William R. Wiley

EMSL

Environmental Molecular Sciences Laboratory

2007 Annual Report

A NATIONAL USER FACILITY
FOR THE SCIENTIFIC COMMUNITY

PNNL-17409

Environmental Molecular Sciences Laboratory

2007 Annual Report

March 2008

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Overview

This Fiscal Year 2007 Annual Report describes the research and accomplishments of staff and scientific users of the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL), located in Richland, Washington.

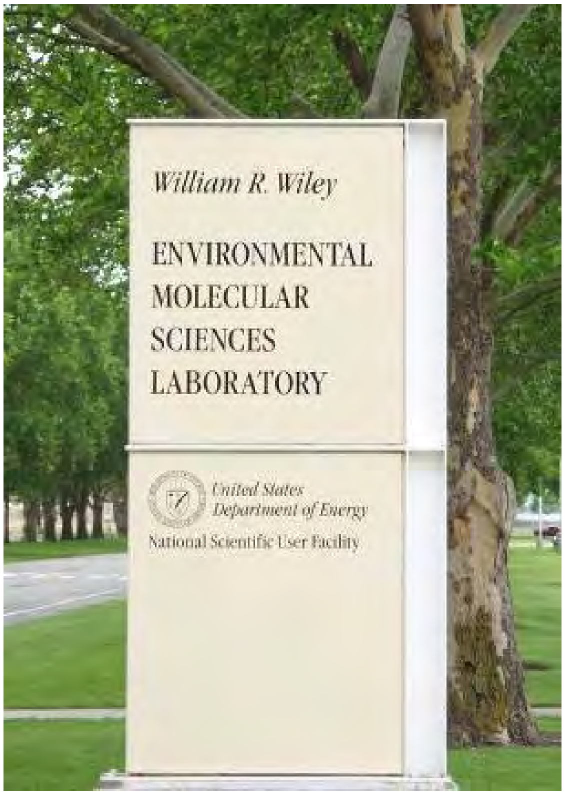
Mission

> *EMSL, a national scientific user facility at Pacific Northwest National Laboratory (PNNL), provides integrated experimental and computational resources for discovery and technological innovation in the environmental molecular sciences to support the needs of DOE and the nation.*

EMSL strives for simultaneous excellence in 1) high-impact science and marquee capabilities, 2) outstanding management and operations, and 3) exceptional user outreach and services, and uses these tenets to deliver its mission and implement its strategy. The central focus of EMSL's strategy is delivery on the mission of the scientific user facility. In addition to its mission, EMSL has a vision and strategy that show where the scientific user facility intends to be in the next 10 years and the progress that will be made during the next 5 years, respectively.

EMSL Resources

EMSL is a national scientific user facility available to researchers worldwide from academia, industry, and national laboratories. EMSL scientific users pursue the understanding of molecular systems essential to scientific breakthroughs and discoveries for a broad set of DOE missions in energy, environment, climate, and national security. Staff at EMSL develop and maintain extensive advanced research and development capabilities that are used to generate new scientific knowledge. EMSL delivers substantial value to its scientific users by understanding their needs, creating responsive new ideas and capabilities, and delivering exceptional results—all achieved through the expertise of staff, demonstrated excellence in management and laboratory operations, and high-value partnerships with its scientific users.



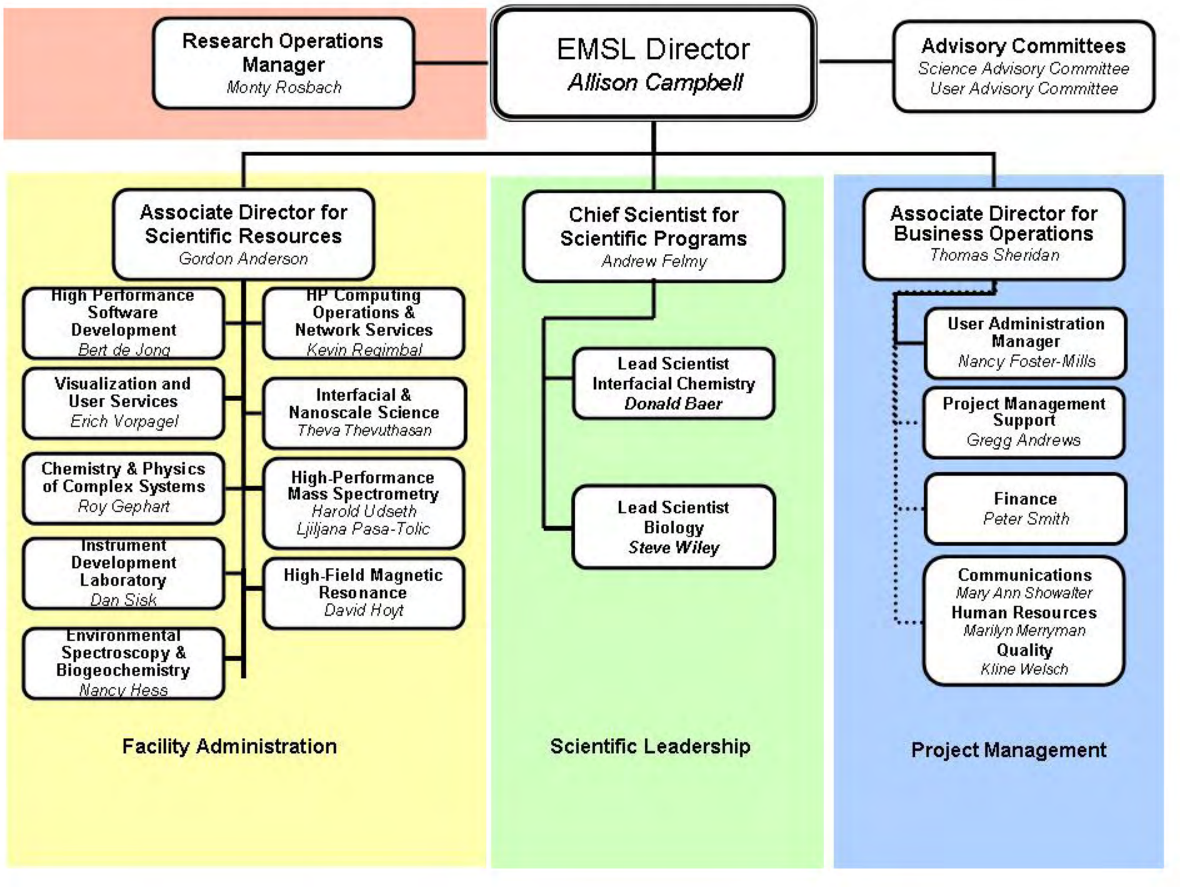
EMSL is a DOE national scientific user facility located at Pacific Northwest National Laboratory in Richland, Washington.

The operating budget for EMSL is provided by DOE Office of Biological and Environmental Research (BER), while the research conducted within the facility is beneficial to the DOE Office of Science and many funding agencies, including other offices within DOE, the National Institutes of Health, the National Science Foundation, and the Department of Defense.

Since beginning operations in October 1997, EMSL has provided advanced and one-of-a-kind integrated experimental and computational resources to scientists engaged in fundamental research in the physical, chemical, and biological processes that underpin environmental remediation and other important scientific issues facing DOE and the nation. In addition to physical resources, EMSL provides unprecedented technical support and expertise, providing its scientific users a highly efficient and focused resource that enhances their work.

Organization

In Fiscal Year 2007, EMSL was managed by a Director, an Associate Director for Scientific Resources, an Associate Director for Business Operations, a Research Operations Manager, a Chief Scientist and Lead Scientists, and Scientific Facility Leads (as shown in the organization chart below).



In addition, two advisory committees— the Science Advisory Committee (SAC) and the User Advisory Committee (UAC)—provide advice to the EMSL Director on longer-term scientific direction and short-term, user-related issues, respectively.

Science Advisory Committee

The independent SAC provides objective advice on long-term science direction to the EMSL Director related to topics such as:

- EMSL's focus on national priorities and science challenges
- strategy for accomplishing EMSL's vision
- potential opportunities for transferring science to applications
- stewardship.

The SAC is comprised of distinguished scientists from academia, national laboratories, and research institutions across the United States who provide expertise in EMSL's major capability areas of biology, environmental science, molecular science, and theory. The committee reports to the Director, PNNL. Responsibilities and activities of the SAC include:

- providing advice on scientific direction for the EMSL user program
- recommending appropriate balance of instrument time for Grand Challenges, general scientific users, and capability development activities
- assisting EMSL with formulating policies related to facility scientific output, scientific impact of the EMSL user program, user access, and other issues, as needed
- performing periodic reviews of scientific impact from the various elements of the EMSL scientific user program.

