science, Cornell University, Ithaca NY, USA, M.-L. Saboungi, CRMD, 1B Rue de la Férollerie, 45071 Orléans Cedex 2, France

Certain living bodies are able to survey inside hostile environments in which the life seems to be completely impossible. In order to understand origins of their resistance, numerous studies were carried out on these animals and plants species. Previous works have shown that to protect themselves against the hazards of drying and freezing, they are secreting mono- or poly-saccharides. The presence of these solutes increasing the glass transition temperature, the sugar solution is able to vitrify inside the protein structure of the membrane and maintain that structure against further dehydration.

The particularity of these sugars is to exhibit unusually high glass transition temperature proving the major role of the dynamics in this phenomenon. Our recent study was focused on the dynamics of sugar molecules in aqueous solutions confined in environments trying to mimic those of living cells. The confinement was successfully realised inside silica gel containing deuterated sugar solutions in the desired concentrations. These samples were studied by quasielastic neutron scattering for the dynamical properties and by small angle neutron scattering for the structural properties. The SANS measurements on the gels without sugar give us an average pore size diameter of the silica matrix around 18-19 nm. The dynamics studies have shown that for this pore diameter the dynamics was not significantly affected by the confinement. Nevertheless, the same properties than those observed in the bulk solutions (decreasing of the dynamics with the increasing of sugar concentration, clustering of sugar molecules) were observed in our case showing the validity of the synthesis method (Lelong, G. and al.; submitted to J. Chem. Phys).

I/PI.53**EFFECTS OF CeO₂ DOPING ON THE SUPERCONDUCTIVITY OF THE YBaCuO SUPERCONDUCTORS**

This work was supported by Korea Research Foundation Grant (KRF-2004-041-D00293)

Sang Heon Lee, Department of Electronics Engineering, Sun Moon University Asan, Chung Nam, 336-840, Korea

The electromagnetic properties of CeO₂ doped and undoped YBaCuO superconductor were evaluated to investigate the contribution of the pinning centers to the magnetic effect. It was confirmed experimentally that a large amount of magnetic flux was trapped in the CeO₂ doped sample than that in the undoped one, indicating that the pinning centers of magnetic flux are related closely to the occurrence of the magnetic effect. It is considered that the area where normal conduction takes place increases by adding CeO₂ and the magnetic flux penetrating through the sample increases. The results suggested that CeO₂ acts to increase pinning centers of magnetic flux, contributing to the occurrence of the magnetic effect. All the doped CeO₂ could be successively separated from 123 phase by applying the partial melt process. Superconducting transition temperature of the samples was as high as 90K regardless of CeO₂ content up to 5 wt%. The separation of the dopant from the superconducting phase resulted in the constant T_c regardless of CeO₂ content. The CeO₂ was converted to fine BaCeO₃ particles which were trapped in 123 matrix during the peritectic reaction.

Session III : Magnetic nanomaterials

Session chairs :

- I-III.01** 14:00 -Invited- ORGANIZING MOLECULAR NANOMAGNETS
D. Gattschi
- I-III.02** 14:45 -Invited- Si/SiO₂ NANOPARTICLE HETEROSTRUCTURES FOR ELECTRONIC MEMORY APPLICATIONS
M.L. Ostraat
- I-III.03** 15:15 DESIGN OF HYBRID ORGANIC-INORGANIC LAYERED STRUCTURES COMBINING MAGNETIC AND OPTICAL PROPERTIES
A. Demessence, M. Werner, G. Rogez and P. Rabu, IPCMS-GMI, 23 rue du Loess, B.P. 43, 67034 Strasbourg Cedex 2, France
Intercalation of organic molecules into inorganic layered materials is an efficient way for building up new organic-inorganic architectures [1] where each sub-network may exhibit its own physical property.
In this respect, the chemistry of layered transition-metal hydroxides, M₂(OH)₃A (M = Co, Cu, Ni, Mn and A = NO₃⁻, CH₃CO₂⁻, Cl⁻), with botallackite or brucite-type structure is well adapted for the design of hybrid materials with outstanding magnetic properties [2]. The A anions located in the interlayer space may be easily substituted by organic species. This species can act as pillars or connectors between the magnetic layers, and, due to strong chemical bonds between inserted molecules and metal-based layers, interaction between sub-networks is favoured. Our strategy is to use such organic molecules to combine a new physical property with the magnetic ones afforded by the inorganic host. We will present the synthesis and properties of new hybrid compounds combining magnetic and optical properties such as chirality and luminescence using hydroxycarboxylates, thiophenecarboxylates and OPV. For the later, it has been shown that the magnetic ordering may influence the luminescence of inserted organic moieties [3].
[1] Special Issue, Chem. Mater. 2001, 13.
[2] P. Rabu et al., Magnetism : Molecules to Materials, Ed. by J. S. Miller and M. Drillon (Wiley VCH, Weinheim, Germany) 2001, 357-395.
[3] J.-M. Rueff et al., Chem. Mater, 2004, 16, 2933-2937.
- I-III.04** 15:30 SPIN LIFETIME ENHANCEMENT PROBED IN A SINGLE AU NANOPARTICLE
A. Bernand-Mantel, P. Seneor, L. Calvet, N. Lidgi, V. Cros, K. Bouzehouane, S. Fusil, C. Deranlot, A. Vaures, F. Petroff and A. Fert, Unité Mixte de Physique CNRS/Thales, Domaine de Corbeville 91404, Orsay, France and Université de Paris-Sud, 91405 Orsay, France
Spin injection in metal nanoparticles or clusters can give rise to outstanding effects due to the interplay of spin-dependent tunneling and electrical charging effects. Spin accumulation is expected to be enhanced owing to the discrete energy levels and the large charging energies, when the particle size is sufficiently small.
We investigate Coulomb blockade and spin accumulation effects in a single nonmagnetic metallic nanoparticle. A layer containing gold clusters of a few nanometers in diameter embedded in an oxide layer of alumina is grown by sputtering. After an optical lithography process, the fabrication is carried out using a conductive tip AFM where the nanoindentation process is electrically monitored in real time. With this technique, we contact particles of a few nanometers size. We observe Coulomb steps in the I-V curves which are characteristic of a current flowing through a single nanoparticle. Magnetoresistance effects are found when the two electrodes are ferromagnetic. Comparison of the I-V characteristics in both parallel and antiparallel configurations allows a simple estimation of the spin lifetime in nanoclusters. Direct evidence for a spin lifetime enhancement of 3 orders of magnitude in gold nanoparticles is found.
- I-III.05** 15:45 MAGNETIC NANO-COMPOSITE MICELLES AND VESICLES
S. Lecommandoux(a), O. Sandre(b), F. Chécot(a), J. Rodriguez-Hernandez(a), R. Perzynski(c), (a)Laboratoire Chimie des Polymères Organiques (LCPO), UMR 5629 CNRS-ENSCP, University Bordeaux 1, 16 avenue Pey Berland, 33607 Pessac, France, (b)Laboratoire Liquides Ioniques et Interfaces Chargées, UMR 7612 CNRS, Université Pierre et Marie Curie, 4 place Jussieu, case 63, 75252 Paris cedex 05, France, (c)Laboratoire Milieux Désordonnés et Hétérogènes, UMR 7603 CNRS, Université Pierre et Marie Curie, 4, place Jussieu – case 78, 75252 Paris cedex 05, France
Novel magnetic nano-composites are obtained by the self-assembly in water of polypeptide based diblock copolymers polybutadiene-b-poly(glutamic acid) combined with hydrophobically modified g-Fe₂O₃ nanoparticles. These hybrid supramolecular objects are either filled micelles (3-d) or hollow vesicles with a magnetic membrane (2-d), which deformation under an applied magnetic field has been evidenced. These nanoparticles are also able to respond to stimuli such as pH and ionic strength due to the presence of the polypeptide block, thus forming what we called multi-responsive nanocapsules. These superparamagnetic self-assembled hybrids offer attractive potentialities in biomedicine and biotechnology due to their dimensions (0.1-0.5 microns) small enough to stay for some time in the blood circulation, and to the properties brought by the iron oxide nanoparticles: possible manipulation by an external magnetic field gradient, local heating by a radio-frequency field for cancer radio-therapy, labeling of organs to enhance the contrast in Magnetic Resonant Imaging.

16:00

BREAK

Session IV : Nanoporous systems

Session chairs :

- I-IV.01** 16:30 -Invited- SUPRAMOLECULAR APPROACHES TO NANOPOROUS MOLECULAR MAGNETIC MATERIALS. FROM NANOSCALE CLUSTERS TO 3-D MAGNETS
J. Veciana
- I-IV.02** 17:15 -Invited- NEW FUNCTIONAL HYBRID MATERIALS - NANOPOROUS MATERIALS
Filipe A. Almeida Paz(a), Fa-Nian Shi(a), Joao Rocha(a), Tito Trindade(a) and Jacek Klinowski(b), (a)Department of Chemistry, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal, (b)Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K.
- I-IV.03** 17:45 A ROUTE TO HEAT RESISTANT SOLID MEMBRANES WITH PERFORMANCES OF LIQUID ELECTROLYTES
M-A. Néouze, J. Le Bideau, A. Vioux, Institut Gerhardt, UMR CNRS 5637, CC 007 Université Montpellier 2, 34095 Montpellier, France and F. Leroux, Laboratoire des Matériaux Inorganiques, UMR CNRS 6002, Université Blaise Pascal, 63177 Aubière, France
Immobilization of ionic liquid within a robust oxide network has been carried out. Ionic liquid are well known as electrolytes due to their high ionic conductivity and their wide decomposition potential (up to 6 V), combined with their chemical stability, non volatility and non flammability. They proved to be competitive in electrochemical devices, such as solar cell and fuel cells. For such applications, polymer membranes swollen with ionic liquids offer an attractive way to immobilize ionic liquids, however the thermal stability of such systems remains limited by the organic nature of the polymer. Here we present a new family of transparent, temperature-resistant (up to around 600 K) solid electrolytes whose preparation and shaping are very easy and cheap. Numerous applications could be addressed (fuel cells, solar cells, electrochromic devices, chemical probes...), by tuning the properties of ionogels upon playing on the sol-gel method, on the nature of the sol-gel precursors and on the choice of the ionic liquid. The synthesis consists in a non-hydrolytic sol-gel route carried out in an ionic liquid R⁺X⁻, typically using a mixture of TMOS and formic acid. The ionogels show a conductivity of the same order of magnitude as that of bulk ionic liquids (e.g. 3.10⁻² S.cm⁻¹ and 8.10⁻² S.cm⁻¹ around 500 K for R⁺ = 1-butyl-3-methylimidazolium and X⁻ = bis(trifluoromethylsulfonylimide)).

18:00-19:00

POSTER SESSION II

19:00

AWARD CEREMONY

The symposium organizers and the candidates to the graduate student award are requested to attend.

CONFERENCE RECEPTION

POSTER SESSION II
Wednesday, June 1, 2005
18:00 – 19:00

I/PII.01 DYNAMIC COMPETITION OF PHOTOOXIDATION AND DISSOLUTION OF Si IN ALKALINE ELECTROLYTES: FORMATION OF NANOSTRUCTURES

K. Skorupska(a), M. Aggour(a), Eder Goncalves(a), Ralf Hunger(b), M. Kanis(a), M. Lublow(a), Elmar R  ther(a), T. Wilhelm(a), H. Jungblut(a) and H.J. Lewerenz(c), (a)Hahn-Meitner-Institut, Glienicke Str 100, 14109 Berlin, Germany, (b)TU Darmstadt, FB Materialwissenschaften, Germany, (c)Department of materials Science and Engineering North Carolina state University Research Building 1, 1001 Capability Road, Raleigh, NC 27695, USA

NaOH and KOH are the commonly used silicon etching agents for micromachining of silicon wafers. The anisotropic etching of Si in alkaline solution allows the fabrication of microdevices requiring a precise three-dimensional structure. This fabrication of precisely dimensioned silicon microstructures for devices such as accelerometers, pressure sensors and ink jet nozzles is of current industrial interest. The fabrication of future nano-dimensional devices requires a detailed understanding of the dissolution mechanism and of the origin of anisotropy.

The dissolution of Si in alkaline solution can be chemical or mixed chemical and electrochemical. It is known that the etch rate depends on the applied potential in electrochemical experiments and models have been developed to explain the purely chemical as well as the mixed dissolution. In this work, we investigate the dynamic competition of oxidation and dissolution of illuminated n-Si by combining chemical surface analysis (synchrotron radiation photoelectr. Spectr., SRPES) and structural characterization (atomic force micr., AFM). SRPES and AFM are done after electrochemistry on float zone n-Si<111> in dilute alkaline solution. The photooxidation of H-terminated Si (111) results in oxide stress which leads to small cracks through which, particularly for the ultrathin films prepared here, electrolyte can reach the silicon surface. The resulting nanopit formation under potential control (which itself, together with the light intensity controls the oxide thickness) is investigated using AFM. The initial and subsequent oxide formation is analyzed by SRPES. The anisotropy of the etch rate between Si and its oxide results in a self organized nanostructure. Future design possibilities of surface nanotopographies are outlined.

I/PII.02 GISAXS STUDY OF GOLD IMPLANTED GLASS

B. Pivac, P. Dubcek, I. Kovacevic, R. Boskovic Institute, P.O. Box 180, Zagreb, Croatia, S. Bernstorff, Sincrotrone Trieste, SS 14, km 163.5, Basovizza (TS), Italy, R. Mu, M. Wu, A. Ueda, Fisk University, Nashville, TN 37831, USA, B. Vlahovic, NCCU, Durham, NC, USA

The interest in metal nanocrystals is focused on their nonlinear optical properties, as they are expected to have a large third order nonlinear susceptibility. To explore the possibility of tuning the surface and shape of metal nanocrystals we implanted gold in glass. Gold ions of an energy 1.1 MeV and doses of 1, 3, 6 x 10¹⁶ ions/cm² were implanted in fused silica and Vycor glass. All samples were subsequently annealed from 900 to 1100°C in air. Rutherford backscattering was employed to characterize the gold profile after each step. The grazing incidence small-angle X-ray scattering (GISAXS) method with synchrotron light was used to study the morphology and the distribution of gold nanoparticles formed in the substrate. It is shown that the performed thermal treatment significantly affects the Vycor glass leading to larger pore radius, while it is not affecting the properties of silica glass. Samples of fused silica implanted to the highest doses but without annealing, already begin to show signs of clustering which is further pronounced upon annealing. Similar behavior in Vycor glass is largely dominated by the present pores. Specially upon annealing the difference between the two substrates is clearly visible confirming our expectation that existing pores will modify metal nanoclustering.

I/PII.03 AC CONDUCTANCE OF (Co_{0.45}Fe_{0.45}Zr_{0.10})_x(Al₂O₃)_{1-x} NANOCOMPOSITES

Anis Saad, Al-Balqa Applied University, P.O.Box 2041, Amman 11953, Jordan, A.B. Fedotov, I.A. Svito, A.V. Mazanik, Belarusian State University, Minsk, 220050 Belarus, B.V. Andrievsky, A.A. Patryn, Technical University of Kozsalin, Voronez, Kozsalin 119899, Poland, Yu.E. Kalinin, A.V. Sitnikov, Voronezh State Technical University, Voronez 250770, Russia

The influence of composition on AC carrier transport of composite films containing amorphous CoFeZr nanoparticles in amorphous aluminium oxide matrix has been investigated. The films with 3-5 nm thicknesses and variable composition 30 at.% < x < 60 at.% were sputtered on single substrate from the compound target in the chamber with argon-oxygen gas mixture. AC conductance measurements were performed in frequency range of 102-106 Hz at the temperatures from 80 to 330 K. DC conductance measurements were also carried out for this temperature region. The measurements have shown the presence of 3 composition regions where frequency-temperature dependences of conductance revealed different behavior. For the samples with the metallic alloy concentration 40at.% < x < 55at.% AC conductance does not depend significantly on frequency and is characterized by activation temperature dependences as for DC conductance. For the samples with x < 40at.% the frequency dependence of AC conductance is governed by power law R(w) ~ w^{-s} (s ≈ 2) at low temperature region (< 120 K) on conservation of its activation temperature dependences only for low frequencies (less 400 Hz). For the samples with x > 55at.% the power law R(w) ~ w^{-s} is disturbed although temperature dependence of AC conductance is remained.

I/PII.04 WITHDRAW

I/PII.05**NANOSTRUCTURES “METAL NANOPARTICLES ON SEMICONDUCTOR SURFACE”: INFLUENCE OF SUBSTRATE SURFACE ON OPTICAL PROPERTIES**

N.L. Dmitruk, T.R. Barlas, O.V. Kondratenko, V.R. Romanyuk, Institute for Physics of Semiconductors of NASU, Pr. Nauki 41, 03028, Kyiv, Ukraine V.V. Gozhenko, L.G. Grechko Institute of Surface Chemistry of NASU, G. Naumova str., 17, 03164, Kyiv, Ukraine I.N. Dmitruk, Kyiv National Taras Shevchenko University, Pr. Glushkov 6, 03127, Ukraine

Nanostructures were produced by photostimulated deposition of gold from aqueous solution of gold salt on flat and patterned GaAs surfaces, performed by anisotropic chemical and holographic photochemical etching. Surface microrelief serves as template for gold nanoparticles deposition. The shape and sizes of metal clusters were examined by AFM and SEM.

To characterize the optical properties of nanosystems we used multi-angle-of-incidence and spectral ellipsometry, and the reflectance spectroscopy of polarized light at several angles of incidence. In actual spectral region 300-900 nm we observed plasmon resonance in Au nanoparticles. The plasmon minima location depends on the nanoparticles sizes, the gold amount on surface, etc. To describe optical data different models of effective medium approximation and new approach for polarizability of gold clusters on the surface were used. It is proposed a generalization of the microscopic theory of the electrostatic response of a system of spheres on a substrate. The generalized theory allows to treat spatial systems of spherical particles of different sizes, made of different materials and located arbitrary near a boundary surface. For a system of two spheres above a substrate, an analytical expression for the sphere's polarizability is obtained in the dipole approximation, and the substrate influence on the polarizability and the optical properties of a nanodimensional sphere is analyzed. The dipole interaction between the sphere and substrate is shown to lead to splitting of the sphere's eigenmode into a set of four resonances. Expression for the resonant frequencies, frequency of the sphere's polarizability, and the strengths of the resonant modes are obtained.

I/PII.06**NEW HYBRID ORGANIC-INORGANIC MATERIALS BASED ON TITANIUM OXIDE GELS FOR PHOTONIC APPLICATIONS**

O. Kameneva(a,b,c), A. I. Kuznetsov(a,d), L. A. Smirnova(b), L. Rozes(c), C. Sanchez(c), N. Biturin(d), K. Chhor(a), P. Marteau(a) and A. Kanaev(a), (a)Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions, URP1311 CNRS, 93430 Villetaneuse, France, (b)Lobachevsky State University, 603950 Nizhniy Novgorod, Russia, (c)Laboratoire de Chimie de la Matière Condensée, UMR 7574 CNRS, Université Pierre et Marie Curie, 75252 Paris cedex 05, France, (d)Institute of Applied Physics RAS, 603950, Nizhniy Novgorod, Russia

Unique photophysical properties of monolithic wet titanium oxide gels have been recently reported [1], which allow considering them for photonic applications. However, high fragility of the gel samples limit their practical use.

In the present communication we report on the production of new hybrid organic-inorganic materials including two interpenetrating networks: the polymeric titanium oxide gel and the organic polymer based on 2-hydroxyethyl methacrylate. Efficient coupling between gel and polymer structures allows conserving useful properties inherent to each of the component. In particular, it assures both (i) rapid scavenging of photoexcited holes and (ii) trapping and long-term conservation of photoexcited electrons [2]. The EPR measurements show that the electrons are stored in the gel structure as Ti(3+) centers. The hybrid material is characterized by a higher glass transition temperature and a higher thermal stability of the organic framework than that of poly-2-hydroxyethyl methacrylate. High mechanical rigidity of the hybrid material allows preparation of samples by mechanical processing and subsequent polishing, attaining the optical quality of the surface. High transparency and photonic sensitivity combined with thermal and mechanical stability and polishing ability of new hybrid materials allow producing optically active samples of a desired shape for photonic applications. References: [1] A. I. Kuznetsov, O. Kameneva, A. Alexandrov, N. Biturin, Ph. Marteau, K. Chhor, C. Sanchez, A. Kanaev, Phys. Rev. E 71 (2005) 1. [2] A. I. Kuznetsov, O. Kameneva, L. A. Smirnova, L. Rozes, C. Sanchez, N. Biturin, K. Chhor, P. Marteau, and A. Kanaev, EMRS 2005 (Symposium J).

I/PII.07**ASSEMBLY OF ALUMINA-BASED NANOPARTICLES DOPED WITH Ag CLUSTERS AND THEIR OPTICAL, MECHANICAL AND ELECTRICAL PROPERTIES**

A.R. Phani, L. Lozzi and S. Santucci, INFN and Department of Physics, University of L'Aquila, via Vetoio, 67010 Coppito, L'Aquila, Italy

Nanometer-sized ultrafine particles of metals and semiconductors display many intriguing properties including optical nonlinearity properties, which are quantitatively and qualitatively different from respective bulk materials. It is a challenging task to deposit such films on to plastic substrates (polycarbonate, polyacrylic etc.) at low temperature and cost effective technique such as sol-gel. In the present investigation, alumina has been chosen as matrix because of its high hardness, chemical resistance, and scratch resistance. Nanostructured Al₂O₃ as well as boehmite AlOOH (on plastic substrates) thin films with 10-12 nm size have been prepared by sol-gel process and subsequently the films were doped with different concentrations of Ag nanoclusters. The alumina-based thin films have been deposited on quartz, polycarbonate and polyacrylic substrates at room temperature and then subjected to annealing at different temperatures ranging from 100°C (plastic substrates) to 400°C (quartz) for 30 minutes. The reduction of Ag₂O to Ag has been performed by two processes, one during the formation of nanoclusters by treating with NaBH₄ reducing agent and other by treating in H₂ atmosphere. The structure formation and chemical composition of these films were examined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) technique respectively. The size of the nanoclusters of Ag in the alumina-based matrix was examined with high-resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM) techniques. Electrical conductivity of the films with various concentrations of Ag were also measured with four-probe sheet resistance technique.

