William R. Wiley EMSL Environmental Molecular Sciences Laboratory

EMSL Report

August 2007 – September 2007

The W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) is a U.S. Department of Energy (DOE) national scientific user facility located at Pacific Northwest National Laboratory (PNNL) in Richland, Washington. EMSL is operated by PNNL for the DOE Office of Biological and Environmental Research. At one location, EMSL offers a comprehensive array of leading-edge resources in six research facilities.

Access to the capabilities and instrumentation in EMSL facilities is obtained on a peer-reviewed proposal basis. Users are participants on accepted proposals. Staff members work with users to expedite access to the facilities and scientific expertise. The Monthly Report documents research and activities of EMSL staff and users.

Research Highlights

On September 28, the EMSL celebrated 10 years of operation as a national scientific user facility. In a ceremony held on the anniversary, a plaque was presented to Mrs. W.R Wiley in recognition of Dr. Wiley's vision and success in moving EMSL from a vision to a reality. M. Kluse, PNNL Director, M. Weis, DOE Pacific Northwest Site Office, and R.D. Smith, EMSL High Performance Mass Spectroscopy Facility, spoke at the event noting that, "Without the support of DOE, our staff, the scientists, and our users and their families, EMSL could not build on its success in the coming decade." Approximately 200 staff, users, and family members attended the event.

Covalent Immobilization of Peptides on Self-Assembled Monolayer Surfaces

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The high selectivity inherent in mass spectrometry and ion beam chemistry may provide unprecedented control for preparation of novel substrates for biorecognition studies and biomaterials for stimulated protein and cell adhesion.

Covalent immobilization of peptides on solid supports plays an important role in biochemistry with applications ranging from characterization of molecular recognition events at the amino acid level and identification of biologically active motifs in proteins to development of novel biosensors and substrates for improved cell adhesion. Self-assembled monolayers (SAMs) provide a simple and convenient platform for tailoring chemical properties of surfaces. Existing techniques for linking peptides to SAMs are based on solution-phase synthetic strategies and require relatively large quantities of purified material.

In this highlight, we report a novel approach for highly selective covalent binding of peptides to SAMs using soft-landing (SL) of mass-selected ions. Soft-landing is defined as intact deposition of ions onto suitable substrates at hyperthermal (i.e., less than 100 eV) energy levels. Recent studies have demonstrated that SAMs are excellent deposition targets for SL because of their ability to dissipate kinetic energies of the projectiles and their efficiency in trapping captured species. It has been proposed that SL could be used for controlled preparation of protein arrays.

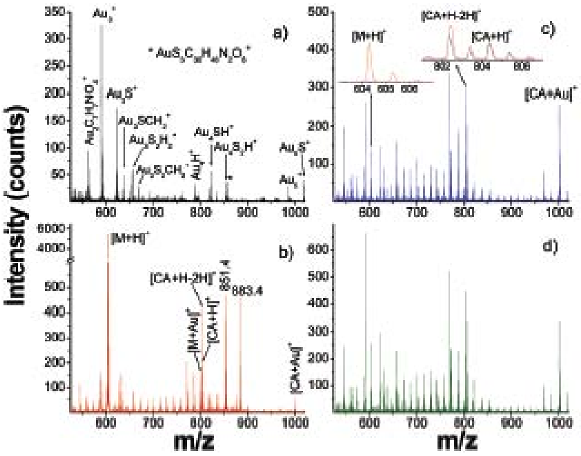

Figure 1. TOF-SIMS spectra of unmodified NHS-SAM (a); NHS-SAM with 1 ng soft-landed c(-RGDfK-) before (b) and after (c) rinsing; and NHSSAM following 2 h solution-phase reaction (d).

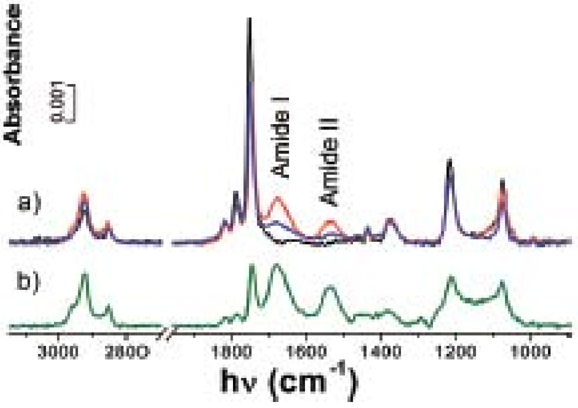

Figure 2. IRRAS spectra of unmodified NHS-SAM (a, black); NHS-SAM with 18 ng soft-landed c(-RGDfK-) before (a, red) and after (a, blue) rinsing; and NHS-SAM following 2 h solution-phase reaction (b, green).