The committee meets annually at EMSL and the 15 members serve staggered 4-year terms. The current members of the SAC are as follows:

- Len Spicer, Duke University (Chair)
- Mark A. Barteau, University of Delaware
- Gordon E. Brown, Jr., Stanford University
- Charles T. Campbell, University of Washington
- Marvin Cassman, Consultant
- Gregory Choppin, Florida State University
- Ian Farnan, Cambridge University
- Barbara J. Finlayson-Pitts, University of California, Irvine
- George W. Flynn, Columbia University
- David J. Galas, Battelle

- Samuel Kaplan, University of Texas-Houston Medical Center
- Julia Rice, IBM Almaden Research Center
- Peter J. Rossky, University of Texas at Austin
- James M. Tiedje, Michigan State University
- Mary F. Wheeler, University of Texas at Austin.

User Advisory Committee

The UAC is an independent body of experts from academia, industry, and the national laboratory system that is charged with providing objective, timely advice and recommendations to EMSL leadership. The Committee reports directly to the EMSL Director and serves as the official voice of EMSL's scientific user community in its interactions with EMSL management.

The responsibilities of the User Advisory Committee include:

- providing a clear channel for the exchange of information and advice between EMSL scientific users and management
- providing a formal vehicle for EMSL scientific users to transmit concerns and recommendations to the EMSL Director
- designing and overseeing the EMSL User Meetings
- providing advice and recommendations to the EMSL Director on how to facilitate the effective use of EMSL
- nominating active scientific users for future membership to the committee.

EMSL's refreshed User Advisory Committee met for the first time at EMSL in May 2007.

In Fiscal Year 2007, EMSL's SAC solicited nominations among the EMSL scientific user community for members of a refreshed UAC. This resulted in 31 excellent candidates, from which the scientific user community elected 14 members that represented all instrument sets and facilities. The newly formed UAC met for the first time at EMSL in May 2007. The committee members are:

- Theresa L. Windus, Iowa State University (Chair)
- Valérie Copié, Montana State University
- Scott Fendorf, Stanford University
- Vicki H. Grassian, University of Iowa
- Wayne Hess, Pacific Northwest National Laboratory
- Kerry Hipps, Washington State University
- Patricia M. Irving, InnovaTek, Inc.
- Anne M. Johansen, Central Washington University
- Sarah C. Larsen, University of Iowa
- Martin McIntosh, Fred Hutchinson Cancer Research Center
- Karl T. Mueller, Pennsylvania State University
- Lisa Porter, Carnegie Mellon University
- Paul G. Tratnyek, Oregon Health & Science University
- Angela K. Wilson, University of North Texas

Science Themes

EMSL established key science themes that focus the strengths of the facility and its scientific user program on increased scientific impact. Science themes guide user outreach efforts, help prioritize investments in equipment and staff, and guide review of scientific user proposals. The objective of science themes is to define and develop key collections of scientific user projects that, taken together, can significantly and positively impact an important area of environmental molecular science.

EMSL's four science themes are:

- **Atmospheric Aerosol Chemistry.** A global- to molecular-scale understanding of aerosol processes and their impacts.
- **Biological Interactions and Dynamics.** Developing a molecular-scale understanding of cells and biomolecules to provide a science-to-solutions approach to biological systems.
- **Geochemistry/Biogeochemistry and Subsurface Science.** A molecular-level understanding of subsurface fate and transport and biogeochemical cycling.
- **Science of Interfacial Phenomena.** Tailored interfacial structures for dynamics, reactivity, and transport.

Proposals and Scientific User Access Modes

EMSL scientific users are encouraged to submit proposals in response to periodic or continuous calls for proposals. By responding to different calls for proposals, scientific users have the opportunity to choose from different options regarding the speed of access and the length of time over which a proposal may remain active. Different options for the type of proposal, type of access, and proprietary status are available to optimize scientific impact and facilitate evolution of EMSL capabilities and science to address cutting-edge science questions.

Calls for Proposals

- **Science Theme Call.** Scientific users are encouraged to submit proposals that fit into major areas of current and growing user activity associated with scientific challenges that address topics of societal importance. To highlight EMSL's science themes, theme-based calls for proposals occur at least once a year. Science theme proposals are valid for one year and can be extended twice for a total period of three years. Some EMSL resources may be especially dedicated to science theme proposals.
- **Grand Challenge Computational Call.** EMSL sends out a call for Computational Grand Challenges once a year, providing that computer time is available on its supercomputer. The call includes research applications in biology, chemistry, climate, and subsurface science and is open to all research entities regardless of research funding

source. Computer time for Computational Grand Challenges is allocated for up to three years, with the computer allocation appropriate for the scope of research to be performed.

- **Capabilities-based Call.** The EMSL Capabilities-based call for proposals is focused on new and extended use of EMSL capabilities. Proposals that use EMSL's unique and new or developing capabilities, that apply EMSL capabilities in specific developing areas, or that propose environmentally or other important work that may not fit within the EMSL four science themes will be encouraged. Proposals in response to this call are valid for one year and can be extended only once for a total open period of two years.

- **Open Call.** EMSL scientific users can continue to submit general-use proposals at any time. This type of proposal may not be extended and will be valid for only one year. A new proposal is required each year.

Types of Proposals

- **General.** Use of existing EMSL resources typically falls into this General use category. General use proposals may be submitted to EMSL at any given time throughout the year. General Use proposals are evaluated by peer review prior to work. Proposals may be from individuals or groups who need access to the facility to carry out their research, using existing equipment in the EMSL. The scope of a General Use proposal can vary from a single experiment proposal to full project proposal (valid for multiple visits and substantial access to a range of equipment extended over multiple years). Individual and group proposals, including collaborative proposals with EMSL staff, are encouraged.

- **Partner.** Partner proposals are individuals or groups who not only carry out research at EMSL but have developed an agreement to also enhance the capabilities. Typically they develop the facility instrumentation in some way, bringing outside financial and/or intellectual capital into the evolution of EMSL. These contributions must be made available to the general scientific users and so benefit them as well as the facility. In recognition of their investment of either resources or intellectual capital and in order to facilitate and encourage their involvement, Partner proposals may allocate participants with limited access to one or more facilities over a period of several years, with the possibility of renewal. Partner user activities are negotiated among the teams involved. New Partner proposals can be submitted in response to Science Theme or other calls, but requires information and discussions beyond the two page proposal work description required for a general type of proposal. Partner proposals are subject to the same peer review process as general proposals. Teams planning a partner proposal should have discussions with EMSL team leads before this type of proposal is submitted.

Types of Access

EMSL scientific users can access the capabilities of the user facility in two ways.

- **Standard Access.** Standard access to EMSL facilities can vary from a single visit, single experiment proposal to a full project proposal (valid for multiple visits and substantial access to a range of equipment extended over multiple years). Prior to any work, a proposal must pass peer review. This is the most common mode of access to EMSL capabilities.

- **Rapid Access.** In limited cases, scientific users may need access to EMSL capabilities where rapid turnaround of data is required (e.g. thesis work, project progress, and paper publication or proposal preparation). If approved, a rapid access proposal will be valid for no more than one month of EMSL use. These proposals must clearly justify why Rapid Access is needed. Work on proposals can be started subject to instrument and resource availability and subject to approval of the Scientific Facility Lead. Proposals will undergo internal peer review that will be conducted as work is initiated. However, all other reviews, including ES&H and the business office, must be complete before usage can begin. If scientific users need rapid access for research that they may want to continue, they may also submit (possibly at the same time) a standard access proposal.

Proprietary Status

- **Non-Proprietary Research.** Research and equipment usage conducted at EMSL where the results and information are fully disclosed and disseminated are considered non-proprietary. Authors of non-proprietary proposals may retain rights to intellectual property resulting from the use of EMSL, but the government is granted a nonexclusive license to use the intellectual property.

- **Proprietary Research.** EMSL facilities can be used for proprietary research. DOE requires that such work pay full-cost recovery of the facilities used which includes, but is not limited to, labor, equipment usage, consumables, materials, and EMSL staff travel.

Calls for Proposals in Fiscal Year 2007

- In February 2007, EMSL's second Science Theme Call for Proposals was sent out to scientific users. The call resulted in nearly three times the proposal submissions than the first year, with 279 proposals submitted: 29 for Atmospheric Aerosol Chemistry, 74 for Biological Interactions and Dynamics, 51 for Geochemistry/Biogeochemistry and Subsurface Science, and 125 in Science of Interfacial Phenomena. Based on instrument availability and scientific merit, 202 of the proposals were selected as full Science Theme Proposals, and 50 as limited proposals. Principal investigators were notified in June 2007.

- EMSL's Molecular Science Computing Facility supported 23 three-year grand challenge projects during Fiscal Year 2007. The average annual computer time allocation for grand challenge projects was 477,530 central processor unit (cpu) hours, with individual project allocations ranging from 180,000 to 1,650,000 cpu-hours.

- In April 2007, a capabilities-based call was issued seeking proposals for use of four newer instruments: Single Crystal and Microbeam X-ray Diffraction (XRD); Focused Ion Beam/Scanning Electron Microscopy (FIB/SEM); Transmission Electron Microscopy with Cryo Stage and Tomography; (Cryo-TEM) and Bio-solids Capability on the 900-MHz NMR spectrometer. The call resulted in 19 proposals submitted, with 7 accepted for the FIB/SEM; none accepted for XRD; 3 accepted for Cryo-TEM; and 4 accepted for the 900 MHz NMR bio-solids.