- I/PII.08** SYNTHESIS AND BIO-ADSORPTION OF ROD-LIKE LARGE-PORE PERIODIC MESOPOROUS ORGANOSILICA
Shizhang Qiao, Yonggang Jin, QiuHong Hu, G.Q. Max Lu, ARC Centre for Functional Nanomaterials, School of Engineering, The University of Queensland, Brisbane QLD 4072, Australia
 Highly ordered rod-like large-pore periodic mesoporous organosilica (PMO) were successfully synthesized at low acid concentrations and in the presence of inorganic salt using triblock copolymer P123 as a template. The effect of ionic strength, acidity, temperature and si/template ratios on the mesostructure and macrostructure of PMOs was extensively investigated. The role of inorganic salt and low acidity in the production of highly-ordered mesostructure and the morphology control of PMOs is explained. The adsorption of bovine heart cytochrome c (cyt c) on PMO was studied at different ionic strengths and pHs by comparing with the adsorption on pure silica materials with controlled morphology and pore structure. The results show that the electrostatic interaction between cyt c and PMO surface is more dominant than hydrophobic forces. The PMO with a rod-like morphology has a high cyt c adsorption capacity of 22.22 $\mu\text{mol/g}$ at pH 7.0. The highly ordered PMO materials with uniform morphology, high BET surface area and pore volume may have potential use in bio-adsorption separation, enzymes immobilization and catalysis.
- I/PII.09** NEAR-FIELD SCANNING OPTICAL MICROSCOPY OF InAs QUANTUM DOT LASER DIODES AT ROOM TEMPERATURE
S.I. Jung(a), H.Y. Yeo(a), I.G. Yun(a), J.Y. Leem(b), I.K. Han(b), J.I. Lee(b), (a)Department of Electrical and Electronic Engineering, Yonsei University, South Korea, (b)School of Nano Engineering, Institute for Nanotechnology Applications, InJe University, South Korea
 Detailed near-field scanning optical microscopy (NSOM) studies of InAs quantum dot laser diodes were performed. The high resolution of NSOM provides a detailed mapping of the laser output from the active region. Facet cross sections are imaged with a spatial resolution of <100 nm, below and above the lasing threshold. Observation of spatially resolved spectra near the active region reveals compositional fluctuations as well as absorption and reemission of the lasing mode. Near-field measurements show a relationship between modal emission, waveguide structure, and lateral device size. Topographical images are achieved simultaneously with NSOM images by digitizing the feedback signal which maintains a constant tip-surface gap. It is shown that these data have direct implications on device performance and problems associated with carrier leakage and nonradiative defects.
- I/PII.10** INTERACTIONS BETWEEN POLYMERS AND NANOPARTICLES: FORMATION OF SUPERMICELLAR HYBRID AGGREGATES
J.-F. Berret(a), K. Yokota(b), Y. Lalatonne(c), A. Sehgal(c) and M. Morvan(c), (a)Matière et Systèmes Complexes, UMR CNRS 7057, Université Denis Diderot 140 rue de Lourmel, 75015 Paris, France, (b)Rhodia, Centre de Recherches d'Aubervilliers, 52 rue de la Haie Coq, 93308 Aubervilliers Cedex France, (c)Complex Fluids Laboratory, UMR CNRS - Rhodia n°166, Cranbury Research
 When polyelectrolyte-neutral block copolymers are mixed in solutions to oppositely charged species (e.g. surfactant micelles, macromolecules, proteins etc...), there is the formation of stable supermicellar aggregates combining both components. The resulting colloidal complexes exhibit a core-shell structure and the mechanism yielding to their formation is electrostatic self-assembly. In this contribution, we report on the structural properties of supermicellar aggregates made from mineral nanoparticles and polyelectrolyte-neutral block copolymers in aqueous solutions. Two inorganic systems have been studied, the ultra-fine yttrium hydroxyacetate nanoparticles (radius 2 nm) complexed with anionic-neutral diblocks, and the citrate-coated cerium oxide nanoparticles (radius 5 nm) mixed with cationic-neutral copolymers. Using light, neutron and x-ray scattering experiments, we determine the sizes (~ 100 nm) and the aggregation numbers of the organic-inorganic complexes [K. Yokota, M. Morvan, J.-F. Berret and J. Oberdisse, *Europhys. Lett.*, 69 (2), pp. 284-290 (2005)]. Thanks to its core-shell structure, the hybrid polymer-nanoparticle aggregates exhibit a remarkable colloidal stability with respect to pH-variations, ionic strength and concentration. 100 μm solid films were cast from solutions under vacuum and the structure of the complexes remains unchanged during the film casting. With yttrium hydroxyacetate, we were able to prepare a bulk polymer matrix (of polyacrylamide) in which nanoparticle clusters are dispersed, a technique that could be extended to other mineral nanoparticles.
- I/PII.11** HYBRID NANOCOMPOSITES REINFORCED WITH CARBON NANOTUBES
S. Bhattacharyya, J.-P. Salvétat, C. Sinturel, M.-L. Saboungi, CNRS-CRMD, 1B rue de la Férollerie, 45071 Orléans cedex 2, France
 We have synthesized nanocomposites by integration of functionalized carbon nanotubes, both singlewalled (SWNT) and multiwalled (MWCNT), with different protein molecules, collagen, ferritin and cytochrome C, dispersed in a PVA matrix. Investigation of the thermo-mechanical behavior was performed by dynamic mechanical thermal analysis (DMTA). A negative or positive shift of the glass transition temperature is observed for all the nanocomposites, which is discussed in connection with polymer chain dynamics. We have also observed a spectacular reinforcement effect, analyzed in the framework of the Cox model for most of our nanocomposites. Such materials are potentially biocompatible and could be used as scaffold in tissue engineering.

I/PII.12**COPOLYIMIDES FROM COMMONLY USED MONOMERS, AND THEIR NANOCOMPOSITES**

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The synthesis of copolyimides from aromatic dianhydrides (pyromellitic dianhydride (PMDA), symmetric 3,3',4,4'-biphenyltetracarboxylic dianhydride (sBPDA)) and diamines (4,4'-oxydianiline (ODA), p-phenylenediamine (PDA)) commonly used for the production of commercial polyimides, as well as preparation of their nanocomposites with SiO₂ nanoparticles was performed in order to get new functional materials with improved thermal stability and mechanical properties. The copolyimide films were analyzed by FTIR, WAXD, DSC and TG, and characterized by transition temperatures and the temperatures of 5 and 10% mass loss, as well as tensile properties.

The amorphous films of PMDA/sBPDA-ODA copolyimides at the room temperature had 20% higher ultimate strength and exhibited higher tensile modulus than the reference polyimide (PMDA-ODA). However, lowering the transition temperature of the polyimide by partial change of PMDA monomeric unit by sBPDA reflected itself in lowering of the modulus at higher temperatures. The best performance was exhibited by semi-crystalline films of sBPDA-ODA/PDA copolyimide, which had 40% higher ultimate strength and 250% higher elongation at break at the room temperature than the reference polyimide (sBPDA-PDA), and retained the strength at 200 °C temperature. Unexpectedly, the elongation at break of films of (co)polyimide nanocomposite up to 3 wt% of SiO₂ content increases. Their ultimate strength is similar and thermal stability is better as compared to the baseline polymer. These phenomena as a distinctive feature of (co)polyimide/SiO₂ nanocomposites are also discussed.

I/PII.13**NONAQUEOUS SYNTHESIS OF METAL OXIDE NANOPARTICLES VIA ORGANIC CONDENSATION REACTIONS**

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There is a great demand for transition metal oxide nanoparticles as one envisions a variety of applications, especially in the promising fields of catalysis, electronics and sensing. Nonaqueous synthesis methods possess substantial advantages as the particle formation proceeds in a more controlled fashion, allowing the direct, surfactant-free synthesis of nanocrystalline materials at relatively low temperatures. This work is not only aimed at presenting new methods for the synthesis of metal oxide nanoparticles but also at exploring the underlying reaction mechanisms to achieve a detailed understanding of the synthesis.

Almost all non-aqueous routes to metal oxides reported so far are based on alkyl halide elimination, ester elimination, or ether elimination mechanisms. Here, we prove that more complex organic condensation reactions are also suitable for the controlled formation of metal oxides, which allows the solvothermal synthesis in organic media other than alcohols. Ketones and aldehydes seem particularly attractive, as they are cheap and non-toxic. In contrast to alcohols, they are practically non-reductive. This makes possible the synthesis of metal oxides from metal alkoxides which in alcohols always are reduced to give the metals. In addition, we present a versatile nonaqueous route to metal oxide nanoparticles by reacting metal acetylacetonate precursors with benzylamine. Highly crystalline, phase-pure materials are obtained after solvothermal treatment at comparably low temperatures. The reaction proceeds via a novel mechanism, involving C-C bond cleavage of the acetylacetonate followed by Aldol-like organic condensation reactions, which will be discussed in detail.

I/PII.14**SOLID STATE NMR INVESTIGATIONS OF SURFACTANT TEMPLATED SILICAS AND ORGANOSILICAS**

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A large variety of periodic mesostructured silicas and organosilicas can be prepared from tetraalkoxysilanes, Si(OR)₄ and trialkoxysilanes, XSi(OR)₃ in the presence of surfactants. Many studies have been focussed on a better understanding of the self-assembly mechanism between the siliceous species and the surfactants, that will directly influence the final type of mesostructure ; it is however still rather difficult to propose a good description of the silica walls-surfactant interfaces.

The goal of this work is to use solid state NMR techniques to characterize mesostructured silicas and organosilicas that are templated with cationic surfactants with various polar head groups. These experiments will take advantage of the heteronuclear or homonuclear dipolar couplings that are sensitive to the spatial proximity between two NMR active nuclei. Examples will be given on the use of two-dimensional (2D) heterocorrelation (HETCOR) experiments, based on the ²⁹Si-¹H heteronuclear dipolar coupling to get a precise description of the organic-inorganic interface. 2D ¹H Double Quantum (DQ) NMR experiments under fast Magic Angle Spinning, based on the ¹H-¹H homonuclear dipolar coupling, have also been used to locate the organic groups X, introduced via a trialkoxysilane, that can be either at the surfactant/silica interface or within the silica walls.

I/PII.15**PREPARATION OF MAGNETIC AND CONDUCTING Fe₃O₄/POLY(STYRENESULFONATE)/POLYPYRROLE NANOPARTICLES WITH CORE-SHELL STRUCTURE**

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We report the synthesis of a new class of Fe₃O₄/PSS/PPy nanoparticles possessing both electrical conductivity and ferromagnetic properties. Fe₃O₄ particles were prepared from Fe(Ⅱ) and Fe(Ⅲ) salts in a 28% of ammonium hydroxide aqueous solution at a stirring rate of 300 rpm at room temperature. These nanoparticles were then surface-capped with a series of surfactant-like molecules that contain a 2-bromoisobutyryloxy hydrophobic tail and a phosphonic acid group which was used as a binding head for grafting metal oxide. In turn, the functional tails on the particle surface were utilized as multifunctional initiators for growing polystyrene (PS) chain via controlled free-radical polymerization. The obtained PS chains were converted into water-soluble poly(4-styrenesulfonic acid) structure with soft sulfonation method. Finally, the highly stable Fe₃O₄/PSS/PPy nanoparticles were prepared via the oxidation polymerization of pyrrole using PSS-guided polymerization method. This synthetic route ensures that each core-shell particle contains only one magnetic particle and that the polymer shell evenly encapsulates the core. The thus-prepared materials were characterized by TEM, dynamic light scattering, UV-Vis, TGA, IR, XRD, conductivity and ERS methods.

- I/PII.16** ELECTROCHEMICAL BUILDING OF NANOSTRUCTURED ZINC OXIDE/ CHROMOPHORE HYBRID FILMS FOR LIGHT EMISSION APPLICATIONS
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- I/PII.17** QUANTUM DOTS-BASED IMAGING OF CANCER TISSUE SLICES
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 Quantum dot (QDs), a kind of semiconductor nanoparticle, is recently emerging as a new fluorescent probe applied in biological and biomedical study, especially in cellular imaging. As fluorescent probes, QDs have several predictive advantages, such as broad absorption spectra, narrow and symmetrical emission spectra, excellent photostability, and single-excitation-multiple-emission. For their excellent fluorescent properties, QDs are an ideal alternative for traditional organic fluorescent dyes.
 Caveolin is a specific protein in caveolae, which is expressed in most normal organs and many solid tumors, and particularly in adipocytes, endothelial cells and epithelial cells. Caveolin might constitute a key switch in tumor development through its function as a tumor suppressor and as a promoter of metastasis. Caveolin seems to be rich in potential targets for cancer imaging. CdSe/ZnS core/shell quantum dots had been successfully synthesized in our lab, and modified with immunoglobulin G (IgG) to construct QDs-IgG conjugates capable of bio-recognition. Based on caveolin recognition, such a kind of bioconjugate has been used to image mouse fibroblast cells, tissue slices of normal human bronchus and lung cancer using indirect immunofluorescent technique. Caveolin proteins expressed in epithelial cells of normal human bronchus and in cancer cells of human lung cancer were recognized by QDs-IgG conjugates. All recognition signals are specific for the intended targets, which are brighter and considerably more photostable than organic fluorescent dyes. The results indicate that QDs-based probes can be very effective in tissue slice imaging and offer substantial advantages over organic fluorescent dyes in target detection.
- I/PII.18** OPTICAL PROPERTIES OF POLY(PHENYLENE VINYLENE) OLIGOMER/POROUS SILICON COMPOSITES
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 Nanosized polymers have particular optical properties that have been investigated in several systems. However, many aspects of the formation and of the physical process in these materials have not been fully understood. We have studied the optical properties of poly(phenylene vinylene) oligomers (or OPV) formed inside a porous silicon layer by using different chain lengths and different solvents for dissolving the oligomers. Strong modification of photoluminescence properties of nanosize OPVs is observed at room temperature by a blue shift of the PL spectra, the structure of the oligomers being preserved as proved by Raman scattering experiment. However, the penetration of the oligomers into the nanopores was found to depend on the conformation of the chains, which is in turn conditioned by the use of the solvent to dissolve the oligomer powder.
- I/PII.19** NANOPOROUS SOL-GEL SILICA FILM DOPED WITH NiO AND Au NANOCRYSTALS FOR OPTICAL AND ELECTRICAL GAS SENSORS
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 Films of NiO, a p-type semiconductor with a wide band gap of 4.2 eV, have been recently proposed as a sensitive material for chemoresistive or optical gas sensors. The working mechanism of these materials lies in a change of the electrical resistance or optical transmittance of the material, caused by changes of the free electron density as a consequence of physisorption, chemisorption and catalytic reactions of the measuring gas and the surface of the material. The reaction to the target gas can be improved either by increasing the area of the reacting surface, either by noble metal nanoparticles doping. In this paper we report a sol-gel synthesis of nano-composite thin films which comprises a nanoporous SiO₂ framework with dispersed NiO and gold metal nanoparticles.
 The nanoporosity of the sol-gel matrix provides a path for the gas molecules to reach the functional ultrafine particles embedded in the glass matrix, whereas the reacting NiO metal oxide-gold-charged nanoparticles are responsible for the reversible change in resistance to different gases like H₂, CO and Humidity, as well as a reversible change in the optical transmittance in the VIS-NIR range when exposed to CO. Microstructure development of the nanocomposite has been studied by X-Ray diffraction, transmission electron microscopy and Fourier transform infrared spectroscopy. Nanocrystals precipitate at 400-500 °C and grow with heat treatments. The variation of OH content and porosity have been monitored by FT-IR measurements. The effect upon optical transmittance and resistivity of the residual porosity, testing temperature and gas concentration have been studied as well as the influence of gold nanoparticles. Enhancing of gas sensing properties induced by noble metal clusters has been demonstrated.

I/PII.20**A NEW LOW COST AND RECYCLABLE INORGANIC PRECURSOR TO NIOBIUM OXIDE MESOSTRUCTURES**

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In this study we describe the use of ammoniacal niobium oxalate as an inorganic precursor to assemble niobium oxide mesostructures. This is a stable aqueous soluble niobium complex that can interact with templates molecules through a labile coordination point (neutral route) or by electrostatic interaction (ionic route) with cationic templates. These two synthetic approaches were tested using n-octylamine and cetyltrimethylammonium as structure directing agents.

Transmission electron microscopy (TEM) and powder X ray diffractometry (XRD) confirmed the mesostructures arrangement. The neutral route produced a lamellar mesophase while the ionic route leads to a hexagonal (p6m) one. The XRD patterns also indicated the presence of crystalline domains in the walls of both materials. The influence of synthetic parameters such as pH and molar ratio of reactants on the mesophase formation were also evaluated. Attempts to remove the template by calcination promoted the mesostructures collapse. Other methods for the template removal are under investigation. In conclusion the ammoniacal niobium oxalate replaces the metal alkoxide and chloride precursors with the advantage of being cheap, stable in acidic aqueous solution and easy to synthesize. This compound can be obtained from the niobium oxide, offering a possibility of recycle the mesoporous material after its use.

I/PII.21**MESOPOROUS SUPPORTS FOR NANOSIZED CATALYSTS**

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Low-dimensional systems are extensively investigated in many fields of materials science because of their intriguing functional properties. As far as it concerns catalysis, in recent years several efforts have been devoted to take advantage of Gold and Platinum nanoparticles as catalysts for fuel cell systems. The main problem affecting this kind of applications is the increase of the metallic particles size under operative conditions, that leads to serious deterioration of the catalytic properties. In present work mesoporous materials produced by different colloidal syntheses will be tested as catalytic supports, in order to improve the thermal stability of metallic nanoparticles. The substrate effectiveness will be carefully analysed from a structural point of view. Moreover, the role played by the substrates upon the reactivity of the system and their interactions with the metallic nanoparticles will be in-depth investigated.

I/PII.22**STRUCTURAL AND MAGNETIC STUDIES OF FERRIHYDRITE NANOPARTICLES FORMED WITHIN ORGANIC-INORGANIC MATRICES**

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Nanometric Ferrihydrite particles formed within an organic-inorganic hybrid matrix were obtained by the sol-gel process. The hybrid matrix here reported, named di-ureasil, is composed of poly(oxyethylene) chains grafted to siloxane groups by means of urea cross-linkages. The formation of Ferrihydrite particles was achieved incorporating Iron Nitrate during the sol-gel process, at low pH. The identification of the iron oxide phase and the average structural correlation were previously studied by X-ray diffraction and SAXS [1]. Detailed TEM studies reveal that the Ferrihydrite particles have an average size of 4nm and a log-normal standard deviation of 0.4. The AC magnetic susceptibility shows thermal irreversibility with a blocking temperature (~13K) depending on the frequency following a Néel-Brown law. The imaginary part of the susceptibility allowed a study of the magnetic anisotropy energy barrier for particle moment reversal. Above the irreversibility temperature (~40K) the DC magnetization follows a Langevin function type behaviour considering a magnetic moment distribution modified with a linear term, as found in antiferromagnetic particles with uncompensated moments. We found that the size and moment distributions do not have a simple relation, probably due to surface disorder [2].

[1] N. J. O. Silva et al, J. Mater. Chem., 484-490 (2005). [2] N.J.O. Silva, V.S. Amaral and L. D. Carlos, Cond-Mat/0408134

I/PII.23**CORRELATIONS BETWEEN THE SYNTHESIS PARAMETERS AND THE PROPERTIES OF POLYPYRROLE-MAGNETIC NANOPARTICLES COMPOSITES**

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The aim of the present work is the investigation of hybrid structures obtained by the combination between a well-known conducting polymer polypyrrole (PPY) and magnetic nanoparticles like Fe₃O₄, CoFe₂O₄. Also, the synthesis of the nanocomposites of carbon nanotubes (CNTs)-PPY containing magnetic nanoparticles Fe₃O₄ is reported.

The nanocomposites PPY-Fe₃O₄ and PPY-CoFe₂O₄ were prepared by the oxidative polymerization of pyrrole in aqueous solution containing an oxidant and water based magnetic nanofluid. The magnetic nanofluid was obtained by the chemical coprecipitation method to obtain Fe₃O₄ or CoFe₂O₄ nanoparticles. The polymerization of pyrrole in the presence of CNTs and Fe₃O₄ magnetic nanofluid results in the formation of the nanostructures of CNTs coated with PPY containing Fe₃O₄ nanoparticles.

The properties of the composites were investigated by TEM, SEM, FTIR spectroscopy, d.c. conductivity, X-ray diffraction (XRD), X-ray Photoelectron spectroscopy (XPS) and magnetization measurements.

The nanocomposites PPY-Fe₃O₄ and PPY-CoFe₂O₄ have a core-shell structure where Fe₃O₄ or CoFe₂O₄ is the magnetic core and PPY is the conducting shell.

The XPS investigations of PPY-Fe₃O₄ nanocomposites show that PPY chains contain a high fraction of positively charged nitrogen atoms due to the interaction with the anionic surfactant DBS and Fe₃O₄. The magnetization of the investigated nanocomposites measured versus increasing and decreasing magnetic field shows no hysteresis loop, this behavior being consistent with a superparamagnetic behavior.

