OXIDE NANOMATERIALS: SYNTHESIS, PROPERTIES, AND APPLICATIONS

Wednesday June 23, 2004

Oxide Nanomaterials: Synthesis, Properties, and Applications I	
9:00 – 9:20a	**ENVIRONMENTAL APPLICATIONS OF SYNTHETIC NANOPOROUS CERAMIC OXIDES.** Glen E. Fryxell*, Shas V. Mattigod, Yuehe Lin, and Hong Wu Pacific Northwest National Laboratory, Richland, Washington, USA
9:20 – 9:40a	**THE ORIGINS OF PORE SHAPES IN MESOPOROUS SILICA THIN FILMS.** Rick E. Williford*, R. Shane Addleman, X. Shari Li, Thomas S. Zemanian, Jerome C. Birnbaum, and Glen E. Fryxell Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 989352
9:40 – 10:00a	**MESOPOROUS MATERIALS FOR ANALYTICAL SENSING AND SEPARATIONS OF ENVIRONMENTAL CONTAMINANTS.** R. Shane Addleman*, Shari X. Li, Dean Kuenzi, Chris Aardahl, Oleg B. Egorov, Matthew O'Hara, Brad Busche, Thomas S. Zemanian, Glen Fryxell Pacific Northwest National Laboratory, Box 999, Richland WA 99352
Oxide Nanomaterials: Synthesis, Properties, and Applications II	
10:20 – 10:40a	**IMMOBILIZED ENZYMES IN NANOPOROUS MATERIALS EXHIBIT ENHANCED STABILITY AND ACTIVITY.** Chenghong Lei[1], Yongsoon Shin[2], Jun Liu[3], and Eric J. Ackerman*[1] [1]Biological Sciences Division, [2]Materials Science Division, Pacific Northwest National Laboratory, Richland, WA 99352; [3]Sandia National Laboratories, Albuquerque, NM
10:40 – 11:00a	**SINGLE ENZYME NANOPARTICLES.** Jungbae Kim*, and Jay W. Grate Pacific Northwest National Laboratory, Richland, WA 99352
11:00 – 11:20a	**APPLICATIONS OF MICROBEADS AND NANOPARTICLES FOR BIOSEPARATIONS AND BIOSENSING.** Cynthia J. Bruckner-Lea Pacific Northwest National Laboratory, P.O. Box 999, MS K4-12, Richland, WA 99352
11:20 – 11:40a	**CHARACTERIZING PARTICLES FOR TOXICOLOGICAL STUDIES.** Sarkis G. Ampian* and William F. Moll Sorptive Minerals Institute, Washington, DC
11:40 – 12:00p	**IRON OXIDE SUPERPARAMAGNETIC NANOPARTICLES FOR TUMOR DIAGNOSIS AND THERAPEUTICS.** Miqin Zhang*, Nathan Kohler, Conroy Sun, Omid Veiseh, Jonathan Gunn, Divakar Gupta University of Washington,Seattle,WA 98195