EMSL Scientific Grand Challenges

Since 2004, EMSL has been challenging the traditional approach to research with two Scientific Grand Challenges—complex, large-scale scientific and engineering problems with broad scientific and environmental or economic impacts whose solution can be advanced by applying high-performance scientific techniques and resources. EMSL Scientific Grand Challenges differ from typical research projects in that they are performed by multi-institution (universities, other federal laboratories, and industry), outcome-driven multidisciplinary teams that use a wide variety of EMSL's cutting-edge resources.

Progress in EMSL's two Scientific Grand Challenges can help DOE resolve the enormous problems associated with environmental contamination across the complex, saving DOE and the country hundreds of millions of dollars and reducing risk to humans and the environment. The Scientific Grand Challenges have brought together some of the world's best minds and engage scientists from more than 20 universities and research institutions worldwide.

Biogeochemistry Scientific Grand Challenge

A Scientific Grand Challenge in biogeochemistry, led by PNNL scientists John Zachara and Jim Fredrickson, is studying how organisms exchange energy and electron flux with mineral matter in soils, sediments, and subsurface materials. This exchange occurs across a mineral-microbe interface that is a minute, but chemically active domain whose molecular workings have perplexed scientists for decades. The Biogeochemistry Scientific Grand Challenge uses EMSL's advanced instrumental capabilities and high-performance computing capabilities to understand the biologic and physical architecture of this remarkably complex domain and the microbe-mediated chemical reactions that occur within it. The research allows scientists to understand this most basic earth-life interaction that is fundamental to the migration of environmental contaminants, to water quality, and to soil fertility and trace metal availability. The following highlight bullets and a more detailed research highlight illustrate the activities under this Scientific Grand Challenge in Fiscal Year 2007:

- EMSL atomic force microscopy was used to show that membrane cytochromes, MtrC and OmcA, purified from *Shewanella oneidensis* MR-1, are able to form a stable bond with the surface of the iron oxide hematite (Fe_2O_3). The force spectra obtained between the pure cytochromes and Fe_2O_3 exhibited a strong correlation with those obtained between living *S. oneidensis* MR-1 cells and Fe_2O_3. These results suggest that *S. oneidensis* MR-1 expresses MtrC and OmcA on the cell surface where the cytochromes make direct contact with an iron oxide and play a prominent role in the terminal electron transfer reaction that occurs between *S. oneidensis* MR-1 and a Fe(III)-bearing mineral during anaerobic respiration. Results were published in *Journal of Bacteriology* 189(13):4944-4952.

- For the first time, PNNL researchers have observed electricity-shuttling by proteins removed from living cells, using purified proteins removed from the outer membrane of the metal-altering bacterium *Shewanella oneidensis*. The research, as reported in the *Journal of the American Chemical Society* [128(43):13978-13979], suggests that proteins rendered portable from the organisms that spawned them could make miniature bioreactor cells feasible. Biofuel cells are not yet powerful enough to be commercially viable, but they offer the promise of breaking down sewage and other biological waste while generating electricity directly from the same process—for example, a self-powering sewage treatment plant.

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

CM Eggleston,[a] J Vörös,[b] L Shi,[c] BH Lower,[c] TC Droubay,[c] and PJS Colberg[a]
(a) University of Wyoming, Laramie, Wyoming
(b) Swiss Federal Institute of Technology, Zürich, Switzerland
(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 (2.4×10^{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, and 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).

Membrane Biology Scientific Grand Challenge

Dr. Himadri Pakrasi from Washington University in St. Louis is leading a Scientific Grand Challenge in membrane biology that uses a systems approach to understand the network of genes and proteins that govern the structure and function of membranes and their components responsible for photosynthesis and nitrogen fixation in cyanobacteria (blue-green algae). A systems approach integrates all temporal information into a predictive, dynamic model to understand the function of a cell and the cellular membranes. These microorganisms make significant contributions to harvesting solar energy, planetary carbon sequestration, metal acquisition, and hydrogen production in marine and freshwater ecosystems. Cyanobacteria are also model microorganisms for studying the fixation of carbon dioxide through photosynthesis at the biomolecular level. The results of this Scientific Grand Challenge are providing the first comprehensive systems-level understanding of how environmental conditions influence key carbon fixation processes at the gene-protein-organism level. This topic was selected because it addresses critical DOE science needs, provides model microorganisms to apply high-throughput biology and computational modeling, and because it takes advantage of EMSL's experimental and computational capabilities. The following highlight bullets and more detailed research highlights illustrate the activities under this Scientific Grand Challenge in Fiscal Year 2007:

- In April 2007, a project review of the Membrane Biology Scientific Grand Challenge was held at Washington University in St. Louis. During the workshop, the science conducted in the past two years was reviewed, with each project lead describing their research and future plans. The participants discussed future strategy for focusing research, publication, and outreach to make a greater impact during the remainder of the project.

- In addition, an advisory committee review was held in August 2007 at EMSL. The committee found that the Membrane Biology Scientific Grand Challenge had made excellent technical progress towards its stated research goals given the relatively short time period of the project. In addition, it was noted that there was clear expansion of the use of EMSL capabilities in a synergistic manner to address a challenging and potentially impactful scientific problem.

Characterization of Two Potentially Universal Turn Motifs that Shape the Repeated Five-Residue Fold-Crystal Structure of a Lumenal Pentapeptide Repeat Protein from Cyanothece 51142

GW Buchko,[a] S Ni,[a] H Robinson,[b] EA Welsh,[c] HB Pakrasi,[c] and MA Kennedy[a]
(a) Pacific Northwest National Laboratory, Richland, Washington
(b) Brookhaven National Laboratory, Upton, New York
(c) Washington University, St. Louis, Missouri

The crystal structure was determined for Rfr32, which is one of 35 pentapeptide repeat proteins (PRPs) in the diurnal cyanobacterium Cyanothece. The structure is dominated by 21 tandem pentapeptide repeats that fold into a right-handed quadrilateral ß-helix, or Rfr-fold. Analysis of the main chain (Φ, Ψ) dihedral orientations for the pentapeptide repeats reveals structural details for the two distinct types of four-residue turns adopted by the pentapeptide repeats in the Rfr-fold, labeled type-II and type-IV ß-turns, that may be universal motifs that shape the Rfr-fold in all PRPs.

HB Pakrasi and his colleagues at Washington University (WU) in St. Louis, Missouri, have recently sequenced the genome of the diurnal cyanobacterium *Cyanothece* sp. PCC 51142. One of the interesting features of the genome, as determined by the annotation team led by WU's E Welsh, is the presence of 35 proteins containing tandem pentapeptide repeats. Such PRPs are identified by the presence of at least eight consecutive repeating five-residues (RFR) approximately described by the consensus motif A[D/N]LXX. While such proteins are scattered throughout the genomes of organisms in both the prokaryotic and eukaryotic kingdoms, PRPs are especially abundant in cyanobacteria. The sheer number of PRPs in cyanobacteria coupled with their predicted location in every cellular compartment argues for an important, yet unknown, physiological and biochemical function. To gain biochemical insights into this mystery, we have determined the crystal structure for one of the 35 PRP in *Cyanothece*, Rfr32, as part of an EMSL Membrane Biology Scientific Grand Challenge project.

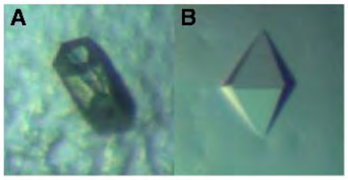


Figure 1. *The two different crystal forms of Rfr32 grown using the hanging-drop, vapor-diffusion method at 6x magnification: A, hollow rods with a hexagonal face, and B, bipyrimides.*

Rfr32 is a 167-residue PRP with an N-terminal, 29-residue signal peptide. As shown in Figure 1, the protein construct of Rfr32 lacking the 29-residue signal peptide crystallized in two different forms that yielded identical structures. H Robinson at Brookhaven National Laboratory collected x-ray data at the National Synchrotron Light Source on these crystals that diffracted to a resolution of 2.1 Å. Figures 2A and B are graphical representations of the structure.