- I/PII.24** PERIODICALLY MESOSTRUCTURED ORGANO-SILICA MONOLITHS WITH HIERARCHICAL BUILD-UP
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 Sol-gel reactions of organo-bridged trialkoxysilanes – typically methoxy- or ethoxysilanes – in the presence of surfactants as structure directing agents are the basis for the synthesis of periodically mesostructured organosilica materials (PMO’s). In the preparation of monolithic materials, substitution of the alkoxy-groups with diols has some distinct advantages. In contrast to the conventional alkoxy-silanes, the water-soluble diol-modified derivatives can be processed without co-solvents, even under neutral conditions (no catalyst is required to start sol-gel reactions). Furthermore, diols show very good compatibilities with lyotropic surfactant phases in water. The synthesis of pure silica materials with periodically ordered mesostructures and unique macrostructures from various diol-/polyol-modified silanes has already been presented by our group. In this work, we extend this approach to the preparation of organo-silica monoliths from ethylene- and phenylene-bridged diol-modified silanes. Gels are directly prepared by true liquid-crystal templating (TLCT) from lyotropic phases of a non-ionic block copolymer in aqueous media. The final organo-functional materials exhibit a highly regular arrangement of mesopores within different macroporous matrixes, e.g. cellular scaffolds. The hierarchical build-up was investigated from the molecular level to the micrometer length scale.
- I/PII.25** HYBRID STRUCTURES BASED ON POLYPYRROLE AND MAGNETIC NANOPARTICLES OF $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ PEROVSKITE MANGANITE
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 The association of conducting polymers with nanostructured magnetic materials represents a new approach in order to obtain composites possessing the properties of each components with specificity effects resulting from the association effect. Potential applications are as: actuators, electromagnetic shielding and electronic devices
 In the present study we report the synthesis and structural electric and magnetic characterization of the nanostructured $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO) / polypyrrole (PPY) nanocomposites.
 The synthesis of this of manganite perovskite LCMO nanograins composites with PPY could be made as following: (i) by using electrochemical polymerization, (ii) in situ chemical oxidative polymerization of pyrrole in the presence of LCMO grains or by (iii) the dispersion of LCMO nanograins in a chloroform solution of the soluble PPY doped with dodecylbenzenesulfonate. The sol-gel method was used to prepare granular nanometric $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ -δ manganites. Two sets of samples with three different grain sizes were obtained by annealing at the temperatures $t_A = 7000\text{C}$ and respectively $t_A = 9000\text{C}$ for 3-4 hours. The final composite was made by dispersion into soluble PPY by using method (iii) as mentioned above
 Standard X-ray diffraction and scanning electron microscopy (SEM) measurements were performed for the two LCMO precursors and, for comparison, on the two sets of LCMO/PPY nanocomposites. Morphological and compositional (surface) characterization were made by the SEM and EDX techniques. The resistivities and magnetoresistivities of composite samples were carried out by using an Oxford Instruments equipment from 4 K to 300 K.
- I/PII.26** SYNTHESIS OF MOLECULE-BASED MAGNETIC NANOPARTICLES
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 The development of nanometer-scaled magnetic nanoparticles has attracted a great deal of attention in modern science because of their technological and fundamental scientific importance. These materials often exhibit new interesting size-dependent physical and chemical properties, which cannot be achieved by their bulk counterparts and could find applications in many fields.
 Numerous bimetallic assemblies with Prussian Blue-like structure based on cyanometallate building blocks form an important family of molecule-based magnetic materials presenting high critical temperatures and interesting physical properties such as photo-induced magnetism. Recently, the spatial confinement in the growth of molecular magnetic materials has emerged as a promising subject for future developments in nanomaterial science. Within the last 5 years, this tremendous activity leads to the successful synthesis of nanoparticles, nanowires, thin films and ordered porous microstructures of cyano-bridged molecule-based magnetic materials. The present work is devoted to the synthesis and study of cyano-bridged molecule-based magnetic nanoparticles obtained following two original different approaches: - The first one deals with the synthesis of soluble nanoparticles using ionic liquid as structuring media. - The second one consists in the use of mesostructured hybrid silica as a nano-reactor to growth and structure nanoparticles at specific sites of the hybrid silica by a step-by-step coordination method.
- I/PII.27** GROWTH OF 3C-SiC NANOWIRES ON NICKEL COATED Si(100) SUBSTRATE USING DICHLOROMETHYLVINYLSILANE AND DIETHYLMETHYLSILANE BY MOCVD METHOD
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 As an important wide band gap semiconductor with high electron mobility, cubic silicon carbide (3C-SiC) nanowires would be favorable for applications in high temperature, high power, and high frequency nanoelectronic devices. In this study, we have grown 3C-SiC nanowires on nickel coated Si(100) substrates using single source precursors by thermal metal-organic chemical vapor deposition (MOCVD) method. Dichloromethylvinylsilane ($\text{CH}_2\text{CHSi}(\text{CH}_3)\text{Cl}_2$) and diethylmethylsilane ($\text{CH}_3\text{SiH}(\text{C}_2\text{H}_5)_2$) were used as a single precursor without any carrier and bubbler gas. The general deposition pressure and temperature were $5.0 \cdot 10^{-2}$ Torr and $800 \sim 1000$ oC, and the deposition was carried out for $1 \sim 4$ h. 3C-SiC nanowires with $40 \sim 100$ nm diameter could grow on substrates at low temperature as low as 900 oC. We can confirm that nickel is a very important role in growth of 3C-SiC nanowires. The initial growth rate of nanowires is strongly dependent on the deposition temperature. The length and width of nanowires are mainly controllable with deposition temperature rather than deposition time. XRD pattern showed that as-deposited SiC nanowires were cubic silicon carbide. Through TEM analysis, we can suggest that an amorphous carbon layer surrounds the as-deposited h-SiC nanowires, and the 3C-SiC nanowire has [111] growth direction with well-crystallized structure. XPS and EDX analyses showed that the as-obtained SiC nanowire has an atomic Si and C composition of about 1.0:1.2, suggesting possible applications for both electronic devices and field emitters.

I/PII.28**MASSIVE SYNTHETIC METHOD OF ROOM TEMPERATURE STABLE NANOPOROUS $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ ELECTRIDE VIA MELT**

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Electrides are ionic compounds in which electrons act as anions. These materials have been studied extensively because of exotic electronic structures, unique chemical and physical properties, and potential applications for electron emitters, thermionic devices, reducing agents, etc. However, the fatal drawbacks such as the thermal and chemical instability of organic electrides at room temperature (RT) have strongly limited the practical applications. Although the synthesis of a RT stable electride using single crystalline $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7) with a nanoporous structure resolved those problems², the synthesis process is not suitable because a single crystal C12A7 is needed as the starting material and because of the long duration of the chemical treatment.

We provide a solution for the instability and complicated synthesis process by synthesizing a RT stable polycrystalline C12A7 electride via a strongly reducing C12A7 "melt", i.e. direct solidification of the melt or crystallization of the transparent glass. The resulting polycrystalline C12A7 electrides exhibited a high electronic conductivity up to 5 S/cm at 300K, and nearly identical mobility ($0.1 \text{ cm}^2/\text{V}\cdot\text{s}$) of the carrier, i.e., loosely trapped electron in the F⁻-like center to the single crystalline samples. The carbon-related anions (C22-), which may be responsible for the formation of C12A7 electride under a strongly reducing atmosphere, serve as a template for stabilizing C12A7 and spontaneously release from the lattice remaining the electrons. This synthetic method is simple and efficient for the use of electrides in practical applications by mass production, facilitating the research of electrides.

1. Y. Toda, et al., Adv. Mater. 16 (2004) 685.

2. S. Matsuishi, et al., Science 301 (2003) 626.

I/PII.29**STUDY ON THE APPLICATIONS OF SiC THIN FILMS TO MEMS TECHNIQUES THROUGH A FABRICATION PROCESS OF CANTILEVERS**

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We have tried to find the most suitable conditions for the deposition process of silicon carbide thin films as a material for MEMS techniques. We have also studied its application to semiconductor processes. To do this, we have tried to fabricate several dimensions of cantilevers (10 μm ~100 μm in length) with these silicon carbide thin films. High quality silicon carbide thin films are grown by metal-organic chemical vapor deposition (MOCVD). This process employs single molecular precursors such as diethylmethylsilane (DEMS), 1,3-disilabutane (DSB) at pressures between 1.0×10^{-4} and 1.0×10^{-5} Torr and a growth temperature in the range of 900~1000°C. For initial patterning of cantilevers, we used two patterning methods and compared them. The first is to etch the previously deposited SiC thin films using mainly SF₆ gas. In this case, Ni metal thin films are employed as a mask material. The second is to use the lift-off process; SiC thin films are deposited on patterned oxide thin films, which are then treated with HF solution. To get three-dimensional cantilever-shaped SiC thin films, we chemically etched silicon substrate with strong alkaline solution such as TMAH at 80°C. The chemical stability of SiC thin films was inspected through SEM images. Finally, a high resolution of probe tips on the cantilevers was achieved using electron-beam deposition in carbon atmosphere.

I/PII.30**TEMPLATING OF ORGANIC/INORGANIC HYBRID MATERIALS**

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A combination of bottom-up and top-down templating strategies was applied to obtain controlled structures in organic/inorganic hybrid materials on the nanometer and micrometer level. Nanostructured silica was synthesized using the sol-gel-method with different precursors such as tetraethyl orthosilicate (TEOS) or ethyleneglycol modified silane (EGMS) and surfactants leading to mesoporous silica monoliths with implemented organic network. External fields were applied to influence the orientation of these precursor/surfactant systems while still in the liquid crystalline state. On the micrometer scale, recently developed photopolymers were used to build soluble moulds by rapid prototyping (RP). The precursor/surfactant mixture was infiltrated into these sacrificial cellular RP moulds and polycondensation of silica was allowed to take place inside the template.

Position resolved small-angle X-ray scattering (scanning SAXS) with synchrotron radiation was used to investigate the liquid crystalline phase of the surfactants and its ordering behaviour in-situ, as well as the resulting nanostructure of the final hybrid material.

I/PII.31**SOLID-STATE SYNTHESIS OF INORGANIC ELECTRIDE WITH MAYENITE TYPE STRUCTURE**

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Calcium aluminate (C12A7) crystal with mayenite structure is a microporous material, which is built up by nanometer-sized cages. A part of these cages are occupied by free oxide ions. Recently, an inorganic electride, namely, C12A7 electride has been reported to be fabricated by substituting free oxide ions with electrons via hydrogenated C12A7. In the present study, we report an alternative method for substituting free oxide ions to prepare C12A7 electride, which is suitable for practical productions. C12A7 crystal was prepared by a solid-state reaction in a stoichiometric mixture of calcium carbonate and alumina powders at 1300 °C for 6 hours in air. The obtained C12A7 powders were heated at 1300 °C, which is below the melting point of C12A7 (1415°C), for 2 hours in a graphite container with lid. The resulting powders were colored dark green. The diffuse reflectance spectra shows that the coloration is due to the strong optical absorption centered at 2.8 eV, which is the same as that observed for the Ca-treated single crystal C12A7 electride.

I/PII.32 NANOCOMPOSITES BASED ON FUNCTIONALIZED NANOTUBES IN POLYANILINE MATRIX BY PLASMA POLYMERIZATION

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The unique architecture and remarkable mechanical and electrical properties carbon nanotubes (CNTs) have great potential that remains, however, unexploited because of poor dispersibility in liquids and problems of processability. Major efforts have, therefore, been devoted towards any modification of the CNTs that could improve their handling. Typically, chemical modification of CNTs is based on severe oxidation processes that often damage the tubes. Mild and single-step electrochemical modification of CNTs still need hard conditions such as halogenation and other intermediate steps. Etching and bonding of different functional groups make it more processable or ready embedded in a matrix is offered as alternative by plasma polymerization. By spraying in plasma stream discharge a dispersion CNT- aniline we succeed to deposit thin layer films on different substrates. FT-IR and Raman spectra show a chemical bonded of the amino group to nanotube surface. Supplementary analysis, AFM and TEM disclose a polymer matrix with uniform distribution of the CNTs. I-V characteristics in a Schottky diode configuration show a combined effect of the conduction mechanisms imposed by SCLC and metallic/semimetallic character of the nanotubes

I/PII.33 SYNTHESIS AND CHARACTERIZATION OF SiO₂ – PANI / PTH NANOCOMPOSITES THIN FILM BY PLASMA POLYMERIZATION

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Encapsulation of inorganic nanoparticles in conducting polymers is the most common and interesting aspect of nanocomposites synthesis. Different metal and metal oxide particles have so far been encapsulated into the shell of conducting polymers giving rise to a host of nanocomposites. These materials differ from both the pure polymers and the inorganic nanoparticles in some of the physical and chemical properties. The synthesis techniques have to be found and optimized to incorporate the inorganic component into the conducting polymer. Inorganic nanoparticles can be introduced into the matrix of a host-conducting polymer either by some chemical methods or by an electrochemical incorporation technique. We report a method to produce thin films nanocomposites with a novel method of plasma polymerization having coupled an atomizer head. The dispersion, monomer-nanoparticles, is directly sprayed into plasma beam. In particular, Polyaniline-SiO₂ (PPAniSiO₂) and PTH-SiO₂ (PTH-SiO₂) were deposited on silicon substrate aiming at nanocomposites with functionalized nanoparticles. The structure investigated by FT-IR, Raman, TEM shown films with strongly bonded SiO₂ nanoparticle to polymer chain. By comparison I-V characteristics of the nanocomposites show a combined conduction mechanism controlled by SCLC.

I/PII.34 STRUCTURAL AND MAGNETIC PROPERTIES OF MANGANITE-SILICON STRUCTURES

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Half-metallic materials with nearly 100% spin polarization such as La_{0.7}Sr_{0.3}MnO₃ (LSMO) manganite are actively investigated nowadays for spintronic applications. Such materials in semiconductor based spintronic devices help to overcome the so called conductivity mismatch limitation for the spin polarized injection. Recently strong efforts are devoted to the integration of Si based technologies in this field. In this context, the investigation of LSMO-Si thin film structures and manganite-Si interface is of great importance for future spintronic development. LSMO films were grown by Channel Spark ablation method on Si substrates covered by 2 nm thick SiO_x layer. The Curie temperatures deduced from MOKE and SQUID measurements indicate film quality close to the epitaxial films (above 320K for 50nm film). Strong room temperature XMCD signal was detected for the first time on LSMO films on Si showing strong spin polarization at the surface. Cross-sectional TEM images indicate sharp interface between SiO_x and LSMO. The LSMO film itself is splitted in two well defined layers also separated by sharp interface too (below 1 nm). The amorphous SiO_x underlayer induces the formation of a transition LSMO layer of few nanometers, and a magnetically robust layer is formed on top of it. The investigated LSMO-Si structures show strong magnetic properties and spin polarisation at the surface, while additional investigations are required for improving the quality of the interface layer.

I/PII.35 MAGNETIC PROPERTIES AND STRUCTURE OF Sm-Fe-X FILMS PROCESSED BY PULSED LASER DEPOSITION

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Sm-Fe thin films 10-50 nm thick, were deposited on a Si wafer coated with ~ 150 nm layer of Ta by ablating different alloys used as solid targets. As a starting material Sm_{13.7}Fe_{86.3} alloy was used. Further on, based on the results of our previous work, where the coercivities of powders obtained from basic Sm-Fe alloy were significantly improved by additive elements [1, 2], also Sm_{13.8}Fe_{82.2}Ta_{4.0} and Sm₁₂Fe₈₆Zr₂ alloys were used as additional targets to prepare thin films and to achieve high coercivities.

Targets were ablated using a molecular fluorine laser at 157 nm [3] at low laser energy of 25 mJ per pulse. The dimensions of the deposited nanocrystals on the Si-Ta substrate varied between 10-500 nm. The composition of the nanocrystals grown by Pulse Laser Deposition (PLD) remains the same as the initial target composition, in contrary to the growth using PLD at longer wavelengths. The magnetic properties measured by VSM, and the morphology and type of the films (observed and analysed by HRTEM/EDX), varied significantly with different experimental conditions.

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I/PII.36**ACID FUNCTIONALIZED COLLOIDS**

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Due to their large specific area, colloidal oxide particles can yield large concentrations of ionizable OH groups and exchangeable protons equivalent to a concentrated acid solution. These acid functions, anchored to the solid particles, are stable during operation in electrochemical devices such as fuel cells or electrochromic cells.

Colloidal zirconia particles were first prepared and purified. Their surface was functionalized by grafting phosphates or phosphonic acids with increased acidity such as sulfophenylphosphonic (SPPA) and sulfofluorophosphonic (SFPA) acids synthesized in the laboratory.

The surface diffusion of proton was studied by NMR relaxation methods that show a behavior ranging from quasi-liquid state for SFPA-grafted system to a local molecular tumbling for phosphate-grafted. This is explained both by the acidity and the high degree of freedom of the rotating species at the surface of the colloids.

The macroscopic proton diffusion was studied by impedance spectroscopy between room temperature and 200°C under various partial water pressures. Conductivity was measured on pressed powders and on composite membranes with the colloids dispersed in neutral (polyvinylidene fluoride PVDF) and basic (polybenzimidazole, PBI) polymers. The impedance is largely dominated by the interparticle or by the particle-polymer transfer.

I/PII.37**AEROSOL GENERATED MESOPOROUS MATERIALS WITH EXPANDED PORES**

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The aerosol based process opens up for an industrially viable method generating well defined mesostructured powders. In contrast to precipitation routes, it enables full control over composition of the products including additives such as dyes, swelling agents and inorganic dopants. However, the use of volatile additives is not suitable since they would evaporate off before any consolidation of the structures occurred. This includes classic monomeric swelling agents like TMB. However, poly propylene glycol (PPG) with a very limited vapour pressure have been demonstrated elsewhere to work well in the preparation of thin mesostructured films with expanded organic domains when using triblock copolymers (EOxPOyEOx) as the templating amphiphilic molecules.

Here, we demonstrate the positive effects of the addition of PPG to the precursor solutions of aerosol based block copolymer templated silica materials. Up to a certain amount, the PPG addition increases the long range order as well as size of the organic domains. This improves the usability of the calcined templated mesoporous materials in e.g. chromatographic- as well as bio separation processes.

I/PII.38**GROWTH AND CONTROLLED OXIDATION IN ELECTRODEPOSITED Sn AGGREGATES FOR GAS SENSORS**

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The electroplating techniques for depositing metal aggregates and films use commonly an electric current to reduce metal ions in solution, but are restricted to conducting substrate. This new electrochemical technique permits coating of insulating or conducting substrates with metals having controlled aggregates size and growth speed. The basis of our approach is the progressive outward growth of the metal from an electrode in contact with the substrate, with the cell geometry chosen so that the electron current providing the reduction passes through the growing deposit.

The nanostructured deposit is composed of branched nano-aggregates from quasi-continuous film to more dendritic morphology with different current condition. When non-continuous buffer gold coating are used, spontaneous mixing of tin atoms into AuSn particles takes place even at room temperature during the electrodeposition, and then, the tin oxidation realized at moderated temperature (100-200°C) induces unmixing of gold from AuSn and the formation of gas sensing SnO₂ nanostructured coating. After a growth mechanism analysis from elaboration conditions and characterisations of these nanoaggregates, we present the first results obtained in the sensors test. Indeed, we have shown that the sensor functions since it is both sensitive to CO and to C₂H₅OH with a rather acceptable reversibility.

I/PII.39**COMPARISON OF BLTO FILMS DEPOSITED BY MAGNETRON SPUTTERING AND PULSED LASER DEPOSITION**

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The Aurivillius phase Bi_{3.25}La_{0.75}Ti₃O₁₂ (BLT0,75), have been recently explored in our institute as substituting materials for PZT [1], thanks to its high-fatigue resistance, larger remanent polarization and low processing temperatures compatible with Si-based IC technology. BLTO is more promising than SBT in view of its lower processing temperature and higher remanent polarization [2]. Among published results, fatigue-free BLT films have been grown on Pt/Ti/SiO₂/Si substrates using various methods like pulsed laser deposition, MOCVD or sol-gel methods.

In this work, after the synthesis of BLTO powder and sintering of 2" targets, BLTO films were deposited by magnetron sputtering and pulsed laser deposition (PLD), using a mixture of argon and oxygen atmosphere, in a pressure range of 5-50 mTorr and a deposition temperature ranging from RT to 550°C. In a first step, the physico-chemical properties of thin films, with thickness ranging from 100 nm to 1 µm, were characterized by XRD, AFM, XPS, SEM and EDXS. In a second step, electrical characterizations were performed on Si/SiO₂/TiO₂/Pt/BLTO/Pt structures. In this paper, we investigate and compare for the two deposition techniques, the effects of deposition parameters and annealing conditions on the physico-chemical properties of the BLT films, i.e. chemical composition, crystalline structure, optical properties and finally electrical properties. In addition, the effect of substrate with a nanostructured network as carbon nanotubes or nanoporous SiO₂ templates are investigated. [1] M.W. Chu, M. Ganne, M.T. Caldes, L. Brohan, J. Appl. Phys. 91,3178 (2002). [2] BH Park et al., Nature, 401,682 (1999).

I/PII.40 LOCAL STRUCTURE OF POTASSIUM DOPED SILOXANE-POLYOXYPROPYLENE SOLID IONIC CONDUCTORS

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Siloxane-poly(oxypropylene) (PPO) hybrid ionic conductors with short polymer chains were prepared by the sol-gel process and doped with potassium triflate (KCF₃SO₃). The local structure around the potassium cations was investigated by complementary X-Ray spectroscopies: diffraction (XRD), photoelectron (XPS) and absorption (XAS) at the potassium K-edge. The neighborhood of the triflate anions was also studied by 19F solid-state nuclear magnetic resonance (NMR). The X-ray absorption near-edge structure (XANES) shows a different behavior depending on the doping level. While for hybrids prepared with low and medium potassium concentrations ([O]/[K] = 8) the cations interact mainly with the ether-type oxygen polymer chains, high doping levels ([O]/[K] < 8) induce the formation of a crystalline complex in the PPO/KCF₃SO₃ hybrid matrix. NMR 19F spectroscopy revealed the presence of a single coordination site in all samples, differently as observed in the triflate doping salt. The combination of EXAFS and XPS spectroscopies allowed us to determine the nature, the number and the average distance of the first neighbors around potassium. These structural features are correlated to the ionic conduction properties.

I/PII.41 GROWTH MODES AND SELF-ORGANIZATION IN THE EPITAXY OF FERROMAGNETIC SrRuO₃ ON SrTiO₃(001)

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We overview our recent research on the epitaxial growth of ferromagnetic and conductive SrRuO₃ films on SrTiO₃(001) substrates. We report on the surface morphology evolution with thickness of films on vicinal substrates of controlled vicinality. Unique growth modes and self-organized structures have been discovered. On low miscut angle substrates, self-organized finger-like SrRuO₃ structures of nanometric size form after an initial 3D growth of island that nucleated along the substrate steps. With additional growth, there is a transition to a 2D growth mechanism since after the coalescence of the finger-like structures an extremely smooth surface of terraces and steps forms and growth proceeds by step flow. The coalescence of the finger-like structures origins an oriented pattern of disordered regions with an impact on the film properties. We demonstrate that the self-organized quasi 1D fingers (and in turn the properties) can be controlled using SrTiO₃ substrates having different miscut angle (up to a critical value) and by using either as-received or TiO₂-terminated surfaces. On substrates with a miscut angle above 1°, there is giant step bunching that forms from the coalescence of early wedge-like islands. We demonstrate that the size of the bunching can be tuned by controlling the density of these islands.

These findings illustrate that growth processes of complex oxides can be unique and promote novel self-organized morphologies.

I/PII.42 TIN CLUSTERS AS NANOBUILDING BLOCKS FOR HYBRID MATERIALS

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One approach to the design of new hybrid organic-inorganic materials relies on the chemical modification of metal alkoxides by suitable organic ligands which, in addition to provide a chemical link between the organic and inorganic components, control the reactivity of these precursors during the sol-gel process. The reaction of metal alkoxides with carboxylic acids, β -diketones or related compounds is also often the first step in the synthesis of metal oxo-clusters of well-defined structure that can be used as versatile nanobuilding blocks in the preparation of hybrid organic-inorganic materials.

In this sense we have modified the tin (IV) isopropoxide with different carboxylic acids obtaining a new dimer of general formula [Sn(OPri)₂(O₂CR)₂]₂ (OPri = (CH₃)₂CHO, R = (CH₃)CCH₂, C₆H₅, CH₃) which structure, as determined by X-ray diffraction and NMR spectroscopy, is based on two seven-coordinate tin atoms, terminal and bridging isopropoxy ligands, and purely chelating carboxylates. The methacrylate derivative has been used as a nanobuilding block in the preparation of new hybrid materials by combining it with different monomers, like methyl methacrylate, styrene and ethyl acrylate. The obtained polymers have been characterized by several techniques. The results show that the dimer is incorporated, without any structural change, in the polymer network by surface-bonded organic bonds cross-linking the polymer chains very efficiently. Consequently, the incorporation of the cluster has improved the thermal properties of the parent polymers allowing their modulation by adjusting the concentration of the cluster.