Self-assembled monolayer surfaces before and after SL are characterized *ex situ* using 15 keV Ga$^+$ time-of-flight secondary ion mass spectrometry (TOF-SIMS) and grazing-incidence, infrared reflection-absorption spectroscopy (IRRAS). Surfaces prepared by SL were analyzed before and after rinsing in methanol. Figure 1b shows TOF-SIMS spectra of the N-hydroxysuccinimidyl ester terminated alkylthiol on gold (NHS-SAM) surface following SL of 1 ng of mass-selected c(-RGDfK-). In addition to common surface-related peaks (Figure 1a), TOF-SIMS spectra obtained following SL contain numerous peptide-related peaks. The spectrum obtained following SL is dominated by the singly protonated, [M + H]+, ion (m/z 604.3). Other major features include [M + Au]+ (m/z 800.2) and peptide-SAM complexes at m/z 851.4 and 883.4. These species are almost completely removed from the surface by sonication and thorough rinsing in methanol (Figure 1c), which suggests that they are loosely bound to the NHS-SAM surface. Interestingly, a significant number of peptide-related peaks are not affected by the rinsing procedure. Moreover, striking similarities between the spectrum shown in Figure 1c and the spectrum obtained for peptide grafted onto the NHS-SAM from solution (Figure 1d) suggest that these features correspond to peptide molecules covalently linked to the NHS-SAM surface. The observed fragmen-tation pattern provides strong support for covalent binding of c(-RGDfK-) to the NHS-SAM surface through the lysine side chain. Other lysine- containing peptides including GRGDSPK and KAAAA were also linked successfully to the NHS-SAM surface by reactive landing.

Although TOF-SIMS is a very sensitive technique for molecules adsorbed on surfaces, secondary ion yields strongly depend on the substrate, coverage, and the binding energy between the adsorbate and the surface. In this study we used IRRAS as a complementary surface characterization technique. Figure 2a compares IRRAS spectra obtained for the unmodified NHS-SAM (black), NHS-SAM following 4 h SL of ca. 18 ng of c(-RGDfK-) (red), and the same surface after extensive sonication and rinsing in methanol (blue). Figure 2b shows the spectrum obtained for the NHS-SAM following a 2-h, solution-phase reaction. Amide bands at 1676 and 1535 cm^{-1} are observed following SL of c(-RGDfK-) on the NHS-SAM surface (Figure 2a). Subsequent rinsing of this surface reduces the intensity of the amide bands by a factor of two, indicating that about half of the observed IRRAS signal originates from peptide bonds of loosely bound c(-RGDfK) molecules. Covalent attachment of peptides to the surface also results in suppression of the bands characteristic of the NHS end-group including the asymmetric stretch of the NHS carbonyls at 1751 cm^{-1}, the asymmetric CNC stretch of the NHS at 1217 cm^{-1}, and the NCO stretch of the NHS at 1074 cm^{-1}.

This study is the first account of covalent immobilization of mass selected peptides on SAM surfaces using SL. We have demonstrated efficient reactive landing of several model peptides onto the SAM of NHS-SAM. This method introduces exceptional selectivity and specificity into the surface preparation step by eliminating the effect of solvent and sample contamination on the quality of the film. In addition, the ability to focus and direct an ion beam at selected spots on the surface with variable sizes allows controllable fabrication of peptide patterns. Details of this research have been recently published in the *Journal of the American Chemical Society.*

Citation

Wang P, O Hadjar, and J Laskin. 2007. "Covalent Immobilization of Peptides on Self-Assembled Monolayer Surfaces using Soft-Landing of Mass-Selected Ions." *Journal of the American Chemical Society* 129(28):8682-8683.

Morphology and Oxide-Shell Structure of Iron Nanoparticles Grown by Sputter-Gas-Aggregation

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Nanometer-sized iron particles have important applications to a variety of technologies related to medical imaging, drug delivery, information storage, cancer treatment, and environmental remediation. Although the smallest nanoparticles are usually round, many useful nanosized particles are large enough to show crystallographic structures with crystal facets. Surface-related chemical and magnetic properties of nanoparticles can be strongly influenced by the nature of the specific surfaces exposed and, for reactive metals such as iron, the oxides that form on the surfaces. Particles produced by a low-temperature, gas-aggregation process have primarily non-equilibrium surface facets exposed. These surfaces contrast with the equilibrium shapes of

particles produced or processed at higher temperatures. The ability to control particle morphology will enable tailoring of the properties of iron nanoparticles.

Iron-metal and iron-oxide nanoparticles have been the subject of extensive research for a wide variety of possible applications. It is no surprise that zero-valence iron (Fe^0) exposed to air or any oxygen-including atmosphere will be quickly oxidized. This nearly instant formation of an oxide layer on the metal also occurs for nanometer-sized iron particles. Therefore, unless protected by some other type of layer, Fe^0 nanoparticles will rapidly become covered by a thin layer of oxide (typically 2 to 3 nm thick). The resulting particles are often described as core-shell structured iron nanoparticles. For some applications, the properties of these core-shell nanoparticles are likely to depend on both the size and shape of the metal particles and the nature of the oxide shell (and the metal-oxide [core-shell] interface). In this paper, we examine the core morphology and shell structure of iron core-shell nanoparticles grown by a sputter-gas-aggregation process, and then compare them to those measured on particles formed at higher temperatures and reported in the literature.