Oxide Nanomaterials: Synthesis, Properties, and Applications III	
1:20 – 2:00p	**IRON NANOPARTICLES FOR SITE REMEDIATION: SYNTHESIS AND CHARACTERIZATION.** Wei-xian Zhang Department of Civil and Environmental Engineering, Lehigh University, Bethlehem, Pennsylvania 18015
2:00 – 2:20p	**SYNTHESIS AND APPLICATIONS OF OXIDE NANOCLUSTERS AND NANOCLUSTER-ASSEMBLED MATERIALS[†].** You Qiang[*1], Jiji Antony[1], Donald R. Baer[2], Sweta Pendyala[1], and Chongmin Wang[2] [1]Physics Department, University of Idaho, Moscow ID 83844-0903; [2]EMSL, Pacific Northwest National Laboratory, Richland, WA 99352 [†]*Research supported by Idaho NSF-EPSCoR, DOE-PNNL, ONR and DOE-EPSCoR*
2:20 – 2:40p	**SYNTHESIS ROUTES TO NANOMETER-SIZED IRON OXIDES.** John C. Linehan[*1], Dean W. Matson[1], John L. Fulton[1], and John G. Darab[2] [1]Pacific Northwest National Laboratory, P.O. Box 999, MSIN K2-57, Richland, WA 99352; [2]Magnesium Elektron Inc., 500 Point Breeze Rd, Flemington, NJ 08822-9111
2:40 – 3:00p	**REACTIVITY OF IRON OXYHYDROXIDE NANOPARTICLES.** Amy J. Anschutz, David J. Burleson, and R. Lee Penn* Department of Chemistry, University of Minnesota, Minneapolis, MN
Oxide Nanomaterials: Synthesis, Properties, and Applications IV	
3:20 – 4:00p	**WATER ON METAL OXIDES: AN EXPERIMENTAL PERSPECTIVE.** Michael A. Henderson Interfacial Chemistry and Engineering Group, Pacific Northwest National Laboratory, Richland, WA 99352
4:00 – 4:20p	**CHEMICAL ACTIVITY OF NANOPOROUS MgO.** Zdenek Dohnalek[*], Ronald S. Smith, and Bruce D. Kay Pacific Northwest National Laboratory, P.O. Box 999, M/S K8-88, Richland, WA 99352
4:20 – 4:40p	**SYNTHESIS AND SPECTROSCOPY OF DOPED OXIDE SEMICONDUCTOR NANOCRYSTALS.** Daniel R. Gamelin Department of Chemistry, University of Washington, Seattle, WA
4:40 – 5:00p	**SYNTHESIS OF COLLOIDAL Mn^{2+}:ZnO QUANTUM DOTS AND HIGH-T_C FERROMAGNETIC NANOCRYSTALLINE THIN FILMS.** Nick S. Norberg[*1], Kevin Kittilstved[1], James E. Amonette[2], Ravi K. Kukkadapu[2], Dana A. Schwartz[1], and Daniel R. Gamelin[1] [1]Department of Chemistry, University of Washington, Seattle, WA; [2]Pacific Northwest National Laboratory, Richland, WA

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OXIDE NANOMATERIALS: SYNTHESIS, PROPERTIES, AND APPLICATIONS I

9:00AM

ENVIRONMENTAL APPLICATIONS OF SYNTHETIC NANOPOROUS CERAMIC OXIDES.

Glen E. Fryxell*, Shas V. Mattigod, Yuehe Lin, and Hong Wu

Pacific Northwest National Laboratory, Richland, Washington, USA

Surfactant templated synthesis of mesoporous ceramics provides a versatile foundation upon which to create high efficiency environmental sorbents. These nanoporous ceramic oxides condense a huge amount of surface area into a very small volume. The ceramic oxide interface is receptive to surface functionalization through molecular self-assembly. The marriage of mesoporous ceramics with self-assembled monolayer chemistry creates a powerful new class of environmental sorbent materials. These nanoporous hybrid materials are highly efficient sorbents, whose interfacial chemistry can be fine-tuned to selectively sequester a specific target species, such as heavy metals (*e.g.* mercury, cadmium and lead), and oxometallate anions (*e.g.* chromate, arsenate), and radionuclides (*e.g.* plutonium, cesium, pertechnetate). Details addressing the design, synthesis and characterization of SAMMS materials specifically designed to sequester species of importance to environmental clean-up, as well as evaluation of their binding properties are discussed.

THE ORIGINS OF PORE SHAPES IN MESOPOROUS SILICA THIN FILMS

Rick E. Williford*, R. Shane Addleman, X. Shari Li, Thomas S. Zemanian, Jerome C. Birnbaum, and Glen E. Fryxell

Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 989352

The synthetically tailored morphologies of mesoporous silica thin films are important for the successful application of these materials to sensing, separations, and catalysis. Sol-gel methods using surfactant templates can produce a variety of mesopore morphologies. One such morphology, composed of long cylindrical micelles aligned parallel to the substrate, is particularly useful for analysis of the stresses that produce the pore shapes. In thin film applications, the drying and calcining stresses deform the micelles from circular to elliptical, and then to somewhat rectangular cross sections if the films are of sufficient thickness. A linear elastic model using an effective medium concept is proposed to describe this morphology evolution in terms of a minimal set of parameters: the film's Poisson ratio and its thickness strain. The circular to elliptical transition (for thinner films) is verified by comparison to independent experimental data. The elliptical to rectangular transition (for thicker films) involves an increasing pressure in the nearly incompressible liquid polymer that fills the micelles. This pressure leads to a departure from the plane stress conditions normally assumed for thin film analysis, and causes localized failures in the silica matrix that will limit the range of mesopore aspect ratios that is attainable in these materials. Limitations and predictive capabilities of the model are discussed.

MESOPOROUS MATERIALS FOR ANALYTICAL SENSING AND SEPARATIONS OF ENVIRONMENTAL CONTAMINANTS

R. Shane Addleman[*], Shari X. Li, Dean Kuenzi, Chris Aardahl, Oleg B. Egorov, Matthew O'Hara, Brad Busche, Thomas S. Zemanian, Glen Fryxell

Pacific Northwest National Laboratory, Box 999, Richland WA 99352

Self-assembled monolayers on mesoporous supports have a number of properties that make them ideal for environmental sensing and separation application. The mesoporous silica structures are produced through a surfactant templated sol-gel process which endows them with large surface areas and a rigid open pore structure. A high density monolayer of selective complexing ligands can be bound to the silica surface. This organically modified silica nanostructure offers high capacity, rapid sorption kinetics, and interfacial chemistry easily tailored for a wide variety of analytes. We will discuss the advantages, challenges and limitations for using mesoporous materials for the analytical sensing and separations of environmental contaminates. Applications to heavy metals and radionuclides material will be presented.

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OXIDE NANOMATERIALS: SYNTHESIS, PROPERTIES, AND APPLICATIONS II

10:20AM

IMMOBILIZED ENZYMES IN NANOPOROUS MATERIALS EXHIBIT ENHANCED STABILITY AND ACTIVITY

Chenghong Lei[1], Yongsoon Shin[2], Jun Liu[3], and Eric J. Ackerman*[1]

[1]Biological Sciences Division, [2]Materials Science Division, Pacific Northwest National Laboratory, Richland, WA 99352; [3]Sandia National Laboratories, Albuquerque, NM

Enzymes (proteins) are the nano-machines of cells. Unlike conventional catalysts, enzymes efficiently perform chemical reactions with extreme specificity under mild reaction conditions. In cells, molecular crowding provides enhanced protein stability and can induce order-of - magnitude enhancements in catalytic reaction rates compared to enzymes in solution. We recently demonstrated that enzymes can be artificially crowded through immobilization on surfaces to thereby increase their reaction rates and stability.

The focus of our research is to utilize proteins in combination with inorganic materials to create devices and materials with exciting new properties and capabilities. Proteins provide superior catalytic abilities over traditional inorganic type catalysts and the simplified reaction conditions of enzymes require less complex engineering than catalytic reactors. To overcome the inherent fragility of enzymes in solution, one focus of our research is to immobilize enzymes in functionalized nanoporous supports (FMS) that could mimic the stabilizing cellular microenvironment.

Nanoscale materials can be combined with enzymes to dramatically improve the durability of enzymes, create localized high concentrations of protein, and reduce costs by minimizing losses. A major caveat is that the enzyme immobilization reaction must not destroy catalytic activity. Studies within our lab have now demonstrated that at least three unrelated enzymes (organophosphorous hydrolase [OPH], glucose isomerase [GI], and glucose oxidase [GO]) linked to a mesoporous material engineered with cavities or pores sized slightly larger than the enzymes resulted in markedly enhanced thermal and chemical robustness of the enzyme without decreasing its catalytic abilities.

We've succeeded in immobilizing large quantities of 3 active enzymes in functionalized nanoporous materials. Our enzyme specific activity is actually higher once immobilized, consistent with 'molecular crowding' effects observed in cells. One of the enzymes we used, oganophosphorous hydrolase (OPH), inactivates chemical warfare agents. After immobilization in FMS, specific activity was double that of free enzyme; the immobilization efficiency was > 200%; and after 54 days of storage, the enhanced specific activity of the entrapped enzyme was still 167% that of free enzyme.