I/PII.43 JAMMING STATE OF BINARY MIXTURE DEPOSITION ON PRE-TREATED SURFACES

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We study, through Monte Carlo simulations, the effect of depositing disks of two sizes on patterned surfaces. We adopt as pattern the tiling of square regions of side a separated from each other of a distance b . A binary mixture of disks, with radii r and R , with $r < R$ is deposited. Following our previous studies [1], we characterize the jamming state of the system by the center-to-center distance distribution functions. We define three distinct distribution functions of the center-to-center distance, accordingly to their particle-pair types, namely, small-to-small-, small-to-large-, and large-to-large-disk. Our study can be of interest to people working, for example, in the fields of self-assembled nanostructures, colloids, lithography, and nonequilibrium statistical physics.

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I/PII.44**THE USE OF HEXAGONAL MESOPOROUS SILICA MATRICES FOR THE PREPARATION OF CONTROLLED-ANISOTROPY IRON NANOWIRES**

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Modern information technologies require development of novel high-density data storage devices due to colossal growth of digital information volume. Today, no other technology can compete with magnetic information carriers in storage density and access rate. One of the most ideal systems which can be used as active component of such devices is diamagnetic oxide matrix with well-ordered porous structure and anisotropic magnetic active elements magnetic nanoparticles inside the pores. Iron-containing nanocomposites based on mesoporous aluminosilicates and zeolites were obtained by thermal modification of intercalated (with Fe(CO)₅) or ion-exchanged (with Fe³⁺) ZSM-5 (Al:Si=1:13.3) zeolite and Al-MCM-41 (Al:Si= 2:15, 1:15, 1:30) at different temperatures (200-650 °C). Incorporation of metal ions was studied by chemical analysis TEM, ED, SAXS, SANS, BET and magnetic measurements. It was showed that particles shape and size are in good agreement with that of the pores. The anisotropy parameters of the magnetic wires were determined by temperature dependence of magnetic susceptibility. It was found the particle length increases with the increasing of the decomposition temperature of the metal complex. The better coercivity values at RT were found to be 670 Oe and 380 Oe for Fe/ZSM-5 and Fe/Al-MCM-41 nanocomposites respectively, which is nearly enough for modern information storage. This work is supported by RFBR (03-03-32182) and INTAS (01-204).

I/PII.45**SYNTHETIC ROUTE TO TiO₂ NANO CRYSTALS WITH CONTROLLABLE STRUCTURE AND SHAPE**

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Due to the potential applications in the field of environmental protection, the photochemistry of TiO₂ is a fast growing area. This level of research activity can be appreciated through the exponential increase of relevant research literature produced over the past decade [1][2][3].

Catalysis is key to the development of photoelectrochemical and photochemical approaches. It is now clear that the TiO₂ substrate plays a very active role in the decomposition and reaction processes, since the surface atoms are incorporated in the reaction products, but some fundamental issues need clarification. At the nanostructure level, a fundamental understanding is needed as to how the size and shape of nanoparticles affect their electron transfer reactions at the molecule-inorganic and molecule-solution interfaces. In conventional sol-gel methods, the hydrolysis rates of the titanium alkoxide precursors were too fast and thus the nucleation and growth were never separated into two steps. Starting from the ([Ti₈O₁₂(H₂O)₂₄Cl₁₈.HCl.7H₂O])[4] precursor, we have shown that the control of polycondensation at the various stages of the synthesis made it possible to obtain gel or solids for which the Ti-O networks dimensionality is well defined: 0D, 1D, 2D or 3D. The details of the precursor hydrolysis by TMAOH and the crystal transformation from 2D to 3D structure will be presented.

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I/PII.46**VISCOMMECHANICAL DETECTION OF VAN DER WAALS BONDS IN CARBON-BASED MATERIALS**

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Secondary bonds have long been identified, as having a determinant effect on the strength of polymers. In this paper, this concept is applied to the study of relatively hard (15-25 GPa) hydrogenated amorphous carbon films. With higher hydrogenation, we note a greater fraction of chain-like segments, a decrease of the graphitic content, a smaller hardness, a larger viscoplastic exponent and an increase in creep. The creep behaviour is consistent with the Burgess model. On this basis, we discuss the influence of the Van der Waals bonds on the dynamic and plasticity of the carbon network.

I/PII.47**SYNTHESIS AND STRUCTURAL PECULIARITIES OF Ce-Zr-La-O NANO-SYSTEM**

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When compared with high temperature solid-state reactions for producing of mixed oxides sol-gel and related soft chemistry methods that use solutions in the initial step of the preparation process, posses many advantages. The most significant one is the impact of catalysis attractive properties to materials obtained due to its high surface area and highly defective structure. Herein we report on successful preparation of the nanocrystalline Ce-Zr-La-O powder by a totally inorganic sol-gel technique.

Experimental results obtained by TEM, XRD, DTA, TG, FTIR, ESR, XPS and BET methods allow as to conclude the incorporation of La(III) into Ce-Zr-O structure leads to the highly dispersed (4-5 nm) c-Zr_xCe_{1-x}O₂ solid solution formation, that is stable up to 1100°. Moreover, the ESR studies showed that the inclusion of La(III) into the Zr_{0.5}Ce_{0.5}O₂ lattice results in increasing of Ce³⁺ defects concentration. This may contribute to the high catalytic activity towards partial oxidation of dry methane. The methane oxidation on composite Ce_{0.45}Zr_{0.45}La_{0.10}O₂-Pt anodes in a model SOFC-type reactor provided 73% CO selectivity with 54% conversion efficiency at 900°C and CH₄:O₂ ratio equal to 2.

This research was supported by INTAS (Project 2001-2162), the NATO Science for Peace program (Project 978002), and FCT, Portugal (Projects BPD/11606/2002 and POCTI/CTM/58570/2004).

I/PII.48**NANOSCALE MANIPULATION OF QUANTUM DOTS IN PHOTOLUMINESCENT NANOSTRUCTURES**

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Inorganic nanocrystals, the so-called quantum dots (QD), are employed here as active layers of nanostructured photoluminescent thin films fabricated with the layer-by-layer (LbL) technique. Thyoglycolic acid (TGA)-capped CdSe quantum dots were assembled with two distinct polyelectrolytes, viz. poly(allylamine hydrochloride) (PAH) and poly(amidoamine) (PAMAM), generation 4 dendrimer. Films containing up to 30 polyelectrolyte/QD bilayers were deposited onto glass or quartz substrates. The growth of the multilayers was monitored with UV-VIS spectroscopy, which showed a linear increase in absorbance at 530 nm with the number of deposited bilayers, indicating that the same amount of material is adsorbed at each deposition cycle. Specific interactions occurring in the films were investigated using FTIR and micro-Raman spectroscopies. Photoluminescence (PL) spectra were collected from the LBL films using an ISS-K2 spectrophotometer with an excitation light at 380 nm. PAH/CdSe films containing 10 bilayers emitted at 555 nm, whereas for PAMAM/CdSe films the emission was red-shifted to 565 nm. Atomic force microscopy (AFM) images revealed an efficient multilayer adsorption, with the substrate surface being completely covered after only 2 polyelectrolyte/CdSe bilayers. The films presented globular topography with RMS roughness of ca. 7 nm for a 5-bilayer film in a 1mm x 1mm scanned area. The adsorption process and the optical properties of the PAMAM/CdSe LbL films were further analyzed layer-by-layer using Surface Plasmon Resonance (SPR), from which a thickness of 3.2 nm was found for a PAMAM/CdSe bilayer. Photoluminescence measurements revealed higher photooxidation of the quantum dots in PAH/CdSe than in PAMAM/CdSe films.

I/PII.49**THE ORIGIN OF DEFECTS FORMATION IN NANOSIZED ZIRCONIA**

E.V. Frolova, M.I. Ivanovskaya, Research Institute for Physical Chemical Problems, BSU, Minsk, Belarus

Metal oxide materials derived with the sol-gel technique possess a number of specific features: (i) nanometer size of particles; (ii) highly defective crystalline structure (in particular, high concentration of oxygen vacancies); (iii) occurrence of metastable phases; (iv) stabilization of metal ions in metastable oxidation states; (v) shift of polymorphic transformation temperatures. Moreover, for the many fields of metal oxides use (nonlinear optics, sensors and catalysis) structural defects are desirable.

In the present work the thermally treated (100-900°C in air) two types of ZrO₂ samples, prepared by ammonia-promoted hydrolysis of the ZrO(NO₃)₂ aqueous solutions followed by washing and drying [1]; precipitates (P)- and sol-gel transition and drying - xerogels (X) [2]; were examined by TEM, XRD, DTA, FTIR and ESR. Under the same heat treatment condition the concentration of Zr³⁺ (axially symmetric signal at g₁=1.976 [2]; 1.979 and g₂=1.958 [2]; 1.965 in d₁ state) became higher in the X-samples rather than in P-samples. The concentration of the Zr³⁺ centers reached the maximum (~10¹⁸ spin/g in X-samples) after calcinations at 500°C in air. The experimental results obtained allow us to conclude that the shift of dehydration process to the structural transformation temperature that is caused by the high degree of zirconia nanoparticles hydration, leads to the increasing of the paramagnetic centers concentration. The mechanism of Zr³⁺ formations in parallel with oxygen vacancy [Zr³⁺;Vo] is described.

The work was supported by INTAS (grant 01-2162).

I/PII.50**IMPROVEMENT OF HEAVY METAL FLUORIDE GLASSES RESISTANCE BY SURFACE RECOVERING WITH TRANSPARENT TIN OXIDE LAYERS PREPARED BY SOL-GEL PROCESS**

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Heavy metal fluoride glasses are due to their high transparency over a wide spectral range a promising material for technological applications, however the main drawback is their poor chemical resistance in humid environments. To improve the chemical resistance of zirconium fluoride glass (ZBLAN) a protective SnO₂ transparent layer was prepared by sol-gel dip-coating process in the presence of Tiron(r) as particle surface modifier agent. After immersion in water during different periods of time both coated and uncoated fluoride glasses were analysed by scanning electron microscopy (SEM), mass loss evaluation, infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS). The results showed for unprotected glass that the surface undergoes a rapid selective dissolution of the most soluble species, while for SnO₂ coated glass the filling of the film nanopores by dissolved glass material results in a hermetic barrier protecting the glass surface. The selective glass dissolution was confirmed by liquid chromatography measurements of the etching solution after each exposure time.

I/PII.51**PHOTOLUMINESCENCE STUDY OF NOVEL SELF-ASSEMBLY ORGANIC-INORGANIC MONO-AMINOSIL HYBRIDS**

R.A. Sá Ferreira, S.S. Nobre, J. Cybinska, L.D. Carlos, Departamento de Física and CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal and S.C. Nunes, V. de Zea Bermudez, Departamento de Química and CQ-VR, Universidade de Trás-os-Montes e Alto Douro 5000-911 Vila Real, Portugal

This work reports on the photoluminescence features of innovative sol-gel derived organic-inorganic hybrids (OIHs), so-called mono-amidosils, whose framework is composed of a siliceous backbone bonded to pendant poly(ethylene) (PE) chains by means of amide bridges. Two mono-amidosils containing 8 and 14 PE repeated units were prepared. The mono-amidosil with longer polymer chains presents a self-assembly lamellar structure, induced by H-bonds. Both hybrids display room-temperature emission assigned to the convolution of two components (in the blue/purplish-blue spectral regions) ascribed to donor-acceptor pairs radiative recombinations, which occur in the NH groups of the cross-links and in the siliceous nanodomains involving oxygen-related defects [1]. The PL quantum yields were measured and compared with those of other OIHs. The effect of the organic chains length will be analyzed, in particular the role of the self-organization.

[1] L. D. Carlos, R. A. Sá Ferreira, R. N. Pereira, M. Assunção, V. de Zea Bermudez, J. Chem.Phys. B. 108, 14924 (2004).

A STRUCTURAL AND CHEMICAL STUDY OF GALLIUM NITRIDE NANOSTRUCTURES: NANONEEDLES, NANOBELTS AND NANOWIRES

A.S.W. Wong(a), G.W. Ho(b), P.M.F.J. Costa(a) and C.J. Humphreys(a), (a)Department of Materials Science and Metallurgy, New Museum Site, Pembroke Street, University of Cambridge, Cambridge, CB2 3QZ, U.K., (b)Nanoscience Centre, University of Cambridge, 11 J.J Thompson Avenue, Cambridge CB3 0FF, U.K.

Gallium nitride nanostructures are technologically attractive due to a promising combination of the electronic and optical characteristics of GaN with the one-dimensional confinement offered by the nanoscale structure. The cylindrical geometry and strong two-dimensional confinement of electron, holes and photons of the nanowires makes these nanostructures particularly attractive as potential building blocks for nanoscale electronics and optoelectronic devices. The catalytic growth method, also known as the vapour-liquid-solid growth mode (VLS) is commonly used and has the advantages for small wire size and position. Another growth mechanism, the vapour-solid (VS) method, does not require the use of any metal catalyst for nanostructure growth. Here we describe the reproducible and high density growth of GaN nanoneedles, nanobelts and nanowires grown with a nickel catalyst on SiO₂ substrates. Structural properties were studied in detail using field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and x-ray diffraction (XRD). Both the TEM and XRD results confirm the crystallinity of the nanostructures. High resolution transmission electron microscopy (HRTEM) reveals that the GaN nanoneedles, nanobelts and nanowires are single crystals. Elemental studies using energy dispersive x-ray spectroscopy in the SEM and scanning transmission electron microscopy (STEM) confirms the nanoparticle at the tip of some GaN nanowires to be nickel. However, no nickel particles are observed at the tip of the nanoneedles and nanobelts. These results suggest that the nanoneedles and nanobelts undergo catalystless growth whilst the nanowires growth can occur with or without the nickel catalyst.

Session V : Functional materials

Session chairs :

- I-V.01** 8:30 -Invited- ORDERED MESOPOROUS MATERIALS AS THE BASIS FOR CONTROLLED NANOSTRUCTURING OF SOLIDS
F. Schüth
- I-V.02** 9:15 -Invited- MULTIFUNCTIONAL HYBRID MATERIALS FOR ENERGY PRODUCTION AND STORAGE DEVICES
Mónica Lira-Cantú, Institut de Ciencia de Materials de Barcelona (ICMAB, CSIC), Barcelona, Spain
Functional Hybrid materials based on conjugated polymers (COPs) and inorganic species provide a wealth of opportunities for the development of novel materials with improved properties. The combination of COPs properties includes electronic and ionic conductivity, electroactivity, catalytic, electrochromic, electrooptical properties, among many others, all of them to add to their processability and polymeric nature. This is the base for the the design and synthesis of novel multifunctional materials where each of these properties or the combination of them interact with those of the inorganic counterpart to produce new materials with tunable properties and technological interest. We present a review of the work developed in our group on the synthesis and development of Functional Hybrid Materials and their application as energy production and storage devices such as batteries, supercapacitors, fuel cells or solar cells. Some examples include our "molecular batteries" or electrochemical capacitors based on the interaction of COPs and electroactive molecules (heteropolyanions, hexacyanoferrate anion). The interaction of COPs with layered oxides (V₂O₅, VOPO₄) for batteries, the application of organic polymers (polybenzimidazol) and polyoxometalates as membranes for low temperature fuel cells or the encapsulation of metal nanoparticles as catalyst in fuel cells, etc.
- I-V.03** 9:45 ENGINEERED COLLOIDAL CRYSTALS WITH TUNABLE OPTICAL PROPERTIES
Pascal Masse, Stephane Reculosa, Serge Ravaine Centre de Recherche Paul Pascal - CNRS, 115 avenue du Dr. Schweitzer, 33600 Pessac, France
Colloidal crystals are expected to have applications in optical devices such as photonic band gap crystals. For these applications, it is critical to fabricate a high-quality colloidal crystal with a controllable organization. We present here an innovative method of building up: 1) binary colloidal crystals which consist of successively stacked crystals formed of colloids of different sizes; 2) planar (2D) defects within 3D photonic colloidal crystals. The method is based on a multi-step process that takes advantage of the ability to grow high-quality, controlled-thickness opals by the Langmuir-Blodgett technique. It allows precise control over the parameters that determine the optical properties of these systems, permitting their tuning. Indeed, successive transfers onto solid substrates of pre-organized two-dimensional arrays of particles (SiO₂, ZrO₂,...) with various sizes allow the formation of 3D colloidal crystals with a perfectly controlled architecture, as shown by Scanning Electron Microscopy. Light transmission measurements were also performed to optically characterize the colloidal structures. In the case of the incorporation of a planar defect in a 3D crystal, the appearance of allowed states in the forbidden photonic band of the host material is evidenced and explained according to theoretical models.
- I-V.04** 10:00 OPAL HETEROJUNCTIONS AS FUNCTIONALISED PHOTONIC CRYSTALS
S.G. Romanov, C.M. Sotomayor Torres, Tyndall National Institute, University College Cork, Lee Maltings, Prospect Row, Cork, Ireland, D.N. Chigrin, Institute of Physics, University of Bonn, 53115 Bonn, Germany, N. Gaponik, A. Eychmueller, Institute of Physical Chemistry, University of Hamburg, 20146 Hamburg, Germany, A.L. Rogach, Department of Physics and CeNS, University of Munich, 80799 Munich, Germany, M. Egen, J. Ye, R. Zentel, Institute of Organic Chemistry, University of Mainz, 55099 Mainz, Germany
Formation of opal heterojunctions is a step towards functional photonic crystals (PhCs), which allows inserting artificial defects in self-assembled materials. The anticipated effects are the engineered confinement of the light and directing the light flow. We discuss the effect of the photonic bandgap (PBG) interface upon the transport, emission and scattering of light.
Hetero-opals were prepared by sandwiching thin opal films assembled from latex beads of different diameters, so that their PBG central frequencies are slightly shifted from each other. One of films was impregnated with light emitting CdTe nanocrystals. Angle-resolved transmission, scattering and emission have been studied. The PBG interface is the main source of light scattering, but it does not destroy the ballistic character of light propagation through the hetero-opal for low angles of light incidence as seen by transmission. This leads to squeezing the scattering directionality diagram in hetero-opals, where the intensity decreases with the angle hyperbolically at the rate of "-3" as compared to "-1.5" rate in single opal film. CdTe emission spectra and directionality diagrams acquire strong anisotropy in hetero-opal. Moreover, the emission directionality becomes enhanced after traversing the passive film similar to scattering data. The emission rate is also becomes affected between two PBGs giving rise to emission non-linearity. Finite difference time domain techniques of model 2D PhC hetero-junction revealed the mismatch of mode group velocity at frequencies between two PBGs that can be the reason for the interface anomaly. Thus, the purposive design of PBG interface mismatch is a key issue for developing 3D PhCs with functionalised optical properties.

- I-V.05** 10:15 SOLUTION PROCESSABLE NANOCOMPOSITE DENDRIMERS BASED ON INORGANIC CORES FOR USE IN ORGANIC LIGHT EMITTING DIODES (OLEDs)
Alan Sellinger(a), Sudhakar Sundarraj(a), Ryo Tamaki(b,c), Richard M. Laine(c), Kazunori Ueno(d), Hiroshi Tanabe(d), Evan Williams(e), Ghassan E.Jabbour(e), (a)Institute of Materials Research and Engineering (IMRE), Singapore, Republic of Singapore, (b)General Electric Company, Niskayuna NY, USA, (c)Macromolecular Science and Engineering; Materials Science and Engineering, University of Michigan, Ann Arbor MI, USA, (d)Canon, Inc., Tokyo, Japan, (e)Chemical and Materials Engineering & Flexible Display Center, Arizona State University, Tempe AZ 85284, USA
 Nanocomposite materials based on inorganic cores that combine the advantages of both small-molecule and polymer approaches to organic light emitting diodes (OLEDs) will be presented. The materials are based on silsesquioxane and cyclic phosphazene cores with multi functional sites that can be decorated with a plethora of OLED functional groups. The resulting materials offer numerous advantages for OLEDs including: high glass-transition temperatures (T_g), high solubility, and high-purity via column chromatography. Initial OLED device performance data is presented that shows a 30% improvement over their molecular counterparts. For example, simple undoped Alq₃-based devices prepared using the nanocomposite material as a hole transport layer have high brightness (>35,000cd/m²), and relatively high quantum efficiency (1.25%).
- 10:30 **BREAK**
- I-V.06** 11:00 MULTILAYER MULTIFUNCTIONAL MESOPOROUS METAL OXIDE THIN FILMS MADE BY INTEGRATIVE TEMPLATING AND ETCHING METHODS
Galo J. de A. A. Soler-Illia, Paula C. Angelomé and M. Cecilia Fuertes, Unidad de Actividad Química, CNEA, Centro Atómico Constituyentes, Av. Gral Paz 1499 (B1650KNA) San Martín, Pcia de Bs.As, Argentina
 In the last decade, a sound library of synthesis protocols for materials with tailored porosity and function has been developed. Integrative synthesis methods should allow to combine nanoscopic matter in composites where spatial separation of regions with different chemical properties is possible, leading to advances in integrated chemical sensors, preconcentrators and bionanomaterials.
 In this work, we produce multilayer thin oxide films by EISA methods, combining mesoscale (surfactants) and micron scale (PEO-based polymers) templates. A variety of mesoporous oxide frameworks (cubic or hexagonal silica, titania, zirconia or mixed oxides) can be synthesized, which can include one or several different organic or biological functions (alkyl, amino, thiol, aminoacid...) attached to the pore surface. Organic functions are added by co-condensation or post-grafting. Macroporous titania layers present distinct nested porosities in the 100 nm-4µm, and in the 2-4 nm ranges; post grafting of functional phosphates or phosphonates allow to functionalise these pores. Successive dip-coating/stabilization cycles combined with template extraction/functionalisation permit to create multilayered thin films presenting tailored porosity in the z axis. The film mesostructure can be affected by the mesostructure of the film situated beneath. A clever choice of the framework (Si, Ti, Zr, V, and mixed oxides) permits to selectively attach organic functions to any preselected layer, by making use of the different surface chemistry features. A variety of optical and transport characteristics can be achieved by selectively etching a determined layer.
- I-V.07** 11:15 MAGNETIC SUSCEPTIBILITY OF COLLOIDAL CDSE NANOCRYSTALS
L.E. Calvet*, V.J. Porter, J. Collins, M. Bawendi, M.A. Kastner Department of Physics and Department of Chemistry, Cambridge MA 02139, USA, *Current Address: Unité Mixte de Physique CNRS/Thales (UMR137), Domaine de Corbeville, 91404 Orsay, France
 The physical properties of colloidal semiconductor nanocrystals (NCs) are currently the topic of much research because of their applications in fields spanning biological imaging to optoelectronics. In many such applications the properties of the NC surface are important because it can have a strong impact on optical properties and serve as an interface for electron transport. We use a superconducting quantum interference device to investigate the magnetic susceptibility of varying size CdSe NCs TOPO capped, doped with Nabiphenyl and cap exchanged with butylamine.
 Semiconducting nanocrystals should a priori have the same diamagnetic susceptibility χdia as the bulk. However, the surrounding capping molecules, whose total number per nanocrystal is directly dependent on the number of surface atoms, results in a change of χdia as a function of nanocrystal radius. From χdia we are able to determine an order of magnitude estimate of the number of capping molecules or doping molecules per nanocrystal. At low temperatures we observe large paramagnetic behavior in sealed TOPO capped NCs that is not present after subsequent treatment. We attribute this to the presence of dangling Se surface bonds. We thus show that magnetic measurements can be correlated with structural characterization, optical absorption and electrical transport to yield a synthesized understanding of the structural properties of CdSe NCs.