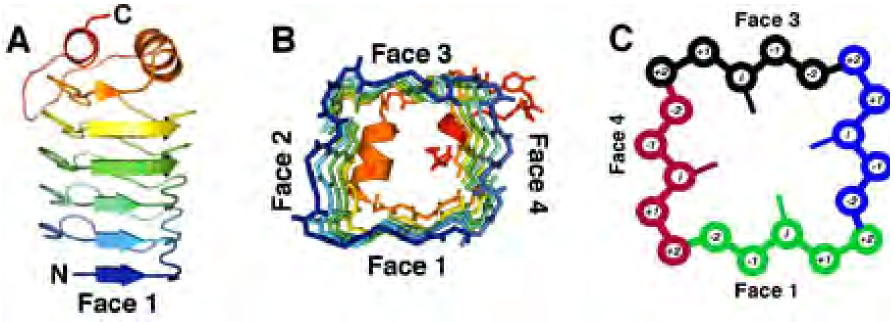


Figure 2. *Graphical representations of the Rfr32 (PDB ID - 2F3L) crystal structure: A, side-view; B, top-view of A viewed from the C-terminal; and C, stylized representation of a complete coil in an Rfr-fold, the higher order structural unit adopted by four tandem pentapeptide repeats. Each pentapeptide repeat is colored differently and is labeled relative to the central residue i.*

The dominant feature is the novel type of right-handed quadrilateral ß-helix, a repeated five-residue fold (Rfr-fold), adopted by the 21 consecutive pentapeptide repeats. This Rfr-fold is reminiscent of a square tower with four distinct faces with each pentapeptide repeat occupying one face of the Rfr-fold. Four consecutive pentapeptide repeats complete a coil that makes a revolution with approximately a 4.8-Å increase every 20 residues. A stylized representation of a complete coil in an Rfr-fold, which is the higher-order structural unit adopted by four tandem pentapeptide repeats, is shown in Figure 2C. The coils of the tower in Rfr32 are held together by short stretches of parallel ß-sheets (Face 1) and ß-bridges (Faces 2-4) (single-residue ß-sheets), which are integral to the quadrilateral shape of the Rfr-fold. There is a regular orientation of the side chains of each pentapeptide repeat. Designating the center residue of each pentapeptide repeat i with the preceding residues labeled i-1 and i-2 and the following residues labeled i+1 and i+2, we observed that the i-2 and I residues all point toward the interior of the tower and pack the middle of the Rfr-fold. The side chain of the i^{th} residue is predominately a large hydrophobic group (Leu or Phe), while the side chain of the i-2 residue is predominately a small and usually hydrophobic group (Ala > Ser, Thr, and Val). On the other hand, the side chains of the i-1, i+1, and i+2 residues all point away from the interior of the tower and form the exterior, solvent-exposed surface of the Rfr-fold. Unlike the side chains that are directed to the interior, which are primarily hydrophobic and form regularly stacked columns, the side chains directed to the exterior are typically hydrophilic and do not assume a regular form.

Figure 3 is a plot of the main chain (Φ, Ψ) dihedral orientations for Rfr32 residues A7-V111 that make up the Rfr-fold. Clearly, two distinct patterns are observed for the five residues constituting each coil on Face 1 and for the five residues constituting each coil on Faces 2, 3, and 4. After thorough analysis of the crystal structures of Rfr32 and MfpA (from *Mycobacterium tuberculosis*), it became evident that each pentapeptide repeat could be grouped into one of two types of four-residue type II and type IV ß-turns. The major differences between the two types of ß-turns is the Ψ and Φ torsion angles of the i and i+1 residue results from an ~90° rotation of the peptide unit between these two residues. Because of the repetitive nature of the pentapeptide repeat sequence, we predict that the regular shape of the Rfr-fold is maintained by these two distinct ß -turns and that they may be universal motifs that shape the Rfr-fold in all pentapeptide repeat proteins. The results of this Scientific Grand Challenge project were published in the journal *Protein Science* (Buchko et al. 2006)

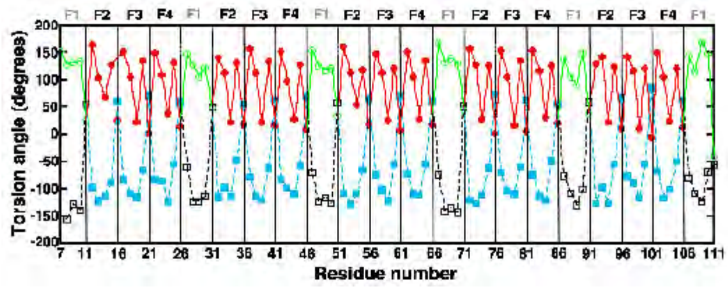


Figure 3. *Plot of the main chain (Φ, Ψ) dihedral torsion angles for the 21 consecutive pentapeptide repeats (A7-V111) that make up the Rfr-fold of Rfr32. The Φ torsion angles are connected with a dashed line and labeled with open black squares for the residues in Face 1 and closed blue squares for residues in Faces 2-4. The Ψ torsion angles are connected with a solid line and labeled with open green circles for residues in Face 1 and closed red circles for residues in Faces 2-4.*

Citation

Buchko GW, S Ni, H Robinson, EA Welsh, HB Pakrasi, and MA Kennedy. 2006. "Characterization of Two Potentially Universal Turn Motifs that Shape the Repeated Five-Residue Fold-Crystal Structure of a Lumenal Pentapeptide Repeat Protein from *Cyanothece* 51142." *Protein Science* 15(11):2579-2595.

High-Performance Sequence Analysis for Data-Intensive Bioinformatics

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(c) Washington University, Saint Louis, Missouri

Cyanobacteria are organisms that are capable of producing energy through photosynthesis and nitrogen fixation. As these organisms represent a large fraction of Earth's total biomass, their energy-producing processes may be a significant source of information related to renewable energy production and environmental cleanup. To fully understand and use these organisms, we modified genetic analysis tools to quickly analyze them at both the genetic and system levels.

Cyanothece is a relatively unstudied cyanobacterium with unique characteristics, including the ability to produce energy through two separate mechanisms: 1) photosynthesis and 2) nitrogen fixation. *Cyanothece* relies on photosynthesis during daylight but "switches" to nitrogen fixation in the absence of light. We might expect this behavior to rely on a "diurnal" cycle, meaning the organism "anticipates" nightfall. However, evidence suggests that circadian cycles play a role in *Cyanothece's* "switching" behavior. Circadian cycles are bio-chemically based processes that react to the change from light to dark. Because switching between nitrogen fixation and photosynthesis requires extensive remodeling of the cell's molecular machinery, we would expect it to be energetically unfavorable, yet *Cyanothece* is a highly efficient organism.

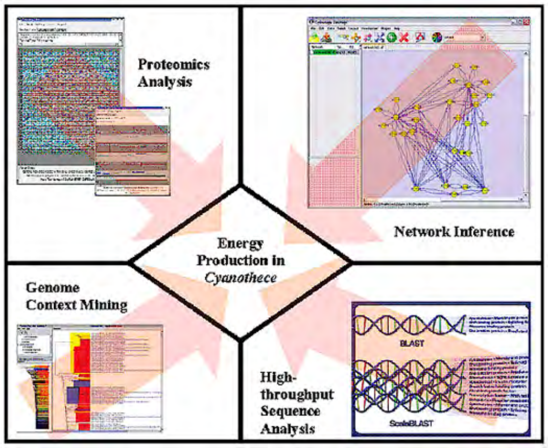


***Figure 1.** The analysis tools involved in discovery of* Cyanothece's *genetic structure include high-throughput sequence analysis, proteomics analysis, Bayesian network inference, and genome context mining.*

To understand how *Cyanothece* is capable of performing such dramatic changes, we need to understand the underlying genetic mechanisms and how those mechanisms affect the organism at the system level. Using ScalaBLAST and other computational tools, we have been able to rapidly annotate *Cyanothece's* genome. We performed a gene context analysis using Similarity Box software. This analysis led to the discovery of two proteins involved in nitrogen fixation. These discoveries were confirmed in a proteomics study using PQuad (a proteomics results browser), which indicated the differential presence of key nitrogenase proteins from samples taken at night. We used SEBINI (a network inference tool) (Taylor et al. 2006) to infer the relationship of these proteins to other nitrogenase proteins. We also were able to confirm the significance of these proteins at the system level through clustering analysis tools, including metabolomic, proteomic, and microarray analyses. More significantly, the tools we modified and made available through this EMSL Grand Challenge project enabled us to accomplish these analyses in a few minutes. In the past, as similar set of analyses would have taken days. The set of tools used in this study are represented in Figure 1.

Citation

Taylor RC, A Shah, C Treatman, and M Blevins. 2006. "SEBINI: Software Environment for BIological Network Inference." *Bioinformatics* 22(21):2706-2708.

Systems Approach to Understanding the Molecular Mechanism of the Light-Dark Cycles of *Cyanothece* sp. 51142

C Oehmen,[a] J McDermott,[a] J Stockel,[b] E Welsh,[b] J Jacobs,[a] T Metz,[a] A Dohnalkova,[c] GW Buchko,[a] and HB Pakrasi[b]
(a) Pacific Northwest National Laboratory, Richland Washington
(b) Washington University, St. LouisSt. Louis, Missouri
(c) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington

Studying complex biological phenomena at multi-levels of detail requires analyzing different types of data from many sources, including imaging technologies, bio-informatics, transcriptomics, and proteomics. As a wider variety of high throughput methods enter mainstream scientific analyses, handling the complexity and volume of data from these disparate sources requires new algorithms for processing, visualization, and analysis.