Over the last few years, potential applications of the core-shell structured iron nanoparticles have been widely explored including their use for drug delivery, enhanced magnetic resonance imaging, information storage, reduction of carbon dioxide, and groundwater remediation. Although the core may have the types of quantum effects characteristic of metal nanoparticles, the whole particle will involve the core and properties of the outer shell. Biocompatibility of the iron nanoparticles for medical applications, for example, may be controlled by the surface properties of the oxide shell. Reduction of carbon tetrachloride by iron also is influenced by the behavior of the surface-oxide layers, which change with time in solution. Most recently, iron nanoparticles have been investigated as the next generation of clean fuel for engines, which again raises questions of oxidation and reduction of iron-iron oxide nanoparticle system.

Work by researchers from PNNL and the University of Idaho has shown that the morphology of iron nanoparticles prepared by a sputtering-gas-aggregation method depends on deposition temperature. Iron nanoparticles deposited at room temperature form morphological structures ranging from cubes confined only by the 6 {100} planes to truncated rhombic dodecahedrons confined both by the 6 {100} planes and 12 {110} planes. No particle was found to have the shape of a regular rhombic dodecahedron (i.e., confined only by the 12 {110} planes). This finding differs from reports in the literature of iron particles deposited at high temperature, where particles were found to form structures ranging from regular rhombic dodecahedron (all {110} planes) to truncated rhombic dodecahedron confined both by the 6 {100} and 12 {110} planes. Particles deposited at high temperatures did not show the morphology of a cube (only confined by the 6 {100} planes). These results, combined with those found in the literature, suggest that by using a low-temperature process, synthesis parameters can be altered to select particle morphology with a possibility of optimizing particles for specific chemical or magnetic properties.

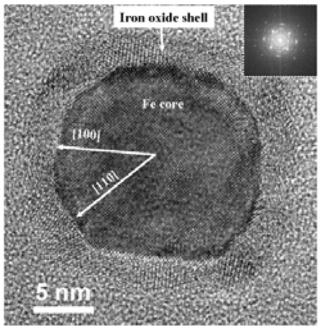

Figure 1. High-resolution transmission electron microscope image of the core-shell structured iron nanoparticle.

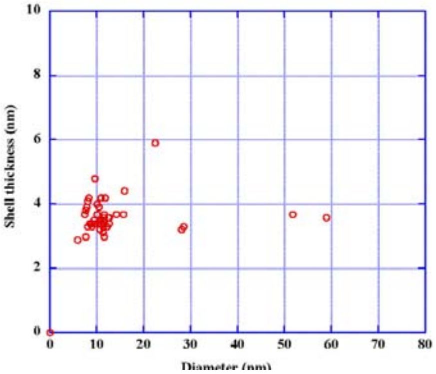

Figure 2. Measured shell thickness as a function of particle dimension.

These data show that the temperature and nature of the nano-particle formation and deposition process can be used to influence the shapes of nanoparticles formed. Core-shell nanostructured iron particles formed by the sputter-gas-aggregation process and deposited at room temperature show a morphology ranging from a cube (i.e., defined by the 6 {100} planes) to a truncated rhombic dodecahedron (i.e., defined by the 6 {100} planes and truncated by the 12 {110} planes) (Figure 1). No particles were found with a morphology of a regular rhombic dodecahedron (i.e., defined only by the 12 {110} planes). This contrasts with the iron particles deposited at high temperature for which the morphology of the particle ranging from a regular rhombic dodecahedron to a truncated rhombic dodecahedron, and no cube was formed. A cas ube morphology represents a configuration of high surface energy for the bcc structured iron. The transition to a lower energy shape appears to be effectively inhibited at lower temperatures. The cube defined by the 6 {100} planes shows a characteristic inward relaxing along the <100> and <110> direction. The oxide shell on the Fe {100} plane maintains an orientation relationship: Fe[001]// Fe_3O_4[001] and Fe(0-20)//Fe_3O_4(4-40), which is the same as the oxide formed on a bulk iron surface through thermal oxidation. The oxide-shell thickness shows no significant dependence on the particle size (Figure 2). These results, along with those found in the literature, suggest that synthesis parameters can be altered to select the particle morphology and orientation of the crystalline oxides that form on the surface of iron nanoparticles with a possibility of optimizing particles for specific chemical properties.