- I-V.08** 11:30 DEVELOPMENT OF NANOCOMPOSITE COATINGS AS UV AND VISIBLE LIGHT HOLOGRAPHIC RECORDING MATERIAL BY PHOTO-INDUCED DIFFUSION OF NANOPARTICLES
M. Mennig, P.W. Oliveira, S.S. Yip, H. Schmidt, Leibniz-Institut für Neue Materialien gem. GmbH, Im Stadtwald, Gebäude 43 A, 66123 Saarbrücken, Germany
 Nanocomposite coatings with high refractive index nanoparticles functionalized with photopolymerisable groups have been developed as UV and visible light holographic recording media. Due to irradiation, partial polymerisation in the system generates a gradient of carbon double bond concentration between the polymerised and unpolymerised region, which leads to the diffusion of functionalised particles from non-irradiated areas into the light irradiated areas as a result of thermodynamic potential differences. Such a photo-induced diffusion causes an increased concentration of high index nanoparticles in the partially polymerised region and consequently resulting in refractive index modulation of the system. In this connection, nanoparticle containing composites are prepared and coated on plastic substrates by wet coating techniques. The films are subjected to wavelength-dependant polymerisation through specific wavelength exposures by holographic techniques. The holographic exposure showed a full crosslinking of the polymerisable groups, which brings about an effective holographic information recording on the film produced.
- I-V.09** 11:45 Withdraw
- I-V.10** 12:00 TUNING THE PROPERTIES OF NANOSTRUCTURED INORGANIC-ORGANIC HYBRID POLYMERS OBTAINED FROM METAL OXIDE CLUSTERS AS BUILDING BLOCKS
U. Schubert, Y. Gao, F.R. Kogler, M. Yupa, Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9, 1060 Wien, Austria
 Transition metal oxide clusters with suitable organic groups bonded to their surface are prepared by controlled hydrolysis of metal alkoxides in the presence of unsaturated carboxylic acids or by ligand exchange reactions. The pre-formed clusters are then polymerized in the presence of organic co-monomers by various polymerization techniques to form cluster-reinforced polymers. The properties of the cluster-crosslinked hybrid polymers are distinctly different to those of the parent polymers and are influenced by (i) the cluster proportion, (ii) the kind of cluster, (iii) the ratio of functional and non-functional capping ligands, and (iv) the polymerization conditions. The variation of these parameters allows modifying the materials properties of the hybrid materials, such as swelling behavior, thermal stability, etc., and introducing cluster-specific properties into the polymers, such as special magnetic properties.
- I-V.11** 12:15 NANOSCALE RINGS, DOTS AND RODS ON SOLID SUBSTRATE BY SHADOW NANOSPHERE LITHOGRAPHY
 A. Kosiorek, W. Kandulski, H. Glaczynska, M. Olek, M. Giersig, Caesar - Research Center, Dept. Nanoparticle Technology, Ludwig-Erhard-Allee 2, 53175 Bonn, Germany
 Shadow Nanosphere Lithography (SNSL) is a low-cost, time-efficient method used for preparation of large-area, two-dimensionally ordered particle arrays. It uses the monolayer of polymer spheres as a mask for metal evaporation process. Control over the apertures in the mask by its temperature processing and silica coating will be presented and example templates of particles downscaled from 200 to 30 nm, with preserved original nanosphere spacing, will be shown. Variation of the geometry of evaporation setup during the process allows preparation of the simple morphologies such as ring, rod, and dot particles. Experimental results are confirmed by computer simulations, which also show the possibility of creating periodic arrays of any other desired geometrical shapes. The templates are characterized by the size, spacing and shape of the particles. Control over these conditions is very important in nanodevice designing as well as in ground research. SNSL allows an outstanding control of the size and morphology of particles, in comparison to its "older sister" - Nanosphere Lithography (NSL), where the size of the triangle-shaped particles depends only on the spacing in the template. The results will be presented soon. (Accepted by Small.)
 [1] A. Kosiorek, W. Kandulski, P. Chudzinski, K. Kempa, M. Giersig, "Shadow Nanosphere Lithography: Simulation and Experiment" Nano Letters, 2004, Vol. 4, No. 7, 1359-1363
- 12:30 **LUNCH**

Session VI : Solid state approach of hybrids

Session chairs :

- I-VI.01** 14:00 -Invited- FLEXIBLE GUEST SORPTION AND TRAPPING BY METAL-ORGANIC FRAMEWORKS
M. Rosseinsky
- I-VI.02** 14:45 -Invited- ARTIFICIAL ATOM SOLIDS BASED ON NANOCRYSTAL QUANTUM DOTS: SYNTHESIS AND ELECTRICAL PROPERTIES
G. Redmond
- I-VI.03** 15:15 FORMATION MECHANISM AND PHYSICO-CHEMICAL PROPERTIES OF MESOSTRUCTURED THIN FILMS OF TUNGSTEN OXIDE WITH HIGHLY CRYSTALLINE FRAMEWORK OBTAINED FROM NOVEL BLOCK COPOLYMERS
Bernd Smarsly, Torsten Brezesinski, Markus Antonietti, Christian Erpen, MPI of Colloids and Interfaces, Potsdam, Germany
Mesoporous metal oxide thin films have attracted significant attention due to their potential use in photocatalysis, electrochromic devices, sensing etc. A straightforward preparation method is sol-gel chemistry in combination with a suitable structure-directing amphiphilic block copolymer. In the present study, for the first time crystalline mesoporous WO₃ films were fabricated. WO₃, showing a high crystallization temperature, was used as an ideal model system to reveal the crystallization mechanism and to study the influence of mesoporosity on electrochromism. Our approach is based on the use of novel block copolymer templates, showing optimized templating properties, in combination with appropriate temperature treatment conditions. The polymer (KLE) has long hydrophilic PEO and poly(ethylene-co-butylene) hydrophobic blocks, possessing advanced templating properties in terms of thermal stability and hydrophilic-hydrophobic contrast. The crystallisation and mesostructural changes upon temperature treatment were studied by small- and wide-angle x-ray scattering, TEM, HRTEM and AFM. These investigations showed that the crystallization starts after decomposition of the polymer template and is a solid-solid transition from an almost dehydrated amorphous oxide to the crystalline form, i.e. KLE stabilizes an amorphous form at high temperatures. Electrochromic investigations on WO₃ films, coated on FTO substrates, showed an increased response of mesoporous films compared to non-porous and amorphous ones, clearly demonstrating the positive effect of the presence of accessible mesopores, probably by facilitating the diffusion of electrolytes.
- I-VI.04** 15:30 THE STRUCTURAL AND DIELECTRIC PROPERTIES OF THE CORE-SHELL STRUCTURE CERAMICS DERIVED FROM NANOSCALED BST CORE MATERIAL
H.Y. Tian, J.Q. Qi, Y. Wang, H.L.W. Chan, and C.L. Choy, Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China
A nanoscaled Ba_{0.5}Sr_{0.5}TiO₃ (BST) powder was successfully synthesized using a modified hydrothermal process at a low temperature (~80°C). The grain size of BST is close to 17–20 nm, as calculated by XRD patterns and confirmed by TEM and SEM measurements. A perovskite structure core material of the nanoscaled BST was successfully self-wrapped by a non-ferroelectric oxide MgO and solid solution compounds Mg_{0.9}Zn_{0.1}O under ultrasonic dispersion. The dielectric properties were investigated. The results show that there are great decreases in dielectric constants and loss tangent after BST wrapped by MgO and Mg_{0.9}Zn_{0.1}O, lower loss was obtained by employing an additional pre-annealing process at 1150°C for 2 hrs because of improvement of calcinations of the ceramics. Above the Curie temperature, the dielectric tunability and loss of the BST@10%Mg_{0.9}Zn_{0.1}O are between 5–45% and less than 0.5%, respectively. The figure of merit (FOM) is between 20 and 90.
- I-VI.05** 15:45 HYBRID NANOSTRUCTURED MATERIALS BY SUPERSONIC MOLECULAR AND CLUSTER BEAMS
T. Toccoli, N. Coppède, F. Siviero, A. Pallaoro, S. Chiarani, L. Aversa, A. Boschetti, M. Nardi, R. Verucchi and S. Iannotta, IFN-CNR, Istituto di Fotonica e Nanotecnologie Sezione di Trento, Italy
We propose a new approach for nanostructured hybrid materials that, exploiting the properties of the supersonic beams, allows engineering interfaces and interactions at the nanoscale for applications in photovoltaics, gas sensing, biofunctionality, etc. Our approach is based on the codeposition from Supersonic Molecular Beams seeded by molecules (SuMBE) [S. Iannotta and T. Toccoli, J. Polymer Science B, 41 (2003) 2501] and clusters produced by PMCS [P. Piseri et al. Current opinion in Solid State & Materials Science, in press]. The main feature of this approach is the control of the energy and state of aggregation of the precursors in the beam that gives an unprecedented control on the properties of the materials. Nanocrystalline metal oxides, have been deposited at room temperature without the need of any thermal annealing, while highly ordered organic films have been grown on different substrates. We show very relevant effects on the performance of devices such as gas sensors and PV cells. A newly developed UHV growth system allows the simultaneous deposition of inorganic precursor (i.e. nano-oxides, rare earth, etc.) and organic, using up to three supersonic beams. Our approach is uniquely suitable to engineer at the mesoscale the hybrid nanostructures. Nanocrystalline TiO₂ films decorated with pi-conjugated molecules have been characterized by spectroscopic ellipsometry, XPS and UPS, showing an effective ability to tailor chemical physical properties.

15:50

BREAK

Session VII : Polymeric materials

Session chairs :

I-VII.01 16:30 -Invited-

SYNTHESIS AND CHARACTERIZATION OF NOVEL FILM-FORMING
(CO)POLYMER/CLAY COMPOSITE LATEXES
E. Bourgeat-Lami

I-VII.02 17:00

HYBRID POLYION COMPLEX MICELLES AS PRECURSORS FOR POLYMER-
STABILIZED METAL HYDROXIDE NANOPARTICLES

Nicolas Sanson, Corine Gerardin, François Fajula, Laboratoire de Matériaux Catalytiques et
Catalyse en Chimie Organique, UMR ENSCM UMI CNRS 5618, Ecole Nationale
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France

Anionic-neutral double hydrophilic block copolymers were used to control the growth and
morphology of hybrid particles. Suspensions of sterically stabilized metal hydroxide
particles were obtained by hydrolysis of metal cations in the presence of the copolymers.
The metal-complexing polyelectrolyte block ensures a controlled growth of the inorganic
phase as the complexing functions act as poisons of the inorganic polycondensation
reactions, whereas the neutral block ensures steric stabilization of the colloids.

The first synthesis step is the induced assembly of the copolymers in the presence of the
oppositely charged multivalent inorganic species. The formation of the hybrid polymeric-
inorganic nanoaggregates is induced by complexation of the metal cations. The micellar
aggregates present core-corona architectures extensively characterized by light and neutron
scattering techniques. The hybrid polyion complex micelles are then used as adjustable
supramolecular precursors for the formation of metal hydroxide particles. Hydrolysis of
metal ions in the micellar core leads to mineralization of the colloids. The size and the
morphology of the hairy particles can be tuned by adjusting the copolymer-to-metal ratio,
the metal prehydrolysis ratio and the relative polymer block lengths. Moreover, the particle
structure could be changed from a core-corona to a core-shell architecture.

I-VII.02 17:15 -Invited-

BUILD-TO-ORDER ASSEMBLY OF MULTIMATERIAL FILMS
G. Decher

17:45-19:00

POSTER SESSION III

POSTER SESSION III

Thursday, June 2, 2005

17:45 – 19:00

I/PIII.01

HARD CARBON NANOSTRUCTURES PREPARED USING CONVENTIONAL SCANNING ELECTRON MICROSCOPES AND DUAL FOCUSED ION BEAM SYSTEMS

P. Lemoine and J.P Quinn, University of Ulster, Newtonabbey, U.K.

Traditionally, studies on Scanning Electron Microscopy (SEM) contamination are aimed at removing these hydrocarbon films. Recently, this electron-beam induced deposition of carbon has been utilised to form single electron transistors, field emitters and negative resists for nanolithography. Most works focus on producing devices and nanostructures, however, few characterisation or growth studies have been published. In the present article, these layers were produced on silicon substrates and were characterised by atomic force microscopy (AFM), Raman spectroscopy and nanoindentation. The Raman spectra of the contamination layers displayed a broad asymmetric peak, over-imposed on a sloping background. These features are similar to those of hydrogenated amorphous carbon (a-C:H) films grown by PECVD although the D and G peak positions and the ID/IG ratio indicate that the films grown by contamination contain larger sp² clusters. Indeed, the nanohardness of this same film (140nm thick) measured at a depth of 50nm is 10.617 GPa; they are softer than optimised a-C:H films grown by PECVD (~20GPa) and this is consistent with the Raman data. Nonetheless, this contamination layers is harder than would be expected for a pure graphitic or polymeric film on silicon. As shown by previous studies, the organic adsorbates from the oil pumps are cross-linked into a dense amorphous carbon overcoat. Preliminary work using a dual focused ion beam (FIB) system and a naphthalene gas injector shows that high aspect ratio nanostructures can be built to repair or create AFM probes.

I/PIII.02

PROPERTIES OF Ce-Zr-La-O NANO-SYSTEM WITH RUTHENIUM MODIFIED SURFACE

E. Frolova, M. Ivanovskaya, Research Institute for Physical Chemical Problems, BSU, Minsk, Belarus; V. Sadykov, G. Alikina and A. Lukashevich, Borekov Institute of Catalysis SB RAS, Novosibirsk, Russia

Ceria-containing ceramics, particularly ceria-zirconia phases, is attractive for a variety of application, such as sensors, fuel cells, luminescent materials and redox catalysts. Since the defective structure and high temperature stability and dispersity of the samples are the most essential peculiarities of materials under consideration it is very important to develop the methods alloying to control these structural features. The effect of Ce-Zr-La-O preparation method on the structure and catalytic properties of materials obtained have been studied. We examined powdered Ce-Zr-La-O samples (Ce:Zr=1:1, La=10.30 mol.%) derived from thermally treated sol-gel products and xerogels (X) and precipitates (P). FTIR-spectra of only Ce_{0.45}Zr_{0.45}La_{0.10}O₂; X-samples contains band at 1856 cm⁻¹ attributed to the vibration of bonded with surface RuO_x. ESR measurements of P- and X-samples calcined at 600°C in air indicate the appearance of axial Ce³⁺ paramagnetic signals. The concentration of the Ce³⁺ defects after Ru-containing solution impregnation reached its maximum (~10¹⁹ spin/g) in Ce_{0.45}Zr_{0.45}La_{0.10}O₂; X-sample. This very sample posses the highest catalytic activity in methane conversion reaction. According to the XPS data the conversion into colloidal solution as well as 10 mol.% La(III) content favors the fine chemical interaction between the components that result in catalytic activity.

The work was supported by INTAS (grant 01-2162).

I/PIII.03

ELECTROCHEMICAL PROPERTIES OF A RUTHENIUM COMPLEX IN LANGMUIR-BLODGETT FILMS AND CARBON PASTE ELECTRODES

K. Wohnrath(a), C.A. Pessôa(a), P.M. dos Santos(a), J.R. Garcia(b), A.A. Batista(c), O.N. Oliveira Jr.(d), (a)DeQuim/UEPG, Av. Carlos Cavalcanti, 4748, CEP 84030-900, Ponta Grossa, Brazil, (b)DEQ/UNICENTRO, Guarapuava, Brazil, (c)DQ/UFSCar, São Carlos, Brazil, (d)IFSC/USP, São Carlos, Brazil

The electrochemical properties of mer-[RuCl₃(dppb)(4-pic)] (dppb=Ph₂P(CH₂)₄PPH₂, 4-pic=CH₃C₅H₄N), Rupic, in CHCl₃ are governed by the formation of species such as [Ru₂Cl₅(dppb)₂], [Ru₂(dppb)₂Cl₄(4-pic)] and trans-[RuCl₂(dppb)(4-pic)₂] upon the reduction of [RuCl₂(dppb)]₂. The overall behavior depends on whether Rupic is immobilized in cast or Langmuir-Blodgett (LB) films, or incorporated into a carbon paste electrode (CPE). In cyclic voltammograms, one redox process appears for LB/Rupic films and CPE/Rupic, at E_{pa}=0.35 V, E_{pc}=0.25 V vs SCE, and E_{pa}=0.32 V, E_{pc}=0.24 V vs Ag/AgCl, respectively. This redox process was ascribed to the Ru(III)/Ru(II) charge transfer. For cast films the redox pair was poorly defined, with E_{pa}=0.27 V and E_{pc}=0.20 V. The reason for the difference lies in the phase separation and formation of aggregates onto ITO for the cast film, in contrast to the LB film. With aggregation, the formation of species occurring in solution is impaired for Rupic in cast films. The electrochemical properties for Rupic in LB films and incorporated into CPE allowed the electrocatalytic activity of Rupic to be exploited in sensors for dopamine and ascorbic acid.

I/PIII.04

Withdraw

I/PIII.05

SOLID-STATE SYNTHESIS OF INORGANIC ELECTRIDES WITH MAYENITE TYPE STRUCTURE

S. Narushima, S. Ito, Research Center, Asahi Glass Co.,Ltd., 1150 Hazawa, Kanagawa-ku, Yokohama 221-8755, Japan, S. Kim, M. Miyakawa, K. Hayashi, M. Hirano, and H. Hosono, Frontier Collaborative Research Center, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Calcium aluminate (C12A7) crystal with mayenite structure is a microporous material, which is built up by 3-dimensionally connected nano-meter-sized cages. A part of these cages are occupied by free oxide ions. Recently, an inorganic electride, namely, C12A7 electride has been reported to be fabricated by substituting free oxide ions with electrons via chemical treatment using metal Ca. In the present study, we report an alternative method for substituting free oxide ions with electrons to prepare C12A7 electride, which is suitable for practical productions. C12A7 crystal was prepared by a solid-state reaction in a stoichiometric mixture of calcium carbonate and alumina powders at 1300 °C for 6 hours in air. The C12A7 powders obtained were heated at 1300 °C, which is below the melting point of C12A7 (1415°C), for 2 hours in a graphite container with lid. The resulting powders were colored dark green. The diffuse reflectance spectra show that the coloration is due to the intense optical absorption centered at 2.8 eV, which is the same as that observed for the Ca-treated single crystal C12A7 electride. The concentration of clathrated electrons in cages was evaluated to be of the order of 10²⁰ /cm³.

I/PIII.06 ONE-STAGE TEMPLATE SYNTHESIS OF MESOPOROUS SILICAS CONTAINING THIOUREA FUNCTIONAL GROUPS

Yu.L. Zub, O.I. Gona, A.A. Chuiko, Institute of Surface Chemistry, NAS of Ukraine, 17 General Naumov Str., Kyiv 03164 Ukraine, N.A. Yaroshenko, Institute of Sorption and Endoecology Problems, NAS of Ukraine, Kyiv, and A. Dabrowski, LCSU, Lublin, Poland

Sulfur-containing organosilicas have attracted significant interest of researchers since the sorbents on their basis have high selectivity to heavy and noble metal ions in comparison with their oxygen- and nitrogen-containing analogues. At the same time it is obviously that parameters of sorbents porous structure also will influence on their selective sorption properties. In this work an attempt to study an influence of geometric factor on the selectivity on the example of mesoporous silicas functionalized with thiourea group was made. Sorbents were obtained using one-pot template synthesis. Tetra-alkoxysilanes (or bis(trialkoxysilanes)) and trifunctional silanes of $(RO)_3Si(CH_2)_3NHC(S)NHR'$ (R' = alkyl or aryl) composition were used as precursors and ionogenic micelle-formative surfactants (tetraalkylammonium and N-alkylpyridine halogenides), also some nonionogenic surfactants of Triton type were used as templates. It led - after template extraction - to functionalized silicas with various nanosized pores. It is shown that at using of such sorbents having good kinetic characteristics the geometry of their pores in case of some metals really influences on specific adsorption properties.

I/PIII.07 COMPARATIVE CHARACTERISTIC OF STRUCTURE AND PROPERTIES OF HYBRID ORGANIC-INORGANIC ADSORBENTS FUNCTIONALIZED BY AMINE- AND THIOL- GROUPS

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Hybrid organic-inorganic adsorbents were obtained by sol-gel method using two systems: a) $Si(OR)_4 + (RO)_3Si(CH_2)_3L$ and b) $[(R)_3Si]_2R' + (RO)_3Si(CH_2)_3L$ (where $R=Me$ or Et ; $R' = -(CH_2)_2-$, $-(CH_2)_2-$ or $-C_6H_4-$; $L=NH_2$, $-NH(CH_2)_2NH_2$, $1/2=NH$, or $-SH$). The composition, structure and structural-adsorption properties of synthesized xerogels on the basis of data IR and Raman, ^{13}C and ^{29}Si CP/MAS NMR spectroscopy, thermal analysis, SEM, TEM, AFM and adsorption method are established. It is shown, that by varying of nature of functional groups, ratio of reacting alkoxysilanes and other conditions of synthesis it is possible purposefully to influence on the content of ligand groups in a surface layer and parameters of a porous structure of hybrid adsorbents. Comparative description of structure, including surface layers, parameters of a porous structure and sorption properties of obtained xerogels in relation to the pairs of some organic samples and ions of metals is carried out. Comparison of factors which determine the structure and adsorption behavior of hybrid materials of these two classes is also carried out.