Our approach could be used to make more sensitive sensors, for decontamination, and to develop advanced separations based on the high specificity of protein-mediated interactions. We can produce large quantities of the materials, so it need not be limited only to research purposes.

SINGLE ENZYME NANOPARTICLES

Jungbae Kim*, and Jay W. Grate

Pacific Northwest National Laboratory, Richland, WA 99352

We have developed single-enzyme nanoparticles (SENs), which dramatically stabilize alpha-chymotrypsin by surrounding each enzyme molecule with a porous composite organic/inorganic network of less than a few nanometers thick. The synthetic procedure, entailing enzyme modification and two orthogonal polymerization steps yields nanoparticles containing a single enzyme, which can be observed by transmission electron microscopy. In experiments with chymotrypsin, incorporation into the nanostructure dramatically increased the enzymatic stability. Furthermore, the nanoscale structure around the enzyme is sufficiently thin that it does not impose a significant mass transfer limitation on the substrate. We have also prepared SENs containing trypsin for the protein digestion in proteomic analysis. These nanoparticles can be further immobilized onto nanostructured matrices that provide a large surface area for attachment. Several examples of successful processing will be given in this presentation. These new nanostructures are very promising for many applications including biosensors, bioreactors, microfluidic devices, decontamination, remediation, antifouling, and protective layers.

APPLICATIONS OF MICROBEADS AND NANOPARTICLES FOR BIOSEPARATIONS AND BIOSENSING

Cynthia J. Bruckner-Lea

Pacific Northwest National Laboratory, P.O. Box 999, MS K4-12, Richland, WA 99352.

The detection of microorganisms in environmental samples often requires extensive sample preparation for the purification and concentration of biomarkers (cells, proteins, or nucleic acids). In addition, approaches are needed for the rapid and sensitive detection of multiple organisms. This presentation will highlight some research at Pacific Northwest National Laboratory involving the use of microbeads and nanoparticles composed of materials such as silica, iron, and quantum dots for bioseparation and biosensing. Superparamagnetic microbeads that contain iron oxide nanoparticles are functionalized with antibodies and used for automated cell concentration from environmental samples, to enable the detection of only10 cells/mL. Porous silica microbeads are used for automated concentration and purification of RNA, to enable the simultaneous detection of microorganisms by mRNA analysis on microarrays. In additions, quantum dots are being developed for use as optical reporters to enable rapid and sensitive biodetection.

CHARACTERIZING PARTICLES FOR TOXICOLOGICAL STUDIES

Sarkis G. Ampian* and William F. Moll

Sorptive Minerals Institute, Washington, DC

Comprehensive particle characterization is essential for any meaningful biological study of respirable particles. A simple XRD pattern and an obligatory BET measurement are insufficient. Excellent examples are the toxicological studies of respirable quartz particles of markedly different origins, which show markedly different biological activities. Naturally-occurring respirable quartz in the atmosphere appears to be markedly less toxic than the crushed quartz created in various man-made processes.

A current series of toxicological experiments studying are comparing the activity of quartz extracted from Wyoming bentonite, a surrogate for natural quartz with a crushed quartz, DQ12. This initial exploratory investigation shows markedly different values for a variety of measurements. These measurements include domain size, morphology, thermal response, surface area, and particle size, as well as chemical analysis and scanning and electron microscopy.

Preliminary toxicological results from a 28 day study show significantly lower quantitative and qualitative effects of the quartz separate vs. DQ-12. Underway is a more comprehensive 90 day study that will elucidate the data more fully, particularly the behavior of the inflammatory response. The study will examine the particles recovered from tissue throughout the experiment to determine any biologically induced changes in them. Of particular interest is the “fine particle effect,” that can lead to a high initial inflammation that lessens over time.

These types of studies should always be a part of any toxicological study of particles.