This research work has published in the June 27, 2007, edition of Nanotechnology (Wang et al. 2007)., The paper was chosen as an Institute of Physics Select (IOP Select) article (http://Select.iop.org) The paper also was highlighted by the Nanotechweb (http://nanotechweb.org/articles/journal/6/6/3/1), was selected as a feature article of Nanotechnology (http://www.iop.org/EJ/journal/-page=featured/0957-4484/1), and was mentioned on the cover of Nanotechnology (volume 18. issue 27).

Citation

Wang CM, DR Baer, JE Amonette, MH Engelhard, Y Qiang, and J Antony. 2007. “Morphology and Oxide Shell Structure of Iron Nanoparticles Grown by Sputter-Gas-

Aggregation." *Nanotechnology* 18(25): 255603. Available at http://www.iop.org/EJ/toc/0957-4484/18/25.

Electron Paramagnetic Resonance Studies of Radiation Damage to DNA

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When DNA is exposed to radiation, the DNA is damaged and free radical sites are formed in the process. Cells usually do a good job of repairing this damage, but if there are multiple free radical sites in near proximity, the DNA may be permanently damaged, leading to health problems such as cancer. The goal of this work is to determine how close together the free radicals need to be to interfere with normal DNA repair. This new information will lead to a better understanding of the repair mechanism.

When DNA is exposed to γ-ray irradiation, either naturally or from a radioactive source, free radicals are created at the sites where the DNA absorbs the electromagnetic energy. These free radicals produce defects in the DNA that need to be repaired so that the encoded information is not corrupted. When the sites are widely spaced, the cell does a good job in repairing the defects, but if the defects are too numerous and are in close proximity, the cell does a poor job in repairing the damage. The science theme of this project is to study the conditions under which the repair mechanisms work poorly, thus leaving damaged DNA that can lead to cancer and other diseases.

Electron paramagnetic resonance (EPR) spectroscopy is an excellent tool for studying free radicals in biological systems, including proteins and DNA. By using a new technique called double electron electron resonance (DEER), it is possible to estimate the distance between free radicals in DNA and proteins. While this is a powerful tool, it is still new, and there were some questions about data collection and analysis. DEER is a multi-pulse technique in which a spin echo is created for one spin, and the other spin is irradiated during part of the evolution time. This extra irradiation, or pump pulse, alone has the potential to disrupt the signal being observed, whether there is a second free radical present or not. Using the pulsed-EPR capability in the EMSL, we analyzed this effect (Bowman and Maryasov 2007), determined it was large enough that it could not be ignored as many researchers have done using DEER, and quantified the magnitude of the effect. While it does disrupt the measurements, it also can be used to calibrate the pump pulse and optimize the sequence.

Part of the project will be to study the interaction of metalloproteins, which repair the DNA, with damaged DNA. The metals in the proteins will be paramagnetic, and some will not be of spin ½. Before studying these mixed systems, we have been able to perform a detailed analysis of the dipolar interactions between free radicals and paramagnetic centers when using the DEER sequence.

Direct work on the science theme project has included preliminary measurements of a few DNA samples that have been subjected to intense γ-ray irradiation at 77 K. The experiment was run at low temperature to prevent reaction of the free radicals before they can be studied by EPR spectroscopy. The DEER spectra show multi-phasic decays that indicate an overlap of radical spurs at the highest doses. This is an encouraging indication that these samples span the range from isolated, non-interacting spurs to a more-or-less homogeneous distribution of radicals once the spurs completely overlap at the highest dose.

Citations

Bowman MK and AG Maryasov. 2007. "Dynamic Phase Shifts in Nanoscale Distance Measurements by Double Electron Electron Resonance (DEER)." *Journal of Magnetic Resonance* 185(2):270-282. DOI:10.1016/j.jmr.2006.12.011

VIPER: An Advanced Software Package to Support High-Throughput LC-MS Peptide Identification

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VIPER (Visual Inspection of Peak/Elution Relationships) combines a host of useful functions and capabilities to facilitate and standardize analysis and processing of data generated in liquid chromatography-mass spectrometry (LC-MS)-based, high-throughput proteomics analyses. The VIPER software was recently described in the journal Bioinformatics and publicly released at http://ncrr.pnl.gov/software.

VIPER is an advanced software package developed to support peptide identification and quantitation in PNNL's high-throughput proteomics data processing pipeline, which is located in EMSL.

VIPER uses a graphical user interface to generate two-dimensional plots that display the monoisotopic masses observed in each mass spectrum (Figure 1), as well as LC-MS features discovered when VIPER groups related data points by mass and elution time (Monroe et al. 2007). This software also maps the observed LC-MS features onto known accurate mass and time tags in reference databases to identify peptides (Zimmer et al. 2006).

VIPER can run in an automated mode in which it loads and processes data based on customizable, user-defined settings. It is primarily intended to work with monoisotopic mass data, as obtained by deisotoping mass spectra from medium to high-resolution mass spectrometers (e.g., time of flight, Fourier transform ion ion cyclotron resonance, or Orbitrap), and it can read several file formats including .CSV, .mzXML, and .mzData.