I/PIII.08 HARD MAGNETS FROM NANOSIZED IRON OXIDE IN SILICA PREPARED BY SOL-GEL

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We have explored the formation of iron oxide in nano-sized particles by sol-gel synthesis. This approach consists of mixing the reactants with TEOS and addition of formamide. Following gelation and drying, the solid is treated at 300°C for 2h before being calcined between 700 and 1000°C for 1h to 10h. This procedure was found to result in controllable particle sizes ranging from 3 to 12nm. For Co and Fe cations, the principal product is $CoFe_2O_4$ with possibly minor quantities of $g-Fe_2O_3$, $a-Fe_2O_3$. For Y and Fe cations, the principal product is the rare and elusive orthorhombic phase of iron oxide $e-Fe_2O_3$ produced by a fortuitous reaction of the aimed $Y_3Fe_5O_{12}$ with the silica matrix. The rate of reaction for the formation of $e-Fe_2O_3$ is time and T dependent. The samples have been characterized by FTIR, x-ray and neutron dif. in conjunction with Rietveld refinement, thermogravimetry, TEM, Mössbauer and SQUID magnetometry. The different iron phases have been identified and Rietveld refinement of the neutron data of $e-Fe_2O_3$ confirms the structure to be analogous to the orthorhombic $AlFeO_3$ and Ga_2O_3 . For $CoFe_2O_4$ the results show an unusual and unprecedented magnetic hardness characterized by large magneto-anisotropy energy and coercive field attaining 22kOe at 2K. For $e-Fe_2O_3$, we have established a coercive field at room temperature of 18kOe increasing to 22kOe at 200K before decreasing dramatically from 20kOe at 150K to zero at 100K. This is accompanied by a large loss of moment at 100K. The transition is characteristic of that of MORIN for $a-Fe_2O_3$ that is due to a re-orientation of the moments. In both regions, above and below 100K, the ground state is that of a canted antiferromagnet.

I/PIII.09 INFLUENCE OF PRECIPITATION AND AGEING MEDIUM ON THE CHARACTERISTICS OF NANO ALUMINA AND a ALUMINA

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Aluminium metal has been hydrolyzed in aqueous - glycerol media composed of various volume % of glycerol. After hydrolysis in the aqueous - glycerol media, the product i.e., precipitate was aged at room temperature and the ageing medium was diluted periodically.

The precipitation and ageing media has influenced the phase composition and morphology of the hydroxides significantly. The morphology of the hydroxide and a alumina powders were examined using TEM and SEM respectively. It has been found that the crystallinity and morphology of hydroxide influenced the morphology of a alumina, importantly the hydroxide powder prepared using 25 % aqueous- glycerol medium, upon calcination yielded spherical a alumina powder.

- I/PIII.10** CORE-SHELL COPPER HYDROXIDE-POLYSACCHARIDE COMPOSITES WITH HIERARCHICAL MACROPOROSITY
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 An original organic-inorganic composite is formed by controlled mineral growth at the surface of alginate gel microspheres. Cu-alginate beads are formed by ionotropic gelling of drops of polysaccharide solution. The controlled hydrolysis of the charge-compensating copper ions leads to the topotactic deposition of hydroxide phases at the outer surface of the microspheres. The mineral shell stabilizes the core of hydrated polysaccharide gel by preventing shrinking by evaporative drying. At the same time, the hydrogel core prevents the dehydration of the hydroxide phase.
 This synergic stability should lead to the development of a range of applications using both the bactericide properties of the mineral and the biodegradability of the organics. Supercritical drying of the core-shell composites leads to a different class of materials. A radial pattern of macroscopic channels is generated by constrained syneresis. The stiffness of the shell resists the shrinkage of the gel and causes 10-100 μm channels to be opened in the macroporous aerogel. The permeability of the shell can be tailored to control the effectiveness of supercritical drying and the level of syneresis of the core. Such a system finds potential applications in systems for biocatalysis or controlled release.
- I/PIII.11** Withdraw
- I/PIII.12** TALC AS THE CATHODE MATERIAL FOR LITHIUM-ION ENERGY SOURCES
 I.I. Grygorchak, B.P. Bachmatyuk, A. Pidluejna, I.M. Bordun, National University "Lviv Politechnic", Kotlyarevskogo Str. 1, r.1, Lviv 79013, Ukraine
 Significant efforts searches of new effective non-polluting cheap cathodic materials for electrochemical devices of generating, transformation and accumulation of energy are made today. The natural layered minerals due to optimum value of distance between layers and chemical stability of a lattice cause great interest in this direction. Experiments with natural silicate - talc with the sizes of particles 5, 1 and 0,5 microns are carried out. The process of lithium intercalation was carried out by electrochemical way in 1M LiBF₄ in γ-butyrolactone. Thermodynamic researches by method of electromotive force with use of a formalism of spectroscopy of chemical potential specify phase transition of the first kind in an interval of values of "guest" loading 1,75 <x <5,5, that can serve as a limiting stage kinetic of intercalation current creation reactions.
 Kinetics researches of intercalation process was carried out by a method of impedance spectroscopy on frequencies 0.01-100000 Hz. Impedance dependences have the common typical kind with dominating stages of transferring of a charge through border talc|electrolyte (R_{ct} - resistance of a stage of transferring of a charge) and diffusions of the entered ions of lithium on guest positions of talc (W - Warburg factor). Modelling of the received impedance data for a voltage 1,2 V has enabled to determine key parameters of process (C_{dl} - the capacity of a double electric layer of border talc|electrolyte) with accuracy ~5 %. On the basis of these researches disclosing intercalation current creation mechanisms in natural minerals and development of technology of their application in chemical power sources is supposed.
- I/PIII.13** PROBING ELECTRON INJECTION AT ORGANIC / INORGANIC SEMICONDUCTOR INTERFACES
 J. Cabanillas-Gonzalez(a), A. Gambetta(a), C. Manzoni(a), G. Cerullo(a), M. Cantoni(a), F. Ciccacci(a), L. Favaretto(b), G. Barbarella(b) and G. Lanzani(a), (a)IFN-CNR, Dipartimento di Fisica, ULTRAS-INFM, Politecnico di Milano, Milano 20133, Italy, (b)Consiglio Nazionale delle Ricerche (CNR), ISOF, Area della Ricerca di Bologna, via Gobetti 101, 40129 Bologna, Italy
 We report femtosecond pump-probe measurements in an oligothiophene spin-coated on top of a GaAs substrate. The differences in energy gap between both semiconductors are approximately 1.2 eV favorable to the oligomer. The differential reflection signal (DR/R) at an excitation energy of 2.3 eV corresponding to the maximum absorption of the oligomer displays a new photoinduced absorption (PA) band centered at 2.2 eV, which cannot be ascribed to the oligomer nor the inorganic semiconductor. The long formation timescale of the PA signal, (~50 ps), as well as its spectral position suggest the likely formation of charged complexes, probably induced by electron transfer at the interface between both materials.
- I/PIII.14** PBCN ORTHORHOMBIC SnO₂ NANOWIRES FOR NANOSIZED GAS SENSORS CHARACTERIZED BY HRTEM AND EELS
 J. Arbiol(a,b), J.R. Morante(b), E. Comini(c); G. Faglia(c) and G. Sberveglieri(c), (a)TEM-MAT, SSR, Universitat de Barcelona, Lluís Sole i Sabaris 1-3, 08028 Barcelona, CAT, Spain, (b)EME, Departament d'Electronica, Universitat de Barcelona, 08028, Barcelona, CAT, Spain, (c)INFM and Università di Brescia, via valotti 9, 25133 Brescia, Italy
 SnO₂ has been found to be one of the materials that present better sensitivity to CO and NO₂ when used as a gas sensor material. In this context, SnO₂ nanowires were synthesized with the aim of explore and study their capabilities as nanosized sensors. In the present work we will show their detailed HRTEM and EELS characterization. The structure of the SnO₂ obtained nanowires was accurately determined, finding that these nanowires crystallized in the Pbcn SnO₂ orthorhombic phase, which is not the usual tetragonal cassiterite phase described for the SnO₂. Nevertheless, in some samples, partial crystallization as SnO₂ Cassiterite precipitates was also found as surface aggregated grains on the nanowires. Until now, various research groups have been able to synthesize SnO₂ nanowires, in some cases, they are presenting tetragonal Cassiterite phase and, in other cases, they found an orthorhombic structure, similar to that obtained by Suito and co-workers when synthesizing SnO₂ layers under high pressure conditions. However, in our case, the orthorhombic structure of our nanowires seems to be different from theirs, and is crystallizing as the Pbcn (space group) bulk SnO₂ found by Mueller et al., also under high pressure conditions. The sensitivity of the Pbcn orthorhombic phase was found to be higher towards CO with respect to the conventional cassiterite in rheotaxial thin solid films based gas sensors, which suggests that SnO₂ nanowires synthesized on this new structure could improve the sensitivity of the single-nanowire sensors fabricated.
- I/PIII.15** = I/PII.51

I/PIII.16**SELF-ASSEMBLY OF MONO-AMIDE ALKYLENE/ SILOXANE HYBRIDS**

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The synthesis of organic-inorganic hybrid materials through sol-gel chemistry is attractive for the development of multifunctional materials. The combination of the appropriate processing conditions with the adequate choice of the organic and inorganic components dictates the morphology, molecular structure and properties of the hybrids.

Recently this concept was used for the production of self-organised silica-based hybrids with long-range ordered lamellar structure [1,2]. These materials are composed of alkylene chains bonded at both ends to a silica network by means of urea linkages. The degree of order of these hybrids is intimately associated with the interactions established: self-association of the urea groups via hydrogen bonding and hydrophobic interactions between the hydrocarbon chains [1,2]. In the present work, we investigate the self-assembly features of novel alkylene/siloxane hybrids (mono-amidosils) in which methyl-terminated alkylene chains are grafted to the siliceous framework through amide groups. The samples were represented by the formula m-A(X), where m denotes mono and X = 4, 8 and 14 represents the number of CH₂ repeat groups of the hydrocarbon segments.

[1] J. J. E. Moreau, L. Vellutini, M. Wong Chi Man, C. Bied, J.-L. Bantignies, P. Dieudonné, J.-L. Sauvajol, Journal of the American Chemical Society, 123 (2001) 7957

[2] J.-L. Bantignies, L. Vellutini, J.-L. Sauvajol, D. Maurin, M. Wong Chi Man, P. Dieudonné, J. J. E. Moreau, Journal of Non-Crystalline Solids, 345&346 (2004) 605

I/PIII.17**FIRST DIRECT SYNTHESIS OF HIGHLY ORDERED MULTIFUNCTIONALISED MESOPOROUS SILICA THIN FILMS**

Ahmad Mehdi(a), Sandrine Dourdain(b), Jean-François Bardeau(b), Catherine Reyé(a), Alain Gibaud(b) and Robert J.P. Corriu(a), (a)Laboratoire de Chimie Moléculaire et Organisation du Solide, Université de Montpellier II, UMR 5637 CNRS, Place E. Bataillon, 34095 Montpellier Cedex 5, France, (b)Laboratoire de Physique de l'Etat Condensé, Université du Maine, UMR 6087 CNRS, 72085 Le Mans Cedex 09, France

Optically transparent and highly ordered mesoporous organosilica thin films functionalized in the channel pores with two different organic groups in various proportions were synthesized by templated-directed co-condensation of tetraethylorthosilicate (TEOS) and a mixture of two distinct and functional organotriethoxysilanes [NC(CH₂)₃Si(OEt)₃ and O=P(OEt)₂(CH₂)₃Si(OEt)₃]. The mesostructured films obtained by evaporation induced self-assembly (EISA) approach were deposited on glass or silicon substrates by dip-coating. They were characterized by Grazing Incidence Small Angle X-ray Scattering (GISAXS) and X-ray reflectivity. We showed that whatever the proportion in organic groups, only 2D hexagonal phase having p6m symmetry was observed for all materials. The bi-functionalization of the channels pores by the organotriethoxysilanes groups are clearly evidenced by using micro-Raman spectrometry.

I/PIII.18**AN ORIGINAL SYNTHESIS OF LARGE-PORE ORDERED MESOPOROUS SILICAS CONTAINING AMINOPROPYL GROUPS**

Ahmad Mehdi(a), Catherine Reyé(a), Stéphane Brandès(b), Roger Guilard(b), Robert J.P. Corriu(a), (a)Laboratoire de Chimie Moléculaire et Organisation du Solide, Université de Montpellier II, UMR 5637 CNRS, Place E. Bataillon, 34095 Montpellier Cedex 5, France, (b)Laboratoire d'Ingénierie Moléculaire pour la Séparation et les Applications des Gaz, LIMSAG, UMR 5633, Université de Bourgogne, 6 Boulevard Gabriel, 21100 Dijon, France

Advanced Functional Nanomaterials - from Nanoscale Objects to Nanostructured Inorganic and Hybrid Materials
Ordered mesoporous silicas with large-pore diameters incorporating aminopropyl groups in variable quantity have been synthesized via the co-condensation of tetraethylorthosilicate (TEOS) and 3-t-butyloxycarbonylaminopropyltriethoxysilane templated with nonionic surfactant P123 under acidic conditions. They were characterized by powder X-ray diffraction, transmission electronic microscopy, nitrogen adsorption-desorption measurements and ¹³C, ²⁹Si NMR spectroscopies. Two independent routes for carbamate deprotection were used. Thermal treatment under vacuum or acidic hydrolysis gave rise quantitatively to mesoporous silica containing aminopropyl groups, which are fully accessible and could allow immobilization of bio-molecules.

I/PIII.19**PHOTO RESPONSIVE ORDERED HYBRID MATERIALS CONTAINING A BRIDGED AZOBENZENE GROUP**

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We investigated the photochromic behavior of bridged azobenzene moieties located in the framework of modified silica prepared by surfactant-directed self-assembly. For that purpose, co-hydrolysis and polycondensation of 4,4'-[(triisopropoxysilyl)propyloxy]azobenzene 1 and tetraethylorthosilicate in the presence of high concentration of Pluronic P123 as structure directing agent was achieved giving rise to a worm-like nanostructured material containing bridged azobenzene moieties within the silica framework. We show that there is a partial and reversible trans-cis isomerization of bridged azobenzene moieties located in the framework of the mesoporous material in spite of their attachment at both ends to the silica matrix. This process does not occur in the corresponding material prepared in the absence of surfactant. This striking result points out the interest of the surfactant templating approach, which induces a regular dilution of the azobenzene moieties in the material. That prevents strong interactions between azobenzene moieties and allows the isomerization process to take place. In contrast, when the material is prepared under the same conditions but without surfactant, the co-hydrolysis and polycondensation of 1 and TEOS gave rise to a material in which the azobenzene moieties are tightly packed, so that the isomerization process is strongly hindered.

I/PIII.20**SYNTHESIS AND CHARACTERIZATION OF SELENIUM CONFINED IN CARBON NANOTUBES**

Jérôme Chancelon, Françoise Archambault, Alain Pineau, Sylvie Bonnamy, CRMD, CNRS/Université, 1B rue de la Férollerie, 45071 Orléans Cedex 2, France

Carbon nanotubes filling raises the possibility of novel nanomaterials synthesis with technologically interesting properties at a nanometric scale. Furthermore it offers the possibility to enhance the physical properties of encapsulated materials.

In the present work, carbon nanotubes having different inner diameters were filled with Se in order to study the filling mechanism as a function of the nanotubes inner diameter and to investigate the influence of confinement on Se structure and nanocomposite properties. For nanotubes filling, a vapor phase method was carried out, because Se is easy to vaporize due to its low melting and boiling points. Experiments were performed in a sealed glass reactor, where the control of Se partial pressure allows to control the nanotube filling rate. Knowing the initial mass of nanotubes, the nanotube mass up-take was plotted as a function of selenium pressure for different filling temperatures. Se filling occurs by steps. In catalytic MWNTs (inner diameter: 3 to 5 nm), it occurs at first for the smaller diameter, then all the opened nanotubes are filled. That means that filling is governed by capillary condensation phenomenon. In SWNTs, three steps are observed probably corresponding to different Se adsorption sites, computation is in progress to take into account adsorption possibilities according to geometry of pores and SWNTs structural organization. After filling, samples were characterized by HRTEM and EDX analysis, X ray diffraction, EXAFS and Raman spectroscopy. Such 1D nanowires are ideal to investigate the influence of confinement on Se structure and properties.

I/PIII.21**EFFECT OF DOPANT ON THE PHYSICAL PROPERTIES OF POLYMER FILMS FOR MICROPHOTONICS**

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The paper presents experimental results concerning the influence of the additives on physical properties of the polymer films. The used additives were metal oxides/inorganic salts in vinyl-polymers solutions. The physical properties of the metal doped polymer films can be significantly modified by the composition of the doping elements and the curing conditions of the polymer. Structural, morphologic, electronic, magnetic and optic properties of the doped polymers were analysed by AFM, SEM, Mossbauer spectroscopy and optical measurements. The film composition and the deposition processes were optimized to allow a better control of the optical parameters (refractive index, transmission), to reduce the processing temperatures and to improve the chemical sensitivity of the films for sensor applications. These compounds can be easily spin coated onto variety of semiconductor substrates, directly patterned. A simpler process for channel waveguides fabrication was developed and experimented.

I/PIII.22**MECHANICAL PROPERTIES OF UV-PHOTOPOLYMERIZABLE HYBRID SOL-GEL FILMS INVESTIGATED BY AFM IN PULSED FORCE MODE**

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Pulsed Force Mode was successfully used to investigate hybrid sol-gel films based on organically modified silicon alkoxides. This technique provides, simultaneously to the surface corrugation analysis, a measure of the local mechanical properties of the material (stiffness and adhesion). Such a study of the tribological properties of the material at a nanoscopic scale is of highest interest to investigate the influence of material synthesis parameters on the architecture of the nanocomposite material. In particular, we emphasize on the influence of the irradiation times and the inorganic synthesis parameters on the mechanical properties of the films. The advantages of this technique are multiple: AFM/PFM appears to be well-adapted for the characterization of thin films and the submicronic lateral resolution of the technique opens the door to the study of micro- or nano-patterned structures.

I/PIII.23**A COMPARISON BETWEEN ACID AND BASIC CATALYSIS OF GLYCIDOXYPROPYLTRIMETHOXY-SILANE BASED SOL-GEL HYBRID MATERIALS FOR PHOTOCURABLE SYSTEMS**

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Organic-inorganic hybrid materials, composed of inorganic oxide structures cross-linked by organic polymers, are promising candidates for electro/optical applications, combining the most important glasslike and polymerlike properties. The study of patterned structures produced by photopolymerization, has been developed on 3-methacryloxypropyltrimethoxysilane based hybrids in which the polymerizable organic function is the C=C bond of the methacrylic group.

A new photosensitive hybrid material is here described, based on 3- glycidoxypropyltrimethoxysilane (GPTMS) and on the cationic photopolymerization of the epoxide groups, which lead to the formation of a PEO organic interpenetrating network. The largely studied epoxy polymerization of GPTMS hybrid systems has generally been achieved during the sol-gel synthesis by using Lewis acids, basic catalysts, as initiators of organic polymerization or by thermal polymerization. The cationic polymerization of the epoxy groups has been extensively studied but its exploitation for the production of patternable films has not been used until now. In this work the authors demonstrate the feasibility of this process, by preparing epoxy based hybrids films and investigate the influence and the consequence of the acid or basic catalysis of the sol-gel process to produce these epoxy based photocurable materials.

I/PIII.24 NEGATIVE DIFFERENTIAL MAGNETIZATION IN NI DISCONTINUOUS LAYERS EMBEDDED IN AN AL MATRIX

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The magnetic properties of discontinuous Ni/AlO_x multilayers strongly depend on the Al spacer thickness. When only one Ni discontinuous film is grown, the hysteresis loops display a conventional shape with a reduced magnetic moment per atom due to a magnetically dead layer at the Ni cluster surface. While, when more Ni discontinuous films are grown, a strong negative differential magnetisation (NDM) is observed that is interpreted as due to an antiferromagnetic coupling between two populations of magnetic entities having different blocking temperatures. The NDM has been observed for an Al spacer thickness up to 8 nm. The samples are made of Ni discontinuous layers encapsulated in a thin AlO_x barrier, they have been synthesised by successive Al or Ni evaporation alternated with in situ oxidation. These steps have been repeated one or three times and always terminated by the evaporation of an Al cap. Structural characterisation has been done by X-ray absorption spectroscopy performed at the Ni K edge and high-resolution transmission electron microscopy. Small Ni clusters, randomly distributed, embedded in an Al matrix, have been identified with an average diameter about 1.5-2.0 nm, but in large part close to coalescence.

I/PIII.25 ORGANIZATION OF METALLIC NANOPARTICLES ONTO ALUMINA SURFACE : APPLICATION TO THE ELABORATION OF VARIABLE CAPACITORS

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Our work deals with the preparation of multilayers such as "metal / dielectric / 2D nanoparticles assembly / dielectric / metal" which are used for the study of a new concept of variable capacitor based on Coulomb blockade [1, 2]. This phenomenon is directly linked to the nanoparticles assembly properties (size dispersion and density). Co and Au metallic electrodes and Al₂O₃ dielectric layers are made by sputtering, whereas the ruthenium nanoparticles are synthesized via the polyol process [3]. These particles are coated with organic molecules, that give them an appropriate functionality to their subsequent attachment to alumina. They are deposited by soaking the alumina layer in the ruthenium solution. The assembly is characterized by TEM. Transport measurements show a capacitance variation with the voltage dependant of the particles density.

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I/PIII.26 THICK ETCH-THROUGH MACROPOROUS SILICON MEMBRANE WITH TUNING THE PORE SIZE AND FAST PORE ETCHING FROM n-Si

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A thick etch-through macroporous silicon (macro PS) has been fabricated either from a medium doped p- or n-type silicon. The resulting macro PS was characterized by scanning electron microscopy (SEM JOEL 6400F). For the p-type, the smooth and straight pores have been obtained only when optimal conditions were adjusted. The electrolyte was 10 (vol%) HF/DMSO (hydrofluoric acid/dimethyl sulfoxide), the applied current has to be low and the etching time has to be long. Higher HF concentration, or without refreshing the HF during etching would cause thinner walls at the upper part of the pores, which appears as thin wire-like structures. For the n-type, a fast pore etching up to 10 μm/min was achieved by using high HF concentration and high applied current. Also, the pore size has been tuned by varying the doping density of the Si wafer, with the same etching conditions. The lower the doping, the larger the pore size and the faster the etch rate. The macropores on the n-type were highly branched and the morphology can be changed with different oxidizing agents when they were mixed with the HF as electrolytes. This highly branched structure is considered advantageous for immobilizing enzymes in biomedical applications. The p-type macro PS can be used as a microfluidic membrane or used as an optical filter.

I/PIII.27 29SI LIQUID NMR INVESTIGATION OF PHOTOPATTERNABLE HYBRID SOL-GEL

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Methacryloxypropyltrimethoxysilane precursor has been involved in the realization of optical elements in crack free thick films (ranging from 15 to 100 µm), through spatially controlled photopolymerization. First, siloxane functions were partially hydrolysed and condensed. Then, using a photoinitiator, free radical photopolymerization was proceeded by irradiating the sample under UV or visible light. Since an organic network is formed in the matrix of the primarily formed inorganic network, understanding the formation of the silicate backbone was of first importance to insure the creation of crack-free thick films through efficient polymerization.