IRON OXIDE SUPERPARAMAGNETIC NANOPARTICLES FOR TUMOR DIAGNOSIS AND THERAPEUTICS

Miqin Zhang*, Nathan Kohler, Conroy Sun, Omid Veiseh, Jonathan Gunn, Divakar Gupta

University of Washington,Seattle,WA 98195

Major challenges in practical use of magnetic nanoparticles as MRI contrast agents include particle magnetic properties, biocompatibility and dispersity, and specific uptake of particles by the cells. We address these problems by (1) developing novel and low cost synthetic processes to synthesize well-dispersed nanoparticles; (2) developing surface modification techniques to produce a smart and integrated nano-bio-system consisting of nanoparticles coupled with PEG-linked ligands to conjugate surface receptors of tumor cells. In this system, the PEG is used as a linker or spacer between the nanoparticles and diagnostic agents to prevent the nanoparticles from agglomeration and improve biocompatiblity. Use of small ligands to target specific cells facilitates particle internalization by cells. In this study, nanoparticle uptake into tumor cells is visualized using fluorescence and confocal microscopy, and quantified using inductively coupled plasma emission spectroscopy (ICP). Surface modification is characterized by Fourier transform infrared (FTIR) and X-ray photospectroscopy (XPS). Our results showed that derivatized particles were internalized into the cancer cells much more efficiently than unmodified nanoparticles. This research provides a framework on which many material surfaces can be modified to meet the needs of variety of biomedical applications.

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1:20PM

IRON NANOPARTICLES FOR SITE REMEDIATION: SYNTHESIS AND CHARACTERIZATION

Wei-xian Zhang

Department of Civil and Environmental Engineering, Lehigh University, Bethlehem, Pennsylvania 18015

Nanoscale iron particles represent a new generation of remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems. Nanoscale iron particles have large surface areas and high surface reactivity. Equally important, they provide enormous flexibility for in situ applications. Research has shown that nanoscale iron particles are very effective for the transformation and detoxification of a wide variety of common environmental contaminants, such as chlorinated organic solvents, organochlorine pesticides and PCBs. Modified iron nanoparticles, such as catalyzed and supported nanoparticles have been synthesized to further enhance the speed and efficiency of remediation. Field tests have demonstrated promising prospective of the nanoparticles for in situ treatment of contaminated soil and groundwater. In this presentation, recent developments in both laboratory and pilot studies will be discussed. Main topics include: (1) synthesis and characterization of supported and unsupported nanoscale iron particles, (2) laboratory evaluation of the nanoparticles for the transformation of common soil and groundwater contaminants, and (3) field demonstration of the nanoscale iron particles for source control and groundwater treatment.

SYNTHESIS AND APPLICATIONS OF OXIDE NANOCLUSTERS AND NANOCLUSTER-ASSEMBLED MATERIALS[†]

You Qiang[*1], Jiji Antony[1], Donald R. Baer[2], Sweta Pendyala[1], and Chongmin Wang[2]

[1]Physics Department, University of Idaho, Moscow ID 83844-0903; [2]EMSL, Pacific Northwest National Laboratory, Richland, WA 99352

We have developed a nanocluster deposition system, which combines a new kind of sputtering-gas-aggregation cluster beam source with an atom beam from magnetron sputtering. A highly intense and very stable beam of oxides (such as ZnO, ion oxides) nanoclusters has been produced. Core-shell nanostructured Fe/ Fe oxides nanoclusters can be also synthesized. Monodispersive cluster size range is between 2 to 100 nm. Usually the deposition rate is as high as 5 Å/s. The cluster concentration in the film is adjusted through the ratio of cluster and atomic beam deposition rates, as measured *in situ* with a rotatable quartz microbalance. This system is used to deposit simultaneously or alternately cluster films, mesoscopic films or multilayers, and offers the possibility to control independently the incident cluster size and concentration, which is of interest for fundamental research and industry applications. Nanocrystalline structures of single clusters have been studied by AFM, XRD and HRTEM. Magnetic properties of clusters and cluster-assembled materials have been investigated by using SQUID and MFM techniques. We found the photoluminescence of ZnO nanoclusters at room temperature is size dependent, changing from 3.13 to 3.45 eV that is important for photoelectronic devices. Fe/Fe oxide core-shell nanoclusters for biomedical and environmental applications will be discussed.