Over the past year, VIPER has been extended to incorporate a range of new features. For example, it now integrates with the LCMSFeatureFinder to find LC-MS features much more rapidly and incorporates an expectation-maximization algorithm to accurately determine the appropriate mass and elution time tolerances to use on the basis of the observed mass and elution time error distributions. VIPER can support DREAMS (Dynamic Range Enhancements Applied to Mass Spectroscopy] datasets, wherein higher-abundance ions are ejected from the ion cyclotron resonance cell in alternating spectra, thereby allowing lower-abundance species to be detected. Importantly, the ease with which external collaborators can use VIPER has also been improved by incorporating the LCMSWarp (Liquid Chromatography-Based Mass Spectrometric Warping and Alignment of Retention Times of Peptides) algorithm into the public version and updating VIPER to support Microsoft Access databases created with the MTDB (Mass and Tag Database) Creator application, which is available at http://ncrr.pnl.gov/software.

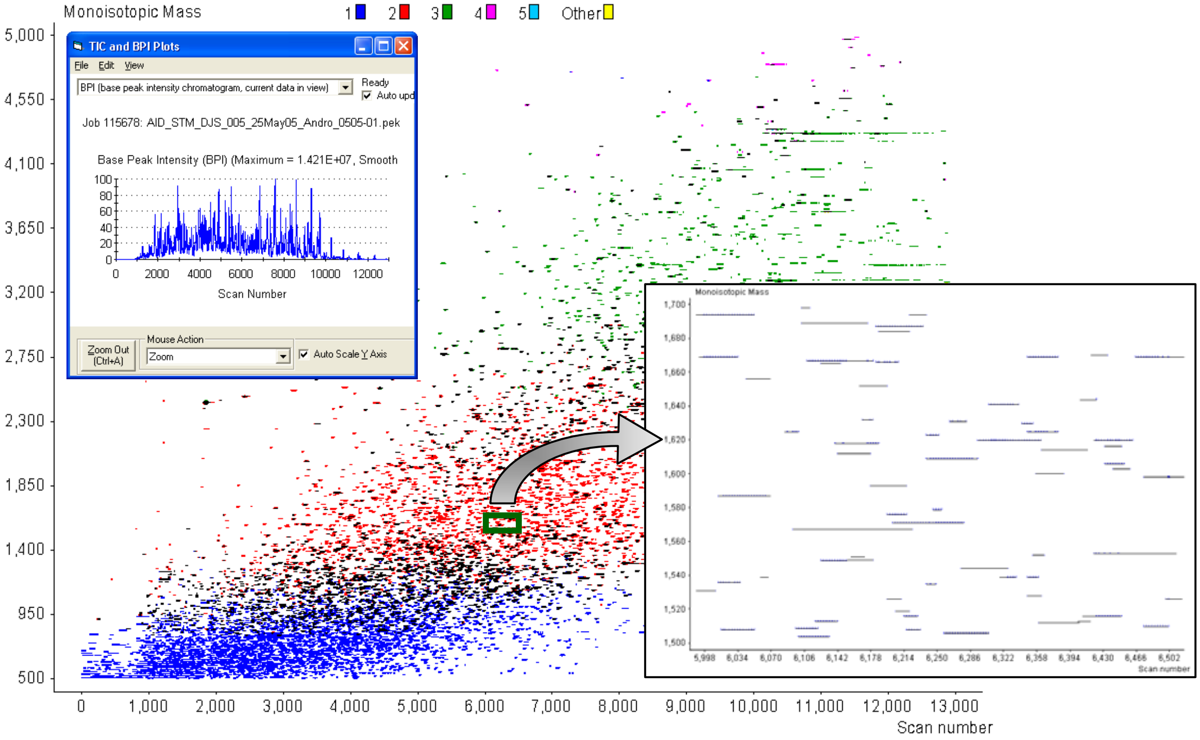

Figure 1. The large graphic shows a plot of monoisotopic masses vs. scan number (time), color-coded by charge state. The upper left inset is a total ion chromatogram of the entire dataset, while the lower right inset shows 68 LC-MS features resolved in both the mass and time dimensions.

Citations

Monroe ME, N Tolić, N Jaitly, JL Shaw, JN Adkins, and RD Smith. 2007. "VIPER: An Advanced Software Package to Support High-Throughput LC-MS Peptide Identification." *Bioinformatics* 23 (15):2021-2023. Supplementary Data available at http://bioinformatics.oxfordjournals.org/cgi/content/full/btm281/DC1). The Supplementary Data include processing details for VIPER, additional screenshots, and a list of 23 selected publications for which VIPER was used for data analysis.

Zimmer JSD, ME Monroe, WJ Qian, and RD Smith. 2006. "Advances in Proteomics Data Analysis and Display using an Accurate Mass and Time Tag Approach." *Mass Spectrometry Reviews* 25(3):450-482.