Liquid 29Si NMR spectroscopy was used to investigate the inorganic network formation. Material preparation required evaporation of the volatile solvents released by the sol-gel process and limitation of the condensation degree. Both conditions were achieved by a drying process at room temperature. The structure and the composition of the dried sols were investigated and compared to non dried sols. Evolution of inorganic species distribution was also studied under increasing aging time or storage temperature. NMR peak fitting pointed out the presence of a large variety of cyclic and linear oligomers in the sol. The structure of the nanocomposite appeared to depend both of the aging time and of the storage temperature. All these results have to be taken into account when tailoring the material for specific optical applications.

I/PIII.28**FLUORESCENCE STUDY OF THE SOL-GEL PROCESS IN HYBRID PRECURSOR**

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Hybrid sol-gel materials have been prepared by hydrolytic polycondensation of methacryloxypropyltrimethoxysilane (MAPTMS). The sol-gel process was followed by fluorescence spectroscopy with 2-naphthol as a probe. It was established that this probe was sensitive to internal solvent chemistry and structural conformation of the silicates. Since the nature of the hybrid precursor led to an inhomogeneous sol, the results presented in this study differ from those relating to precursors with lower molecular weights, such as Si(OMe)₄. The results gave new insights in the sol-gel process and emphasized the influence of a long hydrophobic chain in the hybrid precursor that can be compared to a surfactant. Fluorescence studies revealed fluctuations of the maximum emission intensity and wavelength as a function of time. These fluctuations were attributed to the amphiphilic behavior of the hydrolyzed precursor. They emphasized the reversibility of monomeric silanol aggregates and the changes in hydroxy groups number of the silicate network during the sol aging. The study stresses the importance of an appropriate choice of the photoprobe when monitoring the sol-gel process of hybrid precursors because of the coexistence of nanodomains and bulk phase with highly different local polarities and possible specific interactions of the probe.

I/PIII.29**SECOND-HARMONIC GENERATION FROM LANGMUIR-BLODGETT FILMS OF VARIOUS OPTICALLY NON-LINEAR PYRIDINE AND TERPYRIDINE METAL COMPLEXES**

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Hybrid inorganic/organic compounds can offer a great diversity of tunable electronic properties acting on their second order nonlinear optical (NLO) response.¹ For example, the quadratic hyperpolarizability, measured in solution by the Electric Field Induced Second Harmonic generation (EFISH) technique,² of π -delocalized nitrogen ligands such as stilbazoles³ or terpyridines⁴, bearing a donor group such as a dialkylamino moiety, increases significantly upon coordination to various metal centers reaching values comparable to that of an organic material such as Disperse Red 1 (trans-4,4'-O₂NC₆H₄N=NC₆H₄NEt(CH₂CH₂OH)) currently used in electrooptic polymers.⁵ The current interest for new nanostructured materials with nonlinear optical properties prompted us to study the nanoorganization of this kind of complexes which could lead to a significant NLO response. Thus, in order to obtain a simple model of nanoorganization we investigated the preparation and characterization of monolayer Langmuir-Blodgett films which can allow a non-centrosymmetric packing arrangement of the molecules, and therefore could lead to the achievement of significant NLO properties, and which have been considered the key elements for future molecular technologies for fabricating devices at molecular level.⁶

We found that the molecular quadratic hyperpolarizability of various complexes such as [Ir(CO)2Cl(4,4'-trans-NC₅H₄CH=CHC₆H₄N(Me)(Hexadecyl))], [Os(CO)3Cl2(4,4'-trans-NC₅H₄CH=CHC₆H₄N(Me)(Hexadecyl))], [ZnCl2(4'-(C₆H₄-p-N(Me)(Hexadecyl))-2, 2': 6', 2"-terpyridine)] and [IrCl3(4'-(C₆H₄-p-N(Me)(Hexadecyl))-2, 2': 6', 2"-terpyridine)], measured working in chloroform with a non resonant incident wavelength of 1.907 μ m by the EFISH technique is high and similar to that of previously reported stilbazole and terpyridine complexes.^{3,4} In order to reach a high stability and avoid trans-cis isomerisation, an "Ir(CO)2Cl" complex with an hydroquinoline ligand was also prepared. Its molecular quadratic hyperpolarizability is high ($\chi^{(2)}(1.907) = 618 \times 10^{-30}$ Dcm⁵esu⁻¹) and comparable to that of both the related stilbazole Ir(I) complex ($\chi^{(2)}(1.907) = 755 \times 10^{-30}$ Dcm⁵esu⁻¹) and the hydroquinolinium iodide salt ($\chi^{(2)}(1.907) = 730 \times 10^{-30}$ Dcm⁵esu⁻¹). However it appeared that the second-harmonic generation from the Langmuir-Blodgett films of all the metal complexes investigated is much lower than that of the hydroquinolinium iodide salt. Details of this investigation will be presented here.

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I/PIII.30 ELECTROCATALYTIC OXIDATION OF ASCORBIC ACID AT ACID TREATED MULTI-WALL CARBON NANOTUBE ELECTRODES

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The electrochemical oxidation of ascorbic acid was studied by cyclic voltammetry, differential pulse voltammetry and electrochemical impedance spectroscopy at glassy carbon electrode (GCE) modified with multi-walled carbon nanotubes, MWNTs. Three different types of nanotubes were compared: (i) pristine MWNTs treated in HCl to remove the metal catalyst, (ii) MWNTs refluxed in concentrated HNO₃, and (iii) MWNTs ultrasonically agitated in concentrated HNO₃ and H₂SO₄ in a 3:1 ratio.

The peak current increases with the concentration of ascorbic acid. The oxidation of ascorbic acid at modified electrodes was significantly superior to that observed at bare GCE. The high sensitivity of the CNT electrodes is attributed to the unique carbon nanotube structure and increased surface area providing extra sites for oxidation to occur. Acid treated MWNT electrodes made possible the detection of AA oxidation at the much lower potentials of 0.11 V compared with that of pristine MWNT-GCE and the bare GCE electrode at ~0.3 V. Impedance spectroscopy revealed lower resistance to electrochemical processes at the electrode surface with all types of nanotube modified electrodes. The charge transfer resistance of acid treated MWNT electrodes were two orders of magnitude smaller compared with that of GCE electrode. Also acid treated MWNT electrodes exhibited lower resistance to their pristine counterparts. The study demonstrates that the acid treated MWNT electrodes have greater sensitivity to oxidation and lower impedimetric resistance compared to pristine MWNT. The lower oxidation potentials and resistance of acid treated nanotube electrodes are related to the presence of oxygen groups, attached at the open edges and defect sites as verified by XPS and Raman spectroscopies.

I/PIII.31 = I-V.11

I/PIII.32 MESOPOROUS MATRICES DOPED BY METAL TRANSITION IONS (Cu²⁺, Fe²⁺, Fe³⁺, Co²⁺): EPR INVESTIGATIONS AND NUMERICAL SIMULATIONS

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Electron Paramagnetic Resonance (EPR) experiments are performed on mesoporous silica containing tera-N-propyl cyclam groups doped with metal transition ions in different valence states. The EPR parameters, including g-tensors and hyperfine components are determined and relevant electronic and structural information on the different ions are discussed. The EPR spectra intensities and line-widths are investigated in the temperature range [4K,300K] in the aim to clarify the relative dispersion or the agglomeration of the doping ions in the matrices as well as their possible environment. Thus, for the copper, exhaustive investigations are performed and the shapes of the EPR spectra and their intensities are analyzed taking into account the local environment of the probes in the different matrices. For the cobalt doped matrices, the removal of the orbital degeneracy required for resolved EPR signals is found effective at relatively low temperatures, i.e. below 50K. In that case, a more distorted cobalt environment is suggested from the low symmetry of the corresponding g-tensor which probably correlates with the strong spin-orbit coupling between the 4F fundamental electronic states. As a support of the experimental EPR investigations, numerical simulations of the geometry of metallic ion environments and their electronic properties are carried out and discussed.

I/PIII.33 ELECTROOPTICAL PROPERTIES OF FUNCTIONAL HYBRID GUEST-HOST MATERIALS BASED ON POLYMER-SiC NANOPARTICLES

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The development of synthesis processes of semi conducting SiC nanoparticles have allowed their investigations and evidences of their versatile electronic and optical features were demonstrated. Based on a laser pyrolysis method, different SiC nanopowders can be obtained and systematic studies are carried out as a function of the nanoparticle sizes, surface states and the stabilised crystalline polytypes. These parameters influence also their photoluminescence marked by red emission and induced by oxidation effects and by the involved active electronic centres at the nanoparticle boundaries. In the aim of potential applications, the second step of the process was dedicated to functional materials based on nanosized SiC embedded in host matrices. The more relevant ones are the polymers with regard to their easy preparation, low cost, optical transparency and flexibility. The polymer-nanoparticles interfaces modify the boundary charge density which contributes to the second order optical susceptibility as well as to the refractive index changes. These physical parameters govern respectively the non-linear optics (NLO) and electrooptical (EO) behaviour of the hybrid films. In this context, we have realized functional hybrid materials as polymer/SiC nanocrystals and investigated their EO properties where the interfaces polymer-nanocrystal play a key role. Optimisation of all the process allow us to obtain linear EO parameters in the order of 5-7 pm/V; i.e. in the same order as realized in the standard inorganic monocrystals.

I/PIII.34 OXIDE NANOTEMPLATES FOR SELF-ASSEMBLING "SOLID" BUILDING BLOCKS

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It is widely accepted that the new way for fabricating the new materials (with the intriguing properties) is self-assembling building blocks. In recent years a substantial progress in fabricating such blocks as colloidal particles, polymer blocks and supramolecular aggregates of organic molecules has been achieved. Despite of substantial progress in molecular self-assembly there is still lack of simple blocks made of "solid matter" (e.g. metal, oxides etc.) with well-defined crystal structure and good order.

We propose here that well ordered arrays of metal/metal oxide nanoblocks can be fabricated on a wide range of oxide templates. These oxide templates represent a 2D oxide top-layer, which forms a coincidence structure with the substrate material revealing a long-range Moire pattern. The nano-templates can be fabricated either by depositing an alien oxide film (like FeO/Pt [1]) or oxidizing a metal substrate at appropriate conditions. The last case reveals intriguing phenomena of self-organization of oxide surfaces in a nanostructured 2D-oxide phase [2]. We demonstrate several cases of self-assembly growth of Fe and Cr nano-clusters on FeO(111)/Pt(111), RhOx/Rh(111) and Fe₃O₄(111) nano-templates [3]. In all the cases metal clusters are organized in a well defined arrays with the periodicity of thin film-substrate coincidence lattice. Employing density functional calculations results we discuss the effect of preferential nucleation of metal adatoms on this type of nanotemplates.

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I/PIII.35**HYBRID FUNCTIONAL MATERIALS FOR ENERGY PRODUCTION AND STORAGE DEVICES**

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The integration of electro-ionically active inorganic species in polymer matrices allows for the design of either electrode or electrolyte materials depending on the conducting or insulating properties of the polymer used. Conducting polymers can be used as the basis for a variety of hybrid electrode systems, whereas other polymers such as polybenzimidazoles have been used as electrolyte membranes by themselves or in combination with inorganic solid acids. We will discuss the general approach of hybrid design with this in mind and specifically we will describe our recent results on the use of polyoxometalate-containing hybrids in energy storage and conversion devices. In this respect we have worked in our laboratory on electrochemical supercapacitors and fuel cells but emphasis should be made on the broader potential fields of application of this type of materials.

I/PIII.36**METAL NANOPARTICLES ENCAPSULATED IN CONDUCTING ORGANIC POLYMERS APPLICATION IN ENERGY STORAGE DEVICES**

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Interest on well-ordered superstructures made of metal or metal oxide materials is a growing research area not only from the fundamental point of view, but due to their increasing applications that range from electronic and optoelectronics to medicine-related devices. The use of polymers to encapsulate metal nanoparticles can be tuned in order to limit the size of the particles in to the nanosize level during their synthesis, it also avoids metal agglomeration during their application in different devices, in our case as fuel cell electrode. On the other hand, the application of conducting organic polymers allows the polymer to act not only as synthesis aid but as an electroactive component on the final material. Our research work is focused on the synthesis and application of metal and metal oxide nanoparticles encapsulated in conducting organic polymers and their application energy production and storage devices such as batteries, fuel cells, solar cells, etc. As an example, we show here how these materials help prevent metal agglomeration and catalyst sintering during anode preparation in a solid oxide fuel cell application. Once sintered at high temperatures, the anode present the high porous structure required for good gas transfer reactions, showing also the "pore former" role of the polymer during anode preparation. Several synthesis methods were applied, from surfactant-based to templated-assisted techniques. Some examples include the encapsulation of metal nanoparticles in polymers such as polypyrrole, polyaniline, PEDOT, among others.

I/PIII.37**METAL SPONGES WITH FRACTAL POROSITY FROM SIMPLE COMBUSTION TECHNIQUE**

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The synthesis of open framework materials in a simple fast and reproducible way has been a challenge for many technological applications. Many synthesis routes have been attempted in order to obtain porous structures with large pore sizes and strong magnetic interactions. In this work, we present a fast, non-violent and reproducible single-step combustion method to obtain metallic nickel monoliths with fractal porosity and magnetic properties. The synthesis technique is based on self-sustained combustion reactions which rely on the use of oxidizing and oxidizable (fuel) components. This type of reactions have been widely used for the synthesis of metal oxides, however, we have found out and will present here the application of the method for the synthesis of elemental metals. Indeed, the control of the fuel/oxidant ratio allows for the generation of reducing conditions that can lead to the formation of elemental materials. Furthermore, as it is the case for oxides, the metals resulting from these synthesis present a remarkable microstructure formed by the sintering of metal nanoparticles leading to the growth of foams with fractal porosity. Indeed, observed under different levels of magnification these materials present the same typical microstructure comprised of pores of different sizes, indicating a certain fractal dimension. We will present and discuss in detail our recent results on the preparation of fractal nickel foams as an example of the possibilities of the method.

I/PIII.38**I/PII.52****I/PIII.39****HYBRID POLYMER ARCHITECTURE TO RELEASE SELF-STANDING MULTIMATERIAL FILMS**

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Thin films with multimaterials arranged with nanoscale precision have great potentials for facilitate integration, miniaturisation and multifunctionalisation of the devices. "Layer-by-layer deposition" permits to fabricate multilayer films consist of various materials arranged with nanoscale precision on almost any substrate. If the multimaterial film can be released from the substrate, the obtained self-standing multimaterial films open a wider field of applications, for example separator membrane, medical devices, optical materials. However, the methodology of releasing of those multimaterial films without deteriorations of their properties has not yet established enough.

We developed a new hybrid polymer architecture which releases self-standing multimaterial films by the stimuli of pH change. In this system, the pH responsive multilayer formed via hydrogen-bonds which covers substrate surface releases the multimaterial films constructed onto the pH responsive multilayer. The obtained self-standing film was estimated to be 200 nm in thickness and is several millimeters in width and in length. It was revealed that the existence of the domain isolated from electrostatic interactions in the pH responsive multilayer is the key factor for releasing the upper films. In the presentation, the main principle of the new system, structural features of the hybrid polymer multilayer and the various molecular interactions in the architecture will be discussed.

I/PIII.40**FIRST MAGNETIC MESOPOROUS HYBRID MATERIALS CONTAINING Fe/CYCLAM MOIETIES**

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Mesoporous hybrid materials containing bridged cyclam moieties (cyclam = 1,4,8,11-tetraazacyclotetradecane) in the silicate framework were prepared in the presence of a structure directing agent as well as those containing cyclam moieties located within the channel pores. As cyclam is well known for its remarkable binding ability towards transition metal salts, the binding ability of the cyclam moieties in these materials was tested towards FeCl₂ and FeCl₃. In all cases, it was found that the ratio Fe/cyclam moiety was close to 1/1, which shows that all the cyclam moieties were accessible. In addition, these materials containing cyclam/Fe complexes were studied by ⁵⁷Fe transmission Mössbauer spectrometry at 77K. The first measurements show clearly that the hyperfine structure (i) results mainly from the presence of Fe³⁺ ions, whatever the initial metallic salt is, and (ii) is composed of paramagnetic and magnetically ordered species. This latter species has to be a priori attributed to strongly interacting Fe moments, located in cyclam complexes. Their proportions are dependent on the initial salt (FeCl₃ favouring thus higher content of magnetic Fe ions). Further experiments are in progress to correlate synthesis conditions with the structural and magnetic properties of those mesoporous hybrid materials while zero-field and in-field low temperature Mössbauer spectrometry should provide more information respect to the magnetic nanostructure.

I/PIII.41**SELF-ASSEMBLED NANOTUBES IN ORGANIC SOLVENTS FROM BISAMIDES**

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We developed a series of bisamides that are able to form thermoreversible aggregates in non polar solvents. Their structure have been investigated by electron microscopy. At low concentrations (ca 0.01% mass) the aggregates are mainly helical tapes. At concentrations higher than 0.05%, the bisamides form gels with the solvent, and the aggregates are tubes with lengths of several micrometers and diameters of 25 nm with a low dispersity. SANS and SAXS experiments have been used to confirm the tubular shape of the aggregates and to measure the internal and external radii of the tubes. The bonds that drive the self-assembly have been identified by spectroscopic studies as H bonds between amides and pi interactions between aromatic parts of the molecules.

I/PIII.42**SYNTHESIS AND CHARACTERISATION OF A NOVEL PHOSPHOVANADATE LAYERED HYBRID MATERIAL**

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Much attention has been given over the last years to the synthesis and structural characterization of organic-inorganic hybrid materials given their ability to combine features from both organic and inorganic components, leading to materials with interesting architectures and potential applications.

A novel phosphovanadate layered structure intercalated by 4,4'-bipyridinium cations, (C₁₀H₁₀N₂)(VO₂)₄(PO₄)₂, was synthesised under hydrothermal conditions. The crystal structure was elucidated by single-crystal X-ray diffraction and the material was further characterised using IR, Raman, ¹H, ¹³C{¹H}, ³¹P and ⁵¹V MAS NMR spectroscopies, thermal and elemental analyses. The structure was found to be assembled by an unprecedented secondary tetrametallic V_v building unit (SBU) constructed from a distorted cubane-like {V₄O₄} cluster. The parallel linking in the ab plane, via the phosphate groups, of the SBU leads to a two-dimensional (2D) anionic [(VO₂)₄(PO₄)₂]_n²⁻ layer, topologically described as a distorted (4,4) net, which is perforated by 8-membered rings with an effective cross-section of ca. 2.5×2.5 Å. Charge-balancing and space-filling 4,4'-bipyridinium cations are positioned above and below the anionic [(VO₂)₄(PO₄)₂]_n²⁻ layers. The authors wish to thanks FEDER, POCTI, InTerreg IIIB and FCT for financial support.

I/PIII.43**CUBIC SILSESQUIOXANE-POLYIMIDE NANOCOMPOSITES WITH IMPROVED THERMOMECHANICAL PROPERTIES AND DIELECTRIC PROPERTIES**

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Two series of nanoporous polyimide nanocomposites with well-defined tether architecture have been prepared from octa(aminophenyl)silsesquioxane. TEM, solid-state ²⁹Si NMR, model reaction, density measurement, and WAXD studies show that the nanostructures of the polyimide nanocomposites are well defined and can be adjusted accordingly. The polyimide nanocomposites exhibit tunable dielectric constant with the lowest value of 2.29. The thermomechanical properties of the polyimide have been improved significantly with addition of octa(aminophenyl)silsesquioxane. For example, glass transition temperature increases by ~80°C and storage modulus by 46% respectively as compared to the neat polyimide. Moreover, thermal stability, coefficient of thermal expansion (CTE), hardness, and moisture absorption of the polyimide nanocomposites are also improved significantly.

I/PIII.44**ORGANIC/INORGANIC TRANSITION METAL-THIOPHENE BASED LAYERED MATERIALS: SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES**

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Hybrid Organic/Inorganic system is still an important matter of concern, because it is an efficient way to provide various functionalities where each sub-network exhibits its own property [1].

In particular, the chemistry of layered transition-metal hydroxides, M₂(OH)₃X (M = Co, Cu, Ni, Mn and X = NO₃⁻, CH₃CO₂⁻, Cl⁻), is well adapted for the design of hybrid materials with outstanding magnetic properties [2]. Moreover the X anions located in the interlayer space may easily be substituted by organic species. This species can act as pillars or connectors between the magnetic layers, with strong chemical bonds between inserted molecules and metal based layers. The organic molecules can also bring a new physical property. Recently it has been shown that the magnetic ordering may influence the luminescence of inserted organic moieties [3]. We present here the synthesis and structure-property correlations for a series of hybrid magnetic materials with the layered inorganic framework interleaved by thiophenecarboxylic acids: C₅H₅SCO₂⁻, C₄H₃SCO₂⁻ and C₄H₂S(CO₂)₂. The insertion of the organic molecules into layered transition metal hydroxides can be performed by two ways: anion-exchange with the parent metal hydroxide compounds or direct synthesis with a metal salt. We discuss the modification of the magnetic properties of the inorganic layers caused by the intercalation.

[1] Special Issue, Chem. Mater. 2001, 13.

[2] Rabu, P.; Drillon, M. Adv. Eng. Mater. 2003, 5, 189.

[3] Rueff, J-M; Nierengarten, J-F; Gilliot, P.; Demessence, A.; Cregut, O.; Drillon, M.; Rabu, P. Chem. Mater. 2004, 16, 2933-2937.