[†] *Research supported by Idaho NSF-EPSCoR, DOE-PNNL, ONR and DOE-EPSCoR*

SYNTHESIS ROUTES TO NANOMETER-SIZED IRON OXIDES

John C. Linehan[*1], Dean W. Matson[1], John L. Fulton[1], and John G. Darab[2]

[1]Pacific Northwest National Laboratory, P.O. Box 999, MSIN K2-57, Richland, WA 99352;
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Several methods have been shown to be useful for the synthesis of gram to kilogram quantities of nanometer-sized iron-containing materials. Among the techniques used in our laboratory are Rapid Thermal Decomposition of Solutes (RTDS), Modified Reverse Micelles (MRM), Rapid Expansion of Supercritical Solutions (RESS) and general solution techniques. The diverse materials produced can contain iron ranging from iron (0) to iron (III) with both single phase and multiple phase materials of the common iron oxides obtainable. Crystallite and agglomerate size can also be controlled across a wide range by varying processing and work-up parameters. This presentation will briefly describe the above synthesis methods with emphasize on the strengths and weaknesses for each technique.

REACTIVITY OF IRON OXYHYDROXIDE NANOPARTICLES

Amy J. Anschutz, David J. Burleson, and R. Lee Penn*

Department of Chemistry, University of Minnesota, Minneapolis, MN

Nanoparticle reactivity is critically important to the geochemical cycling of both natural and anthropogenic chemical species. Iron oxides and oxyhydroxides are common and important materials in the biogeochemical cycle of iron and other metals and molecular species, such as arsenic, at and near the Earth's surface. These materials commonly occur as nanoparticles in the 3-10 nm size range. Our work shows that rates of redox using quinones as reducing agents and iron oxyhydroxide nanoparticles as reductants are strongly particle size and phase dependent. Current results show that the surface area normalized rate of redox is substantially faster (as much as 18x) in experiments using ferrihydrite versus goethite nanoparticles. Reactions using ~9x70 nm and ~30x350 nm goethite particles show a surface area normalized rate of redox up to 4x faster using the smaller particles. In addition, growth experiments suggest the possibility of size dependent phase stability of goethite nanoparticles and show that goethite almost exclusively grows by oriented aggregation in environmentally relevant conditions (e.g., circumneutral pH and low ionic strength). Results from high-resolution transmission electron microscopy, X-ray diffraction, low-temperature magnetometry, Mössbauer spectroscopy, and X-ray photoelectron spectroscopy of the synthetic iron oxide nanocrystals before and after reduction will be presented.

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OXIDE NANOMATERIALS: SYNTHESIS, PROPERTIES, AND APPLICATIONS IV

3:20PM

WATER ON METAL OXIDES: AN EXPERIMENTAL PERSPECTIVE

Michael A. Henderson

Interfacial Chemistry and Engineering Group, Pacific Northwest National Laboratory, Richland, WA 99352

Water is perhaps the most important and most pervasive chemical on our planet. The influence of water permeates virtually all areas of biochemical, chemical and physical importance, and is especially evident in phenomena occurring at the interfaces of solid surfaces. The water – metal oxide interaction is of particular importance in fields such as catalysis, electrochemistry, photoconversion, geochemistry, adhesion, sensors, atmospheric chemistry, and tribology. Researchers in all these fields grapple with very basic questions regarding the interactions of water with oxide surfaces, such as how is water adsorbed, what are the chemical and electrostatic forces that constitute the adsorbed layer, how is water thermally or non-thermally activated, and how do coadsorbates influence these properties of water. The attention paid to these and other fundamental questions has been immense in recent decades. In this talk, a sampling of recent experimental findings in the literature on water – oxide interactions are presented with a focus on fundamental studies utilizing single crystal surfaces.