Transparent Thin-Film Transistor Using Self-Assembled Nanocrystals

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As one of the next-generation opto-electronics, transparent circuits have broad potential applications ranging from invisible military detecting systems, clear toys and cards, smart buildings, and interactive media to canopy window displays. *In backlit display devices, transparent active-matrix circuits can increase the life of batteries used to power the devices.*

Currently, the application of transparent circuits is limited by challenges associated with downscaling to the sub-micron regime and poor high-frequency response. One can identify two main reasons for these difficulties. First, most transparent electronic materials are vacuum-deposited inorganic oxides. A common chemical property of these inorganic oxides makes etching at small dimensions difficult: when the top oxide layer is etched, the underlying oxide layer also is attacked. Second, the current method fabricating transparent electronics does not separate circuit manufacturing from material synthesis: layers of oxide are synthesized directly on the device substrate. Synthesis typically occurs under harsh conditions such as elevated temperatures or in energetic plasmas that can damage the existing layers or substrate, especially the plastic transparent layer. These two factors impede the nanoscale development of transparent electronics and fast circuits

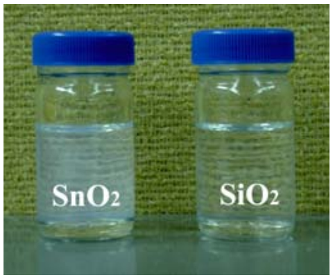

Figure 1. Transparent nanocrystals.

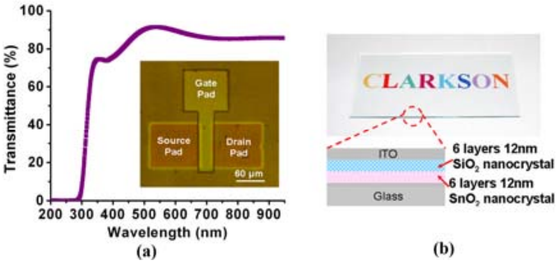

Figure 2. (a) The optical transmittance of the thickest region of a transistor. The inset is the optical micro---graph of a top-gate transistor. (b) Visual effect of a glass slide with all of the layers of the transistor deposited on the surface.

A solution to these difficulties, proposed by scientists from PNNL and Clarkson University, is to separate the material-synthesis step, with its harsh conditions, from the device-fabrication step. In particular, the transparent electronic materials are first synthesized and then transferred onto the device substrate under mild conditions, such as at room temperature. Figure 1 indicates bottled solutions of transparent SnO_2 and SiO_2 nanocrystals. This additive approach also eliminates etching of the oxide multilayer. This innovative solution is expected to advance the state of the art of transparent-electronics production, resulting of smaller and faster circuits. As reported in the April 17, 2007, edition of *Nanotechnology* (Zhang et al. 2007), clear nanocrystals were used as the functional materials for the transistor, and a self-assembly technique was employed to manipulate the nanocrystals. As shown in Figure 2, the resulting transistor is highly transparent with above approximately

85 percent optical transmittance over the visible spectrum. Importantly, the entire process was performed at room temperature when two types of transparent nanocrystals were self-assembled into the device. Etching of the oxide multilayer also is eliminated in this process, and the process is suitable for flexible substrates and for mass production.

This work demonstrates the concept of an innovative process for producing transparent electronics. Next, to further improve process performance, high-mobility nanowires will be produced and transferred onto the device substrate.

Citation

Zhang Q, LV Saraf, and F Hua. 2007. "Transparent Thin Film Transistor with Self-Assembled Nanocrystals." *Nanotechnology* 18:195204(5 pp). DOI:10.1088/0957-4484/18/19/195204.

Use of Quantum-Chemical Computations to Investigate the Sulfur-Poisoning Mechanism in Solid-State Oxide Fuel Cells

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Solid oxide fuel cells (SOFCs) can generate power using a wide variety of fuels including those from fossil, biomass, and other renewable sources. They hold great promise as a future power source, but the catalysts needed for the process are easily poisoned by small amounts of sulfur in readily available fuels. Achieving an understanding of the sulfur-poisoning mechanism of nickel-based SOFCs is essential to rational design of sulfur tolerant SOFCs. Computer calculations combined with experimental results have made great progress toward this goal.

Under typical fuel cell operating conditions, the nickel (Ni) electrode is susceptible to poisoning by sulfur concentrations as low as 0.2 ppm at 700°C, leading to rapid loss of activity. To explore sulfur tolerance on the Ni surface under SOFC operating conditions, interactions between hydrogen (H_2) fuel contaminated with hydrogen sulfide (H_2S) and Ni surfaces were studied using density function theory (DFT) calculations with thermodynamic corrections. A new S-Ni phase diagram based on different temperatures and pressure ratios of H_2/H_2S was produced (Figure 1). This new phase diagram reveals that a clean Ni surface (shown in the white region of the figure) will first adsorb sulfur atoms according to the reaction, $H_2S + \text{surface} \rightarrow S(a) + H_2$ when exposed to small amount of H_2S, crossing the blue line and entering the blue region. The blue region of S(a) cannot be predicted directly from the classical thermodynamic database in the existing bulk S-Ni phase diagrams and, therefore, cannot be used to explain some experimental results.