- I/PIII.45** OPTICAL AND ELECTROPHYSICAL PROPERTIES OF POLYMER-METAL NANOCOMPOSTIES NEAR THE PERCOLATION THRESHOLD
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 Polymer-metal nanocomposites consisting of metal nanoparticles in a dielectric matrix are promising candidates for data storage, sensors and optical switchable devices. Polymers are particularly suitable matrices since they are sensitive to the external thermal, optical, organic vapor or mechanical stimuli, for instance, and the resulting volume change results in the formation of localized plasmon oscillations or percolation paths if the composition is near the percolation threshold in the polymer-metal nanocomposites. This causes a dramatic change in the plasmon resonance and electrical resistivity. Polymer-metal nanocomposites were synthesized by co-deposition and co-sputtering of noble metals (Au, Ag, Cu) and different amorphous polymers (PTFE, PS, PAN etc.). The polymer matrix is formed by polymerization of a reactive gaseous species, which has been generated in the gas phase by thermal or plasma activation of a precursor. Some advantages of VPD process are excellent conformity over complex topography, the possibility of a good composite film uniformity on relative large substrate, and environmentally friendly processing due to absence of solvents. Several methods like TEM, FTIR, XPS, and UV-VIS were used to characterize the nanocomposite films. To tune the plasmon resonance and electrical resistivity we varied particle size and shape as well as the filling factor by varying the deposition parameters. Moreover, we changed the dielectric properties of the metal nanoparticle itself and the properties of the matrix. The electrophysical properties of metal-filled nanocomposites beyond the percolation threshold are shown to exhibit a number of anomalies, which are very sensitive to the external thermal and mechanical impulses as well as to organic vapors.
- I/PIII.46** SELF-ASSEMBLING AND THERMAL STRIPPING OF ORGANO-BIMETALLIC CLUSTERS OF RuCo₃L ON SURFACES
A. Nait Abdi, O. Toulemonde, J.P. Bucher and M. Drillon, Institut de Physique et Chimie des Matériaux de Strasbourg, Université Louis Pasteur, UMR 7504, 23 rue du Læss, B.P. 43, 67034 Strasbourg, France, J. Rosé, P. Braunstein and R. Welter, Laboratoire de Chimie de Coordination, Université Louis Pasteur, UMR 7513, 4 rue Blaise Pascal, 67070 Strasbourg, France
 One of the main difficulty encountered during the elaboration of nanocomposites is to obtain a final product which is homogeneous and shaped. In this context, different nanocomposites have been prepared using either the post-synthetic method or the direct one. Ag-nanoparticles have been immobilized in mesoporous silica for optical applications. The influence of synthesis parameters on particles size has been shown. Furthermore, incorporated particles are still accessible and can interact, for example, with luminescent species. Mesoporous silica was also used as a host system for bactericidal zinc complexes having different structures. Different loadings were achieved and the time dependence of complexes release was investigated. The last study concerns the incorporation of Ba_{0.6}Sr_{0.4}TiO₃ nanoparticles in a silica gel for electric applications. Different nanocomposites were prepared and their dielectric properties were studied. Results obtained were compared with those obtained with Ba_{0.6}Sr_{0.4}TiO₃@SiO₂ core shell nanoparticles. Finally, advantages and disadvantages of the two methods used for the preparation of nanocomposites are discussed.
- I/PIII.47** ELABORATION OF SILICA-BASED NANOCOMPOSITES
V. Hornebecq, P. Llewellyn, V. Zelenak, MADIREL Laboratory, Centre de Saint-Jérôme, 13397 Marseille Cedex 20, France and T. Cardinal, C. Elissalde, C. Huber, M. Maglione, S. Mornet, M. Treguer-Delapierre, ICMCB-CNRS, 87 Av. Dr. Schweitzer, 33608 Pessac Cedex, France and M. Antonietti, Max Planck Institute of Colloids and Interfaces, 14424 Postdam, Germany
 Studies towards the condensation of acetone and phenol to Bisphenol A have been conducted using organically functionalized mesoporous SBA-15. Sulfonic acid sites have been positioned in the SBA framework, and the effects of spacing have been investigated. The dramatic effect on the reaction of unoxidized thiol in the active site has been investigated, and it has been found that thiol is a much more competent catalyst for the reaction in the presence of sulfonic acid catalyst as well.
- I/PIII.48** HYBRID MESOPOROUS MCM-41 TYPE MATERIALS CONTAINING 1,4-DIAZOBUTADIENE CHELATE LIGAND “INSIDE” THE WALLS: SYNTHESIS AND CHARACTERISATION
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 New organic-inorganic hybrid mesoporous MCM-41 type materials have been synthesised by co-condensation of the different ratios of tetraethyl orthosilicate (TEOS) and 1,4 diazobutadiene (DAB) ligand RN=C(Ph)-C(Ph)=NR [R=(CH₂)₃Si(OEt)₃], in the presence of cetyltrimethylammonium bromide as structure-directing agent. Surfactant extraction under mild conditions leaves hybrid mesoporous materials with periodical hexagonal channels, large pore volumes and high specific surface areas. These mesoporous organosilicas were characterised by powder XRD, N₂ adsorption-desorption isotherms, ¹³C and ²⁹Si CP and CPMAS NMR, TEM, FTIR, elemental and thermal analyses. The variation of the TEOS/DAB ligand has a strong influence on structures and morphologies of the hybrid mesoporous materials. ²⁹Si MAS NMR and FTIR spectra confirmed that the Si-C bonds are covalently linked in the silica network. The integrity of the ligand structure is kept after the extraction step as well as the ordered structure.

I/PIII.49**THE DESIGN OF FUNCTIONAL NANOCONTAINERS BASED ON NANOGOLD TEMPLATE: A NEW AND GENERAL ROUTE FOR NANOPARTICLE FUNCTIONALISATION**

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The past decade has seen the use of non-covalent interactions as a key tool to the construction of new molecular and supramolecular architectures that cover a range of scales. In the area of polymer thin films, the most influential area in the use of non-covalent interactions is the electrostatic layer-by-layer assembly, which was introduced by Decher in 1997 (Decher, G. Science 1997, 277, 1232-1237). This technique allows surface modification of any kind and any shape with high throughput and has experienced an explosion of growth in both application and theoretical advances dealing with the design of nanomaterials (over 1000 citations). The popularity of the method is due to the ability to create highly tailored polymer thin films with a nearly unlimited range of functional group in nanoconstructed structures. Nevertheless, this technique was recently reported to be beyond hope by some authors when applied to gold nanoparticle functionalisation (Gittins D.I., Caruso F. J. Phys. Chem. B 2001, 105, 6846-6852). In fact, adsorption (wrapping) of polyelectrolytes onto (around) oppositely charged nanospheres is a problem in colloid science (stabilisation, surface functionalisation), biology (dna-histone complex) and in theoretical physics. Here we report that gold nanoparticles can easily be coated using layer-by-layer (lbl) deposition as the sole method. The resulting core/shell nanoparticles are so well stabilized that they can be centrifuged and redispersed without agitation or use of ultrasound. At an average recovery of about 95% of particles per layer, at least 20 layers can be deposited with a minimum of particle aggregation.

Thus lbl opens a new and general route for the functionalization of nanoparticles even in aqueous media limiting the risk of ligand exchange reactions. In the case of gold colloids, the core can be gently dissolved resulting in empty (hollow?) Nanospheres.

I/PIII.50**POLYANILINE NANOTUBES**

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When aniline was oxidized with ammonium peroxydisulfate in the aqueous solutions of acetic acid, polyaniline nanotubes have been obtained. Their diameter was 100-200 nm. The conductivity of the bulk materials was 0.1-0.3 S cm⁻¹ depending on the acetic acid concentration. The nanotubes are accompanied by a granular polyaniline precipitate as a rule. It is shown that polyaniline nanotubes are produced also when aniline is oxidized in the absence of any acid. Protonated polyaniline has been deprotonated with ammonium hydroxide to obtain a polyaniline base and ammonium salt of the protonating acid. All these components have been analyzed by FTIR spectroscopy. Although the polymerization has been carried out in the 0-1 M solutions of acetic acid, polyaniline was protonated completely by sulfuric acid produced as a by-product from the decomposition of ammonium peroxydisulfate. It is concluded that acetic acid acts as the acidity buffer, enables the formation of nanotubes, but does not constitute their part.

I/PIII.51**SYNTHESIS AND CHARACTERIZATION OF NEW AROMATIC SUBSTITUTED OXO-ALCOXO-TITANIUM CLUSTERS.**

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Metal oxo clusters are of high interest for incorporation in hybrid or organic matrices for change of dielectric and optical properties. In this study, we focused on oxo-alcoxo titanium clusters.

Transition metal alkoxides M(OR)₄ (M=Ti, Zr, Nb...) have a high reactivity towards nucleophilic reagents. The use of carboxylic acid in order to decrease the precursor's reactivity has two reasons. On one hand, the bidentate behavior of the acid leads to new precursors Ti(OR)_{4-x}(OOCR)_x with moderated reactivity, on the other hand, the excess of acid can react with alcohol via esterification, resulting in in-situ produced water needed for the formation of well defined oxo species.

The reaction of titanium alkoxides Ti(OR)₄ (R=Et, Pr, iPr, Bu, ...) with benzoic acid (C₆H₅COOH) or vinylbenzoic acid (CH₂=CHC₆H₅COOH) (to create a strong hybrid interface) leads to the formation of oxo-alcoxo clusters. The resulting crystals have been characterized by ¹³C- and ¹H-NMR, and IR spectroscopy. The structure of some of them have although been established by single-crystal X-ray diffraction. Oxo-alcoxo titanium clusters such as Ti₆O₄(C₆H₅COO)₈(OR)₈ or Ti₆O₆(C₆H₅COO)₆(OR)₆ (R = Et, Pr, iPr) have been prepared.

First copolymerisation of vinylbenzoic substituted oxo clusters with styrene has been done.

I/PIII.52**ONE-STEP TEMPLATE-DIRECTED SYNTHESIS OF MULTIFUNCTIONALISED NANOPOROUS SILICA: ON THE WAY TO INTERACTIVE NANOMATERIALS**

Eric Besson, Ahmad Mehdi, Victor Matsura, Yannick Guari, Catherine Reyé, Robert J.P. Corriu, Laboratoire de Chimie Moléculaire et Organisation du Solide, Université de Montpellier II, UMR 5637 CNRS, Place E. Bataillon, 34095 Montpellier Cedex 5, France

Advanced Functional Nanomaterials - from Nanoscale Objects to The recent use of bridged silsesquioxanes [(R'O)₃Si]_mR (m=2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12), as precursors for periodic mesoporous organosilicas (PMOs) prepared in the presence of structure-directing agent was a remarkable advance in the material science. Indeed, this method allows integrating organic moieties within silica framework leaving the channel pores unoccupied. That is of great interest as that could be a route to prepare materials coupling to physical properties one located in the channel pores and another in the framework. As the presence of gold nanoparticles in a material containing a NLO chromophore is expected to exalt the NLO response, we achieved the co-hydrolysis and polycondensation of a bisilylated azobenzenephosphonium salt with NLO property, 3-mercaptopropyltriethoxysilane and tetraethoxysilane by using the direct liquid crystal templating approach. That gave rise in one step to multifunctional mesoporous silica containing a NLO chromophore in the framework and mercaptopropyl groups able to stabilize gold (0) nanoparticles in the channel pores. We then succeeded to prepare gold (0) nanoparticles with a narrow size distribution (5.5 nm ± 1nm) in agreement with the pore size of the host material. This is the first example of ordered mesoporous materials containing a large functional group in the framework, and another in the channel pores prepared in one step thanks to the L. C. T. approach. This methodology could be a general route for such materials coupling two properties, which could interact.

Session VIII : Biomaterials
Session chairs :

- I-VIII.01** 8:30 -Invited- NANODEVICES FOR DRUG DELIVERY AND TARGETING
P. Couvreur
- I-VIII.02** 9:15 -Invited- DESIGN OF MULTIFUNCTIONAL NANOPARTICLES
E. Duguet
- I-VIII.03** 9:45 NOVEL PHOSPHATE-PHOSPHONATE HYBRID NANOMATERIALS, APPLIED TO BIOLOGY
B. Bujoli(a), D.R. Talham(b), J.M. Boulter(a), B. Alonso(c), P. Janvier(a), M. Pipelier(a), (a)University of Nantes, France; (b)University of Florida, USA; (c)University of Orléans, France
While research at the frontier between Chemistry and Biology is of major importance for the design of new drugs, there is also high potential for developing novel nanomaterials for biotechnology. In this context, we will describe how phosphonic acid chemistry can be applied to the synthesis of biomaterials.
In the first example, a new support for the preparation of DNA arrays is described, in which the biological probes are bound to a monolayer-coated surface through an "inorganic" linkage, in contrast to existing systems based on the attachment of the probes via organic bonding [Bujoli et al. J. Am. Chem. Soc. 2004, 126, 1497]. In the second example, a novel drug delivery system is designed, based on the chemical grafting of a gem-bisphosphonate monolayer on various calcium phosphates. The resulting biomaterials show promising in vivo results for osteoporosis treatment [Bujoli, et al. Adv. Mater. 2004, 16, 1423].
- I-VIII.04** 10:00 CONTAINING ORMOSILS FOR BONE RECONSTRUCTION
M. Manzano, A.J. Salinas and M. Vallet-Regí, Dpt. Química Inorgánica y Bioinorgánica, Fac. Farmacia. Universidad Complutense de Madrid, 28040 Madrid, Spain
The synthesis of organic-inorganic hybrid materials has attracted much attention as a new type of bioactive materials. These hybrids are an alternative to traditional ceramics because of their mechanical properties that can be tailored to match those of the living tissues. Thus, SiO₂-CaO-PDMS (PolyDiMethyl Siloxane) monolith ormosils (Organically Modified Silicates) have been investigated. The organic content (PDMS) gives structural flexibility, while the inorganic content (SiO₂-CaO) brings the requirements to show a bioactive behaviour.
One of the drawbacks of this system when having a high content of PDMS is the hydrophobic character of the monolith surface which decreases the bioactivity of the hybrid. The use of a phosphorous source such as DiEthyl Phosphato Ethyl TriEthoxySilane (DEPETES) allowed the introduction of P into the network, leading to a bioactive behaviour of the new hybrid. Bioactive ormosils were synthesised by the sol-gel process with PDMS, tetraethyl orthosilicate (TEOS), calcium nitrate tetrahydrate and DEPETES as starting materials. The obtained monoliths were soaked into a Simulated Body Fluid (SBF) for different periods of time, and the bioactivity of hybrids was determined by examining the apatite-like layer formation on the surface of the specimens by XRD, FT-IR spectroscopy and SEM-EDX. To obtain a more homogeneous distribution of the organic content throughout the hybrid and to avoid phase separation, it has been used the precursor monomer of PDMS (Dimethyl DiethoxySilane [DDS]) to produce the polymerisation in situ. Thus, organic domains within the inorganic network were avoided. The conditions to obtain bioactive monoliths were established.
- I-VIII.05** 10:15 EMISSION PROPERTIES AND APPLICATIONS OF NANOSTRUCTURED LUMINESCENT OXIDE NANOPARTICLES
T. Gacoin(a), V. Buissette(a,b), D. Giaume(a), J-P. Boilot(a), (a)Groupe de Chimie du Solide Laboratoire de Physique de la matière condensée, CNRS / Ecole Polytechnique UMR 7643, 91128 Palaiseau, France, (b) Rhodia, Centre de Recherches d'Aubervilliers, 52 rue de la Haie Coq, 93308 Aubervilliers, France
Rare earth doped oxide materials are well known for their numerous applications in light emitting devices. An interesting issue is to study the emission properties of nanoparticles, with the aim to study the influence of small size and surface effects on the emission processes, and to use those particles for new applications such as the elaboration of transparent emitting devices or new biological labels.
We describe here the work done in this field by our group concerning highly luminescent rare-earth doped yttrium vanadate (YVO₄:Eu) and lanthanum phosphate LaPO₄:Ce,Tb-xH₂O nanoparticles. Simple aqueous colloidal syntheses were used for the elaboration of concentrated colloids, based on the progressive decomposition of polymeric precursors at moderate temperature (60-90°C). Both types of particles exhibit strong emission (quantum yields of 25% and 45% for vanadates and phosphates respectively), but significantly lower than for the equivalent bulk material. Improvement was obtained through the elaboration of core/shell nanostructures obtained by the controlled deposition of a thin LaPO₄ shell around the particles. Surface derivatization has been achieved through the controlled growth of an organically modified silica shell using a functionalized silane precursor. Two examples will be given concerning the applications of these particles : the first one is the elaboration of transparent emitting thin films, obtained by the dispersion of the functionalized particles in a sol-gel silica matrix. The other one is the use of guanidine fonctionalized particles as biological labels for the single particle detection of sodium channels in cardiac cells.

Session IX : Nanomaterials: processing and catalysis**Session chairs :**

- I-IX.01** 11:00 ORGANICALLY FUNCTIONALIZED MESOPOROUS SILICATES AS CATALYSTS IN THE FORMATION OF BISPHENOL A
 Ryan K. Zeidan, Veronique Dufaud, Mark E. Davis, Caltech, USA
 Studies towards the condensation of acetone and phenol to Bisphenol A have been conducted using organically functionalized mesoporous SBA-15. Sulfonic acid sites have been positioned in the SBA framework, and the effects of spacing have been investigated. The dramatic effect on the reaction of unoxidized thiol in the active site has been investigated, and it has been found that thiol is a much more competent catalyst for the reaction in the presence of sulfonic acid catalyst as well.
- I-IX.02** 11:15 BIOMIMETIC FUNCTIONAL RECOGNITION FOR REGIOSELECTIVE HYDROGENATION
F. Goettmann(a), C. Sanchez(a), P. Le Floch(b), (a)Laboratoire de Chimie de la Matière Condensée, UPMC-CNRS, 4 place Jussieu, 75005 Paris, France, (b)Laboratoire «Hétéroéléments et Coordination» UMR CNRS 7653 (DCPH), Département de Chimie, Ecole Polytechnique, 91128 Palaiseau cedex, France
 Reaching the efficiency and selectivity of enzymatic catalysis is still a dream for chemists. In the most cases, regioselectivity is induced by an interaction between the substrate and the amino acids of the enzymatic holes. For example, the selectivity of the hydroxylation of valproic acid by cytochrome P450CAM relies on H-bonding between the carboxylic acid moiety of the substrate and the OH group of TYR 96.[1] Mimicking such systems requires well designed chemical engineering. Mesoporous materials (with controlled pore size and organisation and well defined surface properties[2]) and supported homogeneous catalysis provide perfect tools for that quest.
 Herein, we present the synthesis and characterisation of a rhodium I phosphanorbornadiene phosphonic acid, grafted on mesoporous mixed zirconia/silica spray dried powders. This complex sits near to the surface and is thus very rigid, as other hybride bidentate ligands described previously. [3] As the zirconia rich surface is known to be Lewis acidic, complexation of a Lewis basic substrate to the wall is supposed to induce a better recognition of the reactive functions of the substrate. Therefore, this system was tested in monohydrogenation of dienes bearing esters or alcohols. Indeed, hydrogenation of methyl bicyclo[2.2.2]octa-2,5-diene-2-carboxylate in methanol proved to be totally regioselective, whereas the homogeneous reduction was at most 80% selective. Working with geraniol confirmed the proposed mechanism. Geraniol complexation to the surface competes with that of methanol so that the selectivity is only of 30% in that medium. In toluene however, the selectivity reaches 70%.
 [1] J. R. Collins, D. L. Camper and G. H. Loew, J. Am. Chem. Soc. 1991, 113, 3736-3727-3743.
 [2] G. J. D. Soler-illia, C. Sanchez, B. Lebeau and J. Patarin, Chem. Rev. 2002, 102, 4093-4138.
 [3] F. Goettmann, D. Grosso, F. Mercier, F. Mathey and C. Sanchez, Chem. Comm. 2004, 1240-1241.
- I-IX.03** 11:30 AEROSOL GENERATED FUNCTIONALIZED MESOSTRUCTURED MATERIALS
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 Surfactant templated mesoporous materials are characterized by a high surface area, accessible mono disperse pores and hydrothermal- and mechanical stability. This class of materials are usually synthesized in small amounts in a batch-wise manner. We have recently developed a small pilot plant for continuous production of well-ordered spherical mesostructured particles with an output exceeding 10g/h. This presentation will briefly outline the synthesis, and focus on the functionalization of these materials. The production method is based on a modified spray drying equipment. In contrast to precipitation based methods, the aerosol process allows for a superior control over composition of the final product. We will show how photochromic dyes can be incorporated into the mesostructured silica particles. These pigments retain the optical properties of the dyes in solution, and are possible to disperse in different matrices that can be processed into films or monoliths. Another example of a one-pot synthesis is the production of mesoporous materials containing iron oxide nanopartricles. The calcined materials display super paramagnetic behaviour and well defined accessible pores that allows for applications ranging from separation processes to immobilisation and recycling of catalysts.

I-IX.04	11:45	<p>STUDY OF SURFACTANT-SILOXANE INTERFACES IN SPRAY-DRIED MESOPOROUS SILICA-BASED SPHERES</p> <p><u>Bruno Alonso</u>, Dominique Massiot, CRMHT, CNRS, Orléans, France</p> <p>The molecular interactions existing between surfactant aggregates and organometallic oligomers control the final texture of materials obtained through self-assembly processes. It appears thus necessary to investigate more systematically the role of the surfactant-oligomers interfaces during the formation of new compounds.</p> <p>Among the various chemical pathways and materials, we have undertaken the synthesis of mesoporous silica-based micrometric spheres using spray-drying techniques. Like for other Evaporation Induced Self-Assembly processes, the texture is kinetically formed during the solvent evaporation step. However, in the case of spheres, special attention has also to be made to the morphological variations during this step. The characterisation by various techniques (SEM, XRD, TEM, NMR) of the as-synthesised compounds allowed to optimise the textural and morphological properties and to describe the surfactant-siloxane interfaces. A correlation has been found between Si-bound organic groups located at these interfaces and the resulting textural properties. This correlation demonstrates the effect of these organic groups. In particular, it could be used in a predictive way for the synthesis of functionalised spheres.</p>
I-IX.05	12:00	<p>CHARACTERIZATION OF POROUS LOW K FILMS AND PORE SEALING TREATMENT ON PATTERNED AND BLANKET WAFERS BY ELLIPSOMETRIC POROSIMETRY</p> <p><u>A. Darragon</u>, J.P. Piel, C. Defranoux, Y. Turcant, J.L. Stehle, SOPRA, 26 rue Pierre Joigneaux, 92270 Bois-Colombes, France</p> <p>Lowering the film dielectric constant by introducing porosity is the dominant strategy as the microelectronic industry targets to achieve future generations of ultra low K ILD materials. The ITRS roadmap mentions the Low K pore size distribution (PSD), as a parameter needed for integration of the Low K, in the next technology nodes. The ITRS roadmap requires also a metrology tool able to detect pore killers. The sealing of the porous dielectric and the deposition of a thin barrier layer on top are critical for the process integration.</p> <p>Ellipsometric porosimetry (EP0) is an effective method for characterization of porosity, pore size distribution (PSD) of porous low K films. Spectroscopic ellipsometry is used to determine the amount of adsorptive, which is adsorbed in the film. The change in refractive index is used to calculate the quantity of adsorptive present in the film. EP gives accurately the pore size distribution and the porosity of the layer. Several examples will be presented for micro porous layers (with pore size lower than 1nm in radius) or macro porous (with pore size larger than 1nm) deposited by spin coating or CVD equipments. The porosity of the layer ranges from few percent up to 40%. A mapping of these parameters will be presented as well.</p> <p>EP is also suitable to evaluate the sealing of a porous layer. Several examples will be presented on both patterned and blanket wafers. A study on several sealing treatment will be presented where the treatment doesn't seal the porous layer, which would lead to a diffusion of the barrier layer if not detected by the proper metrology. EP evaluates the change in refractive index due to the penetration of the solvent through the sealing layer into the porous layer. EP can detect these parameters on 300mm, 200mm or wafer pieces. The small probing surface allows a edge exclusion of less than 3mm.</p>
	12:15	LUNCH