We present integrative, multi-level analysis of circadian cycling in *Cyanothece* sp. 51142 under the auspices of the EMSL Grand Challenge in Membrane Biology project, which is a multi-institutional collaboration among Washington University in St. Louis, Purdue University, Saint Louis University, the Danforth Center in St. Louis, and PNNL. The focus of the Grand Challenge consortium is to understand how cycling of metabolites, gene expression, and proteins leads to physiological changes in *Cyanothece* during light and dark cycles. Integration of correlations across transcriptomic, proteomic, and metabolomic datasets is being accomplished with a novel suite of computational tools developed at PNNL. These integrated tools include Similarity Box (Sofia and Nakamura 2007), an interactive dendogram/clustering tool, PQuad (Harve et al. 2004), a proteomics dataset viewer, SEBINI (Taylor et al. 2006), a network inference environment and ScalaBLAST (Oehmen and Nieplocha 2006), and a high-performance BLAST accelerator (Altschul et al. 1990). Analyzing this large and complex collection of datasets using novel tools and hardware has made it possible to identify vital molecular components in the circadian cycles. Once identified, the goal is to experimentally verify the importance of these components *in vivo*.

Citations

Sofia HJ and GC Nakamura. 2007. "Similarity Box: Visual Analytics for Large Genomic Sets." (submitted to *Bioinformatics*).

Havre SL, M Singhal, DA Payne, and BM Webb-Robertson. 2004. "PQuad: Visualization of Predicted Peptides and Proteins." *Visualization, 2004, IEEE* 473-480.

Taylor RC, A Shah, CC Treatman, and ML Blevins. 2006. "SEBINI Software Environment for Biological Network Inference." *Bioinformatics* 22(21):2706-2708.

Oehmen CS and J Nieplocha. 2006. "ScalaBLAST: A Scalable Implementation of BLAST for High-Performance Data-Intensive Bioinformatics Analysis." *IEEE Transactions on Parallel and Distributed Systems* 17(8):740-749.

Altschul SF, W Gish, W Miller, EW Myers, and DJ Lipman. 1990. "Basic Local Alignment Search Tool." *Journal of Molecular Biology* 215(3):403-410.

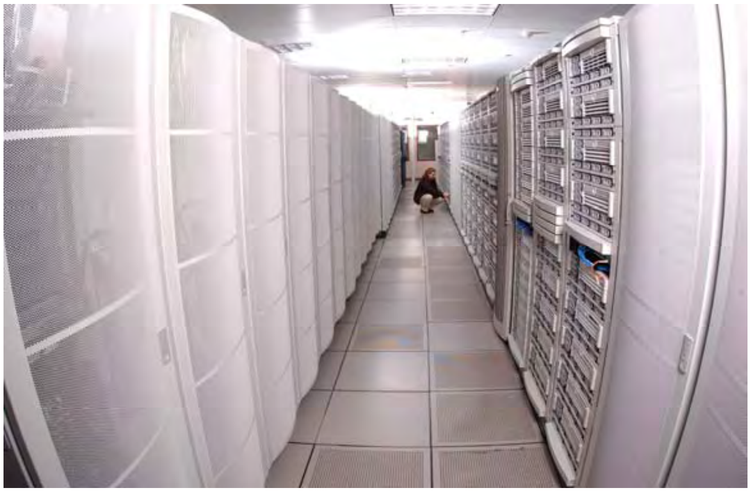
EMSL Highlights

Major EMSL Activities

EMSL Commemorates 10 Years of Operation. On September 28, 2007, 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. William R Wiley in recognition of Dr. Wiley's vision and success in moving EMSL from a vision to a reality. Mike Kluse, PNNL Director; Mike Weis, DOE Pacific Northwest Site Office; Allison Campbell, EMSL Director; and EMSL scientific user Dick Smith spoke at the event noting that, "Without the support of DOE, our staff, the scientists, and our scientific users and their families, EMSL could not build on its success in the coming decade." Approximately 200 staff, scientific users, and family members attended the event.


Mrs. Bill Wiley was a special guest at EMSL's 10-year anniversary celebration on September 28, 2007.

Supercomputer Contract Awarded to HP. In September 2007, HP was selected to deliver to EMSL a new $24-million supercomputer that will help scientific users advance molecular science in areas such as aerosol formation, bioremediation, catalysis, climate change, hydrogen storage, and subsurface science.


In September 2007, HP was selected as the vendor to deliver EMSL's next-generation supercomputing system. The system is scheduled to be fully operational in Fall 2008.

With this new system, EMSL users will be able to study more complex scientific problems with larger and more realistic models and get answers faster by scaling computational models to larger numbers of processors. The system will support a broad range of cutting-edge research, such as discovering safe and effective materials for producing and storing hydrogen; studying chemical processes in bacteria's behavior to address bioremediation and energy production issues; and developing computer simulation tools to aid in environmental cleanup.

The system will be delivered and tested in two phases starting in January 2008 and is expected to be fully operational in Fall 2008. It's architecture will run on HP ProLiant servers and will include an InfiniBand 4x DDR interconnect, 4,620 AMD Opteron™ processors, 37 terabytes of memory and aggregate disk bandwidth of about 950 gigabytes per second enabled by nearly 21,000 disk drives in HP enterprise virtual arrays. Consisting of 18,480 2.2 gigahertz AMD Opteron processor cores, the new HP supercomputer will have an expected total peak performance of about 163 teraflops. DOE's Office of Biological and Environmental Research funded the supercomputer's purchase.

EMSL Celebrates First Permanent Expansion. On January 10, 2007, nearly 175 PNNL staff celebrated the first permanent expansion of EMSL—nearly 4,000 square feet of new floor space in the user facility's supercomputing operations area. The space is slated to accommodate a portion of EMSL's next-generation supercomputer—scheduled for operation in 2008—and the facility's data archive capabilities. The new floor space is the first in a series of planned expansions that EMSL will undergo in the next decade to include a radiological annex and several new office and lab spaces.

EMSL celebrated its first permanent expansion, a raised floor that will house the next-generation supercomputer. From left to right: EMSL user TP Straatsma (PNNL); Kevin Regimbal, Operations Manager of EMSL's Molecular Science Computing Facility; EMSL Director Allison Campbell; David Koppenaal, PNNL Chief Research Officer; Jeff Day, DOE Pacific Northwest Site Office; and Larry Maples, PNNL Facilities and Operations. The ribbon was cut with the giant scissors used at the original ribbon-cutting ceremony of EMSL a decade ago.

EMSL is serving as a model for a new user facility being created by the University of Manchester and the United Kingdom's Nuclear Decommissioning Authority.

EMSL Serves as Model for New User Facility. Representatives from the University of Manchester visited EMSL on July 23 and 24, 2007, to evaluate EMSL as a model for how the university will design and operate its new user facility.

The University of Manchester's Dalton Nuclear Institute is partnering with the United Kingdom's Nuclear Decommissioning Authority to fund creation of the Dalton Cumbria Facility (DCF), which will become part of that country's National Nuclear Lab system. In the planning stages, the DCF is expected to house equipment and facilities associated with research in radiation sciences and engineering decommissioning and, as an outstation to the University of Manchester, will enable research and education activities at the post-graduate level. Instruments will include accelerators and experimental equipment to study irradiation damage and effects on materials and chemical systems used in nuclear environments, as well as cutting-edge computational modeling and simulation tools.

To support Dalton Nuclear Institute's goal of operating the DCF as a user facility, the university delegation is focusing on evaluating the development and operation of world-class user facilities such as EMSL. During the July visit, the representatives gained a good understanding from EMSL staff about EMSL's financial model of operation, organizational hierarchy, stakeholder engagement, project selection and peer review processes, how users are trained and supervised, and measures of performance. According to the university representatives, the visit was a great success, and the DCF and National Nuclear Lab system were expected to adopt several of EMSL's key user systems.

Successful Workshop Held on Future of NWChem. The meeting, "NWChem Meeting on Science Driven Petascale Computing and Capability Development at EMSL," was held at EMSL on January 25 – 26, 2007. Sixty-five experts in software development and computational chemistry attended the meeting to discuss status and future direction of NWChem, how to contribute to the growth of NWChem related to its scientific capability and computational performance within the next 15 years, and parallel implementation and natural linear scaling of coupled-cluster theory of large molecule applications. The information generated by the participants' discussions is being rolled into a strategic plan for further development of NWChem.

User Committee Recommends Completion of DOE Stretch Goal. During the inaugural meeting of EMSL's refreshed User Advisory Committee in May 2007, it was recommended that EMSL had met DOE Office of Biological and Environmental Research Stretch Goal 1.1.2, "Develop and deploy to the user community a minimum of 5 new or improved capabilities/methodologies for investigation of environmental and biology problems verified and validated by EMSL's User Advisory Committee, which provides a recommendation to BER regarding the completion of the measure." The candidate capabilities that helped lead to this recommendation included the Single-Particle, Laser-Ablation Time-of-Flight II spectrometer; Subsurface Flow and Transport Laboratory; NWChem computational chemistry software; cryo-transmission electron microscope; 12-tesla top-down proteomics capability; radioactive material nuclear magnetic resonance spectrometer; and capability for analysis of single-site chemical properties.

EMSL's cryo-transmission electron microscope was one candidate capability that helped EMSL satisfy a DOE stretch goal of developing and deploying five new or improved capabilities to the scientific user community.