The important implication of this new phase diagram is that it can be used to accurately predict conditions for avoiding sulfur poisoning (the blue line) and for explaining reported sulfur tolerance results. To avoid significant sulfur poisoning, experiments show that the maximum H_2S concentration is about 0.05, 0.5, and 2 ppm at 1023, 1173, and 1273 K, respectively. This corresponds to the red dots near the blue line in Figure 1. These results also confirm that sulfur poisoning corresponds directly to the adsorption of sulfur atoms on the surface, which blocks active sites for fuel oxidation. Previous experimental results on sulfur chemi-sorption and formation of Ni_3S_2 all would have been predicted by the phase diagram. A paper based on this research has been accepted for publication in the journal *Electrochemistry Communications.*

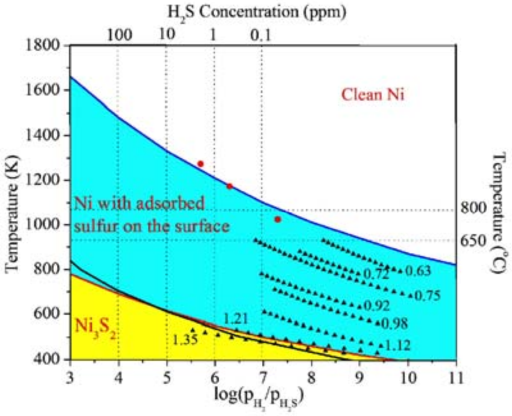

Figure 1. The new predicted phase diagram for the S-Ni system in H_2S/H_2 fuel mixtures. The black line is from the bulk phase diagrams. The red dots are related to the sulfur tolerance experiment. The black symbols are related to the experiment of chemisorbed S(a) with different coverage as indicated by the number adjacent to each set of data points.

Scientific Grand Challenge Highlights

Binding and Direct Electrochemistry of OmcA, an Outer-Membrane Cytochrome from an Iron Reducing Bacterium, with Oxide Electrodes: A Candidate Biofuel Cell System

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(c) Pacific Northwest National Laboratory, Richland, Washington

This research was conducted as part of the Biogeochemistry Grand Challenge and describes how the bacterial protein OmcA could be used in the design of biofuel cells.

Dissimilatory iron-reducing bacteria transfer electrons to solid ferric respiratory electron acceptors. Outer-membrane cytochromes expressed by these organisms are of interest in both microbial fuel cells and biofuel cells. In this project, we used optical waveguide lightmode spectros-copy (OWLS) to show that OmcA, an 85 kDa decaheme outer-membrane c-type cytochrome from *Shewanella oneidensis* MR-1, adsorbs to iso-structural Al_2O_3 and Fe_2O_3 in similar amounts. Adsorption is ionic-strength and pH dependent (peak adsorption at pH 6.5 to 7.0). The thickness of the OmcA layer on Al_2O_3 at pH 7.0 (5.8 ± 1.1 [2σ] nm) from OWLS is similar, within error, to that observed using atomic force microscopy (4.8 ± 2 nm). The highest adsorption density observed was 334 ng/cm^2 (2.4 x

10^{12} molecules/cm^2), which corresponds to a monolayer of 9.9-nm-diameter spheres or sub-monolayer coverage by smaller molecules. Direct electrochemistry of OmcA on Fe_2O_3 electrodes was observed using cyclic voltammetry, with cathodic peak potentials of -380 to -320 mV versus Ag/AgCl. Variations in the cathodic peak positions are speculatively attributed to redox-linked conformation change or changes in molecular orientation. OmcA can exchange electrons with indium-tin-oxide electrodes at higher current densities than with Fe_2O_3. Overall, OmcA can bind to and exchange electrons with several oxides; thus, its utility in fuel cells is not restricted to Fe_2O_3.