CHEMICAL ACTIVITY OF NANOPOROUS MgO

Zdenek Dohnalek*, Ronald S. Smith, and Bruce D. Kay

Pacific Northwest National Laboratory, P.O. Box 999, M/S K8-88, Richland, WA 99352

The chemical activity of, and reagent transport on, nanoporous MgO films are probed using adsorption of various probe molecules. The MgO films employed in this study are grown via reactive ballistic deposition of Mg in the background of O_2 at low temperatures (< 300 K). The films have very high surface area (~ 1000 m^2/g) and high fraction of active, high energy binding sites. As such these films serve as an ideal platform for studies of the catalytic activity of MgO surfaces. The dynamics and kinetics of adsorbate displacement is explored by coadsorption of various weakly bound species (e.g. N_2/CO and N_2/O_2). The exchange of adsorbates between the adsorption sites and facile transport within the film is demonstrated. In case of chemisorption, the dissociation of HCOOH via two distinct channels is seen with $H_2 + CO_2$ and $H_2O + CO$ formation. The overall reaction efficiency and selectivity between these two reaction pathways is determined. The adsorption on flat, high quality MgO(100) surfaces is used as a reference for comparison with the adsorption on nanoporous MgO films.

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SYNTHESIS AND SPECTROSCOPY OF DOPED OXIDE SEMICONDUCTOR NANOCRYSTALS

Daniel R. Gamelin

Department of Chemistry, University of Washington, Seattle, WA

Diluted magnetic semiconductor (DMS) nanostructures such as quantum dots (DMS-QDs), quantum wells, quantum wires, and epitaxial thin films are pivotal architectural elements in many proposed spintronics devices. This talk will present our group's recent advances in the development of direct routes for preparation of freestanding high-quality oxide DMS quantum dots, a target material recently shown to support high-temperature ferromagnetism in thin films. The application of magneto-optical spectroscopic methods (including magnetic circular dichroism and Zeeman spectroscopies) to study the electronic structural properties of oxide DMS-QDs will also be discussed. Finally, data addressing the influence of DMS length scales on high-T_C ferromagnetic ordering will be presented.

SYNTHESIS OF COLLOIDAL Mn^{2+}:ZnO QUANTUM DOTS AND HIGH-T_C FERROMAGNETIC NANOCRYSTALLINE THIN FILMS

Nick S. Norberg[*1], Kevin Kittilstved[1], James E. Amonette[2], Ravi K. Kukkadapu[2], Dana A. Schwartz[1], and Daniel R. Gamelin[1]

[1]Department of Chemistry, University of Washington, Seattle, WA; [2]Pacific Northwest National Laboratory, Richland, WA;

Using direct chemical synthesis to produce oxide diluted magnetic semiconductors free from impurity phases, we have synthesized high quality, colloidal Mn^{2+} doped ZnO nanocrystals in DMSO. Synthesis of these nanocrystals was monitored by electronic absorption and electron paramagnetic resonance (EPR) spectroscopies. Under aerobic reaction conditions, $Zn(OAc)_2$ prevents the oxidation of Mn^{2+} by O_2 towards manganese oxide impurities. Internally doped Mn^{2+}:ZnO nanocrystals of relatively spherical shape and uniform diameters were produced after removing Mn^{2+} ions from the surfaces of the as-prepared nanocrystals using dodecylamine. Simulations of the highly-resolved X-band and Q-band EPR spectra of the surface cleaned nanocrystals confirms substitutional doping of Mn^{2+} in the ZnO nanocrystals with homogeneous speciation. Spin coat processing of these Mn^{2+}:ZnO colloids yielded thin films exhibiting above room-temperature ferromagnetism with saturation moments up to 1.35 μ_B, about an order of magnitude higher than any previously reported saturation moment at room temperature for Mn^{2+}:ZnO. The low temperature solution synthetic technique effectively prevents impurity phase segregation, a common concern of higher temperature vacuum deposition techniques, therefore ensuring the observed ferromagnetism is intrinsic to Mn^{2+}:ZnO.

Department of Chemistry, University of Washington