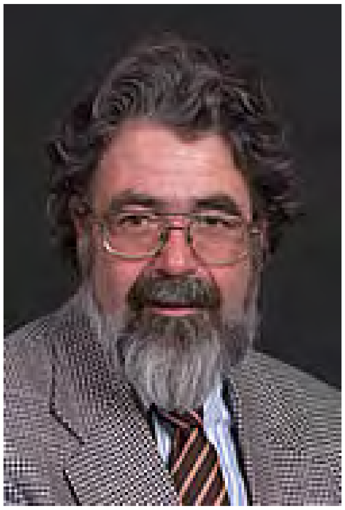
EMSL Staff and Scientific User Highlights

In 2007, EMSL staff and scientific users received continued recognition for progress in development of state-of-the-art capabilities and expertise, and for their professional contributions.

Zachara Honored with Prestigious E.O. Lawrence Award. John Zachara (EMSL scientific user, PNNL) received the E.O. Lawrence Award, which honors scientists and engineers at mid-career for exceptional contributions in research and development that support DOE and its mission to advance the national, economic and energy security of the United States. His research has focused on chemical interactions of toxic metals and radionuclides with mineral surfaces and microorganisms that control the rate at which these contaminants move through soils, sediments and groundwater.

John Zachara (center) with Sam Bodman (left, Secretary of Energy) and Ray Orbach (right, DOE Under Secretary for Science).

Meakin Recognized with Norwegian Award. Paul Meakin (EMSL scientific user, Idaho National Laboratory) was presented with the Gunnar Randers Research Prize for 2007 by King Harald V of Norway for his pioneering research into complex materials and processes. His research has increased fundamental insights in many branches of material science—especially in super-strong fibers and increased oil production. Having published more than 350 scientific publications in more than 50 journals, Meakin was the 79th most-cited physicist in a worldwide survey covering papers published in physics journals from 1981 to 1997. Meakin is an EMSL scientific user under the Geochemistry/Biogeochemistry and Subsurface Science theme.



Paul Meakin

Alex Punnoose

Punnoose Awarded Prominent Honors by Home Institution. Alex Punnoose (EMSL scientific user, Boise State University) received three prestigious awards this year from his home institution. Punnoose received the 2007 Boise State University College of Arts and Sciences Award for Distinguished Teaching and the Award for Distinguished Research—the first BSU professor to receive both awards in the same year. In addition, Punnoose was named winner of the university's 16th Foundation Scholar Award for Research and Creativity. These awards recognize ongoing commitment, expertise, and accomplishment in teaching, research and creative activity, and professionally related service. As a teacher, Punnoose was cited for his dedication and skill in the classroom and for his contributions to developing future scientists. He teaches in both the undergraduate physics program and the graduate materials science program at BSU. His scholarly achievements include publishing more than 65 refereed papers in diverse fields, including spintronics, magnetic semiconductor materials, photonic materials, and other high-profile research areas. His current work at EMSL involves studying the development of ferromagnetism in oxide semiconductor nanostructures; the ferromagnetic properties of these materials make them promising candidates for development of a new generation of computer chips. Punnoose is also using EMSL facilities to study how semiconductor nanoparticles enter cells. This work has applications in the use of nanomaterials in biomedicine.

Satyanarayana Kuchibhatla (right) with one of his mentors, Don Baer, EMSL Lead Scientist for Interfacial Chemistry.

EMSL Graduate Student Recognized by AVS. Satyanarayana Kuchibhatla, a graduate student from the University of Central Florida who is conducting research at EMSL, received an American Vacuum Society (AVS) Graduate Research Award for 2007. The award is established to recognize and encourage excellence among graduate students in the sciences and technologies of interest to AVS. Satya's research focus is understanding and tuning the properties of nanostructured materials, including nanoparticles and high-quality, single-crystal thin films. He was one of seven individuals to receive the honor, recognized by the AVS for his hard work, creativity, and potential for leadership in his profession. He received a $1,000 cash award, a certificate, complimentary AVS membership for 2008, and travel expenses to attend the AVS 54th International Symposium in Seattle in October 2007.

Campbell Receives ACS Award for Distinguished Service. Charles T. Campbell (EMSL scientific user, University of Washington and member of EMSL's Science Advisory Committee) received the Arthur W. Adamson Award for Distinguished Service in the Advancement of Surface Chemistry. This award is administered by the American Chemical Society and is sponsored by the Occidental Petroleum Corporation. Campbell has served on the editorial boards of the Journal of Catalysis, the Journal of Chemical Physics, and other journals, and he has held the position of editor-in-chief of Surface Science since 2002. He has been honored with several awards, including the ACS Award in Colloid or Surface Chemistry in 2001 and the Alexander von Humboldt Research Award in 2003. He received the honor at the ACS 233rd national meeting held in Chicago on March 27, 2007.

Charles Campbell

Dohnalkova Celebrates Renowned Microscopy Award. EMSL researcher Alice Dohnalkova was presented with the Diatome Award for distinguished scientists in the field of microscopy at the Microscopy Society of America meeting in August 2007. The award recognizes scientists who present new and enlightening work in the field of microscopy. She received the award for the best use of ultramicrotomy in the presentation "Creating 3D Reconstruction of Cyanobacterium *Cyanothece* sp. by Alignment of Serial TEM Tomograms." As part of this award, Dohnalkova received a trip to Switzerland to visit the Diatome factory, where precision diamond knives are manufactured for electron microscopy applications.

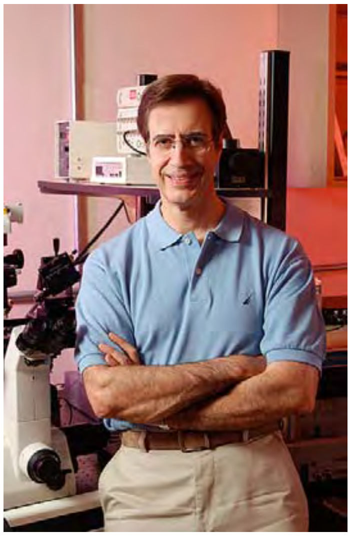
Alice Dohnalkova (left) is congratulated by the Microscopy Society of America's president, Michael O'Keefe (center) and Diatome representative Helmut Gnaegi (right).

Zhao Named Outstanding Post-Doc. Jin Zhao (EMSL scientific user, University of Pittsburgh) was the first-ever recipient external to PNNL to receive the M.T. Thomas Award for Outstanding Postdoctoral Achievement in the 11-year history of the award. The award recognizes Zhao's seminal contributions to the theory of the unoccupied electronic structure and dynamics of solid-adsorbate interfaces, which are of importance to geochemistry, atmospheric science, and energy-related interfacial phenomena. Zhao is a user of EMSL's computational resources. She was honored at an awards ceremony held at EMSL on May 24, 2007.

Jin Zhao

Gephart Recognized by National Academies. EMSL researcher Roy Gephart was invited by the National Academies to participate in a June 2007 workshop on radiation contamination and remediation issues in the former Soviet Union. Hosted by the National Academies and the Russian Academy of Sciences, the workshop participants assessed cleanup problems and provide recommendations for six Russian sites: Kurchatov Institute, Lakes 10 and 11 at Mayak, Andreev Bay, Krasnokamensk Mining Enterprise (Siberia), Almaz Mining Enterprise (North Caucasus), and a site for testing peaceful nuclear explosions (Perm or Ivanovo region). Gephart led one of the workshop's review sessions.

Roy Gephart



Steve Wiley

Wiley Brings Biology Expertise to EMSL Senior Management Team. On October 1, 2006, PNNL researcher Steve Wiley joined the EMSL senior management team as the new Lead Scientist for Biology. Steve, a Lab Fellow, joined PNNL in 2000 and has served as Director of the Laboratory's Biomolecular Systems Initiative. In his new role, he will help develop the scientific vision for potential breakthrough biological research and will work with the other lead scientists to oversee the operational and capital investments EMSL will undertake to maximize its user program.

Jean Futrell

Futrell Honored by ACS for Contributions to Mass Spectrometry. Former EMSL Director Jean Futrell was awarded the 2007 American Chemical Society Frank H. Field and Joe L. Franklin Award for Outstanding Achievement in Mass Spectrometry. This award is the highest recognition given by the ACS for fundamental contributions to mass spectrometry. He was selected for his work developing and modifying mass spectrometry instrumentation for specialized research purposes. His invention of tandem mass spectrometry is deployed in nearly every commercial mass spectrometer available. Futrell's research has answered several fundamental questions about mass spectrometry, including a detailed analysis of the mechanisms of ions. Co-author of nearly 300 peer-reviewed journal articles, Futrell is internationally recognized for his significant scientific contributions. He holds the distinction of Battelle Fellow, the organization's highest technical appointment for international scientific leadership.

Grate Garners ACS Award for Innovative Work. Jay Grate (EMSL scientific user, PNNL) received the 2007 American Chemical Society (ACS) Regional Industrial Innovation Award. He received the honor for his work developing BSP3 Polymer, a unique polymer coating that can be used in chemical detector systems to detect airborne chemical agents. BSP3 makes sensors four times more sensitive to nerve agents and in some systems has enabled faster detection at lower concentrations than was previously possible. Grate received his award at the ACS Northwest Region Meeting in Boise on June 17 – 21, 2007.