Citation

Eggleston CM, J Voros, L Shi, BH Lower, TC Droubay, PJS Colberg. 2007. "Binding and Direct Electrochemistry of OmcA, an Outer-Membrane Cytochrome from Iron Reducing Bacteria, with Oxide Electrodes: A Candidate Microbial Fuel Cell System." *Inorganica Chimica Acta* in press. (doi:10.1016/j.ica.2007.07.015)

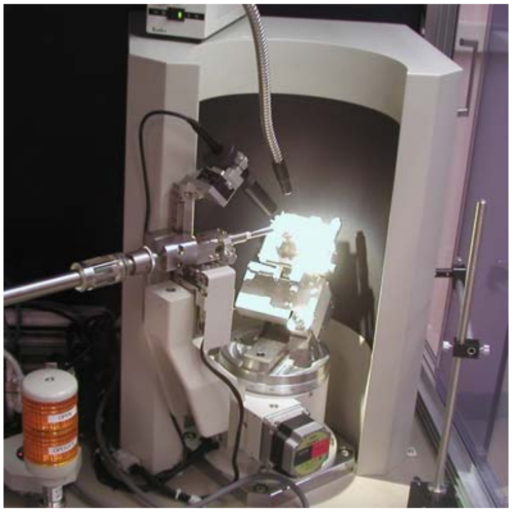
Professional/Community Service

EMSL Scientific Facility Lead Finding Solutions for Contaminated Sites in Russia. Roy Gephart, Scientific Facility Lead for the Chemistry and Physics of Complex Systems Facility, and Don Bradley, Pacific Northwest National Laboratory, recently visited Russia and provided environmental cleanup recommendations. Gephart and Bradley were part of a six-member U.S. delegation that met with Russian representatives in early June. In addition to reviewing the current status of remediation at six Russian sites that are contaminated with radioactive materials, the participants talked about technologies needed to bring the sites to an internationally acceptable level of environmental cleanup. Members of the U.S. delegation were invited to participate by the U.S. National Academy of Sciences. The George Russell Family Fund provided financial support to the collaboration.

EMSL Hosts Microscopy Meeting. EMSL hosted the annual meeting of the Pacific Northwest Microscopy Society (PNMS) on September 20-21, 2007. Over 40 participants from Washington, Oregon, and Idaho, including participants from PNNL, attended the meeting, which was led by current PNMS president and EMSL staff member A Dohnalkova. The scientific program included 20 talks on the latest advances in microscopy in the biological and physical sciences, and a keynote speech that addressed three-dimensional reconstruction and visualization. Participants received a tour of the EMSL facility. Twelve participants attended a hands-on workshop on TEM tomography as demonstrated on the EMSL Tecnai T-12 electron microscope, with complete reconstruction and three-dimensional modeling done a sample provided by one of the participants. The vendors' exhibition featured a compact Hitachi bench-top scanning electron microscope, and an array of optical microscopes suitable for educational outreach programs. The conference banquet, which included student poster-session awards announcements, was held Thursday evening. Several discussions of possible EMSL user collaborations were initiated by visitors during the meeting.

Major Facility Upgrades

Micro-X-Ray Diffraction Capability Now Available to EMSL Users. The x-ray beam can be focused to a 10-micron spot size and is capable of analyzing samples using either an automated x-y stage for planar samples such as petrographic thin sections, sealed capillary tubes for air sensitive powders, or fiber-mounted particulate samples. The detector is a curved image plate and is capable of measuring a large portion of the Ewald diffraction volume at one time. This detector coupled with the bright rotating anode x-ray source will enable rapid data acquisition on even minute samples. Both copper and chromium x-ray wavelengths are available.



Micro x-ray diffractor

News Coverage

A press conference was held September 28, 2007, to announce the new contract with Hewlett Packard for the purchase of a $24 million dollar computer system. The story was covered locally by KNDU (NBC affiliate), KEPR (CBS affiliate), the *Tri-City Herald*, and KONA radio, and nationally by *HPC Wire* (article available at http://www.hpcwire.com/hpc/1805360.html) and *Computerworld* (article available at http://www.computerworld.com/action/article.do?command=viewArticleBasic&articleId=9039701).

The next generation supercomputer will enable EMSL users to advance molecular science in areas such as aerosol formation, bioremediation, catalysis, climate change, hydrogen storage, and subsurface science. Installation of the new system will begin in January 2008, and the system is expected to be fully operational in September 2008. This system will allow EMSL users to study more complex scientific problems with larger and more realistic models, obtain answers in less time by scaling computational models to a larger numbers of processors, and acquire a greater level of detail in simulations and more complete answers to scientific questions.

Visitors and Users

During this reporting period, a total of 330 users benefited from EMSL capabilities and expertise. This total included 222 onsite users and 108 remote users.

Publications

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Presentations

During this reporting period, EMSL staff presented on research performed at the user facility at the following meetings or locations:

- 11th Interational Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, August 29, 2007, Munich, Germany.
- American Association of Aerosol Research, September 25, 2007, Reno, Nevada.
- Conference on Laser Ablation (COLA) 2007, September 25, 2007,Tenerife, Spain.
- DOE Low-Dose Program, First NOTE Annual Meeting, September 15, 2007, Crete, Greece.
- Goldschmidt 2007, August 20, 2007, Cologne, Germany.
- Instrument Development Laboratory Seminar Series, September 11, 2007, Richland, Washington.
- MSCF Operational Assessment Review, August 29, 2007, Washington, D.C.