Jay Grate

Yanwen Zhang

Zhang Offered Appointment at Top Chinese University. Based on her international recognition and scientific advances in the area of ion-solid interactions, EMSL researcher Yanwen Zhang has been awarded a unique offsite Guest Professor appointment at Peking University, one of the top universities in China. There, Yanwen will supervise graduate student research, enhance PNNL-Peking University collaborations, and contribute to strengthening fundamental ion-beam research at the university.


Greg Exarhos

Exarhos Recognized for Outstanding Mentorship. Greg Exarhos (EMSL scientific user, PNNL) received an Outstanding Mentorship Award, which recognizes scientific and technical staff at DOE Office of Science labs whose dedication and leadership significantly contribute to the development of the next generation of scientists. Greg was selected because of his dedication, inspiration and nurturing. According to undergraduate student Adriana Teodoro-Dier, "He often asked for my input and encouraged me to gain autonomy by working alone and asking me questions on what I was doing or on the techniques I learned from someone else. Because he has allowed me to develop my own sense of autonomy and independence, I feel that my confidence as a scientific investigator has increased."


Ken Beck (right) with PNNL interim Director Mike Kluse.

Beck Receives President's Volunteer Service Award. EMSL researcher Ken Beck is the first Battelle staff member to receive the President's Volunteer Service Award. This award, an initiative of the President's Council on Service and Civic Participation, honors America's volunteers and encourages even more Americans to get involved in volunteer activities. Beck served more than 250 hours with the U.S. Coast Guard Auxiliary District 13 and the Black Rock City Emergency Services Department over the last year. That number of hours earned him a Silver Award from the President's Volunteer Service Award program. He was honored June 26, 2007, at the Volunteer Appreciation and Community Service Award reception held in the Battelle Auditorium.

Wang Receives Humboldt Research and Sahlin Awards. Lai-Sheng Wang (EMSL scientific user, Washington State University Tri-Cities) has received a prestigious Humboldt Research Award for his lifetime achievements in nanoscience. Lai-Sheng –a world leader in nanoclusters research—and his colleagues created hollow nanoscale cages of gold atoms, the first known metallic equivalent of the buckyball. He also has pioneered the study of multiply charged negative ions and began the study of solution molecules in the gas phase. The Alexander von Humboldt Foundation presents up to 100 of these awards each year and invites the recipients to conduct research projects of their choice in Germany for 6 months to a year. In addition, he was awarded the Sahlin Faculty Excellence Award for Research, Scholarship, and Arts from Washington State University. The university presents three Sahlin awards each year to recognize excellence in teaching, public service, and research.

Lai-Sheng Wang

Julia Laskin

Laskin Provides Expertise to Mass Spectrometry Book. Julia Laskin (EMSL scientific user, PNNL) was co-editor of the new book *Principles of Mass Spectrometry Applied to Biomolecules*. The book has 16 chapters written by experts in the field of fundamental mass spectrometry and gas-phase ion chemistry. Laskin of PNNL and Lai-Sheng Wang of Washington State University Tri-Cities wrote two of the chapters. Another chapter written by EMSL user Graham Cooks of Purdue University provides information on the EMSL Science Theme proposal he leads.

Shuttha Shutthanandan

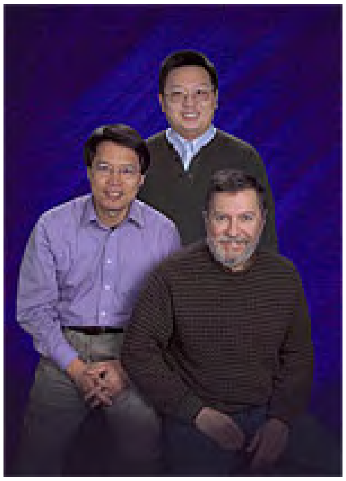
Shutthanandan Honored for Mentorship. EMSL researcher Shuttha Shutthanandan received the 2007 Fitzner/Eberhardt Award for Outstanding Contributions to Science and Engineering Education, awarded by the Pacific Northwest National Laboratory. He received the award at a ceremony held at PNNL on April 26, 2007. Since joining PNNL in 1999, Shutthanandan has enthusiastically mentored several high school, undergraduate, and graduate students as well as university faculty members, post-doctoral fellows, and junior staff at EMSL's ion beam accelerator laboratory. His mentorship has contributed to publication of several papers by his students in internationally peer-reviewed publications, development of a new nanoscience course by a university faculty colleague, and completion of a graduate student's Master's research in one semester.

EMSL User Selected to Serve on the Editorial Board for *Laser Chemistry*. Wayne Hess (EMSL scientific user, PNNL) has been selected to serve on the editorial board of the publication *Laser Chemistry*. With his peers on the board, including experts from universities, research foundations, and government councils, Hess will be involved in decisions regarding accepting or rejecting scientific articles submitted for publication in the journal. *Laser Chemistry* is an international journal that focuses on fundamental studies and applications within the field of laser chemical physics and spectroscopy. Hess was selected to serve on the editorial board because of his experience in laser-induced reactions in solids and at surfaces, including his ongoing studies in laser desorption from wide-band gap materials, metal oxides, and semiconductors.

Wayne Hess

Ram Devanathan

Devanathan Invited to Frontiers of Engineering Symposium. Ram Devanathan was invited to attend the prestigious 2007 German-American Frontiers of Engineering Symposium, organized by the National Academy of Engineering and the Alexander von Humboldt Foundation. About 60 engineers, generally not older than 45, from German and U.S. industry, universities, and national laboratories were invited because of their innovation, articulation, and leadership. The symposium was held in April 2007 in Hamburg, Germany.



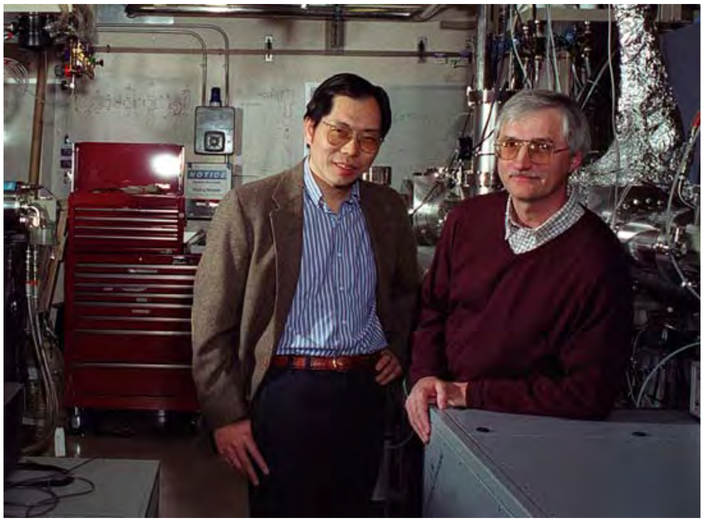
Clockwise from top: Guodong Liu, Chuck Timchalk, and Yuehe Lin.

Richard Barry

Sensor Research Garners EMSL Users Journal Honor, Grant. Yuehe Lin and Guodong Liu, as well as past user Chuck Timchalk, (EMSL scientific users, PNNL) received a 2006 *Environmental Business Journal* Technology Merit Award for designing and testing a nanotechnology-based sensor that detects organophosphate insecticides and nerve agents. The award is given by the journal to recognize notable achievements in the environmental industry. In addition, the trio and their collaborator, Richard Barry (PNNL), were awarded a $3.5-million grant by the National Institutes of Health/National Institute of Neurological Disorders and Stroke to develop nanoparticle-based biosensors. The biosensors will be used for onsite rapid detection of protein biomarkers (biological signatures) in blood and saliva to determine if an individual was exposed to nerve agents. The 5-year grant supports PNNL's Environmental Biomarkers Initiative.

Baer Named to Editorial Advisory Board. Don Baer, EMSL Lead Scientist for Interfacial Chemistry, has been named to the editorial advisory board of *Surface and Interface Analysis*. The journal is devoted to the publication of papers dealing with the development and application of techniques for the characterization of surfaces, interfaces and thin films. Baer has frequently published with his collaborators in this journal and will serve in this capacity with more than 20 of his colleagues from national and international academic, industrial, and government institutions.

Don Baer


Lai-Sheng Wang (left) and Alexander Boldyrev

EMSL Users Featured in *Chemical & Engineering News*. Alexander Boldyrev (EMSL scientific user, University of Utah) and Lai-Sheng Wang (EMSL scientific user, Washington State University-Tri-Cities) were featured in the May 7, 2007, issue of *Chemical & Engineering News*. Their computational studies and gas-phase photoelectron spectroscopy experiments confirmed the existence of delocalized bonding involving the d atomic orbitals of transition metals. Research on the planar $Ta_3O_3^-$ cluster provides the first experimental evidence of a δ-aromatic molecule and suggests that δ aromaticity exists in other planar transition-metal complexes.

EMSL Users Named AAAS Fellows. Five current and past EMSL scientific consultants and users were named Fellows of the American Association for the Advancement of Science (AAAS):

- **Jim Fredrickson** (Pacific Northwest National Laboratory), Biological Sciences: For leadership in the field of microbial ecology and environmental microbiology, with emphasis on subsurface microbiology and biogeochemistry.
- **Dick Smith**, (Pacific Northwest National Laboratory), Chemistry: For leadership in analytical chemistry, specifically in the development of advanced separation methods with high-performance mass spectrometry for high-throughput proteomics.
- **SK Sundaram,** (Pacific Northwest National Laboratory), Engineering: For leadership and innovative contributions to a diverse cross-section of materials sciences, particularly new tools for synthesis and characterization of novel materials, diagnostics and nanomaterials.
- **Bill Weber**, (Pacific Northwest National Laboratory), Physics: For leadership and innovative research on defects, ion-solid interactions, and radiation effects in ceramics, particularly modeling and simulations of radiation damage processes.

- **John Zachara**, (Pacific Northwest National Laboratory), Geology and Geography: For distinguished contributions to environmental science, particularly for his work on the chemical and microbial processes affecting subsurface contaminant transport at the Hanford site.

Fredrickson

Smith

Sundaram

Weber

Zachara

They are five of 449 AAAS members who had this honor bestowed upon them this year because of their scientifically or socially distinguished efforts to advance science or its applications. They were honored with their peers on February 17 at the 2007 AAAS Annual Meeting in San Francisco.

Journal Covers

During Fiscal Year 2007, research by EMSL users and staff was highlighted on six scientific journal covers. The following describe the research that led to these covers.

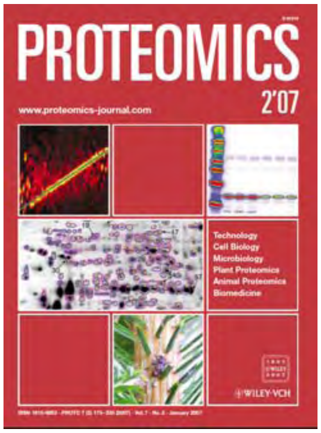
A new class of materials that transmit data based on an electron's spin could revolutionize the world's computers, thanks to scientists at PNNL and their collaborators. The team recently demonstrated a key relationship that brings us one step closer to this new class of materials. Since 2001, certain oxides which are not normally magnetic have been made ferromagnetic by adding a few percent of a magnetic element, such as cobalt. What is new is that this research team has demonstrated for the first time that the magnetism in one such material is directly tied to the presence of additional electrons that convert the material from an insulator to a semiconductor. The material is zinc oxide in which some of the zinc atoms are replaced with cobalt. Cobalt-doped zinc oxide, or materials like it, could be critical in developing revolutionary computer chips to enable spin electronics, or spintronics. In spintronics, circuits would use the electron spin, rather than the electron charge, to carry signals and process information. To develop such chips, researchers must find semiconductors that remain magnetic at and above room temperature. Magnetic means the spin of the electrons that carry the signal is preferentially oriented in one direction. Other such magnetic semiconductors exist, but these materials lose their beneficial magnetic properties well below room temperature, reducing their usefulness.

The research of EMSL users SA Chambers, TC Droubay, CM Wang, KM Rosso, SM Heald, DA Schwartz, KR Kittilstved, and DR Gamelin was featured in the November 2006 issue of Materials Today.

Identical regions of partially reduced TiO_2(110) surfaces with bridge-bonded oxygen vacancy (BBOV) concentrations of ~ 10 % ML (1 ML = 5.2×1014 cm^{-2}) were imaged using scanning tunneling microscopy before and after dosing H_2O at ambient temperature (~ 300 K). Provided the H_2O coverage is less than the BBOV concentration, atomically resolved images confirm that the titration of individual BBOV by dissociative adsorption of H_2O is strongly favored. The products are two hydroxyl species, one positioned at BBOV and denoted OHV and the other, denoted OHB, formed by protonation at either of the two nearest-neighbor bridge-bonded oxygen atoms. Proton hopping along the [001] direction is observed at ambient temperature, with a strong preference for OHB (~

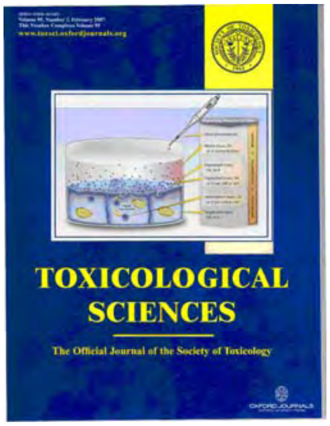
10x) proton motion. This powerful imbalance demonstrates the inequality of OHV and OHB and suggests differences in their charge and/or binding configuration.

The research of EMSL users Z Zhang, O Bondarchuk, BD Kay, JM White, and Z Dohnalek was featured on the cover of the November 2, 2006, issue of the Journal of Physical Chemistry B.



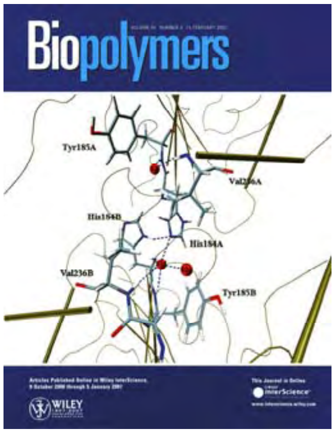
Genomics and proteomics assays hold great promise for revealing molecular events that underlie human disease. Essential to this quest is the ability to effectively analyze clinical samples, but this task is considerably complicated by tissue heterogeneity. Laser capture microdissection (LCM) can be used to selectively isolate targeted cell populations (such as tumor cells) from their native tissue environment. However, the small number of cells that are typically procured by LCM severely limits the proteome coverage and biomarker discovery potential achievable by conventional proteomics platforms. Herein, the use of a nano liquid chromatography-Fourier transform ion clyclotron resonance mass spectrometry (nLC-FTICR MS) platform is reported for analyzing protein digests of approximately 3,000 LCM-derived tumor cells from breast carcinoma tissue, which corresponds to approximately 300 ng of total protein. A total of 2,836 peptides were identified by matching LC-MS data to accurate mass and time (AMT) tag databases that were previously established for the human mammary epithelium and several breast cancer cell lines. The peptide identifications correspond to 1,139 unique proteins confidently identified with 2 or more peptides. Based on categorization by Gene Ontology, identified proteins appear to cover a wide variety of biological functions and cellular compartments. This work demonstrates that a substantial number of proteins can be identified from a limited number of cells using the AMT tag approach and opens a door for high throughput in-depth proteomics analysis of clinical samples.

The research of A Umar, TM Luider, JA Foekens, and L Pasa-Tolic was featured on the cover of the January 2007 issue of Proteomics.



The rapid growth in the use of *in vitro* methods for nanoparticle toxicity assessment has proceeded with limited consideration of the unique kinetics of these materials in solution. Particles in general and nanoparticles specifically, diffuse, settle and agglomerate in cell culture media as a function of several systemic and particle factors: media density and viscosity, particle size, shape and density. Cellular dose then is also a function of these factors as they determine the rate of transport of nanoparticles to cells in culture. Here the principles of particokinetics and dosimetry *in vitro* was developed and applied and outlines an approach for simulation of nanoparticle particokinetics in cell culture systems. Illustrated is where equal mass concentrations (µg/ml) imply equal doses for dissimilar materials, the corresponding particle number or surface area concentration doses differ by orders of magnitude. When rates of diffusional and gravitational particle delivery are accounted for, the trends and magnitude of cellular dose as a function of particle size and density differ significantly from those implied by NMC doses. Fifteen nm Ag nanoparticles appear ~4000 times more potent than micron sized cadmium oxide particles on a cm2/ml media basis, but are only ~50 times more potent when differences in nanoparticle delivery to adherent cells are considered. Conclusions are that simple surrogates of dose can cause significant misinterpretation of response and uptake data for nanoparticles *in vitro*. Incorporating particokinetics and principles of dosimetry would significantly improve the basis for or nanoparticles toxicity assessment, increasing the predictive power and scalability of such assays.

The research of J Teeguarden, P Hinderliter, G Orr, B Thrall, and J Pounds was featured on the February 2, 2007, issue of Toxicological Sciences.



The dynamics and structure of Serratia marcescens endonuclease and its neighboring solvent are investigated by molecular dynamics. Comparisons are made with structural and biochemical experiments. The dimer form is physiologic and functions more processively than the monomer. The researchers previously found a channel formed by connected clusters of waters from the active site to the dimer interface. Here, the researchers show that dimerization clearly changes correlations in the water structure and dynamics in the active site not seen in the monomer. Their results indicate that water at the active sites of the dimer is less affected compared with bulk solvent than in the monomer where it has much slower characteristic relaxation times. Given that water is a required participant in the reaction, this gives a clear advantage to dimerization in the absence of an apparent ability to use both active sites simultaneously.

The research of C Chen, BW Beck, K Krause, TE Weksberg, and B Montgomery Pettitt was featured on the cover of the February 15, 2007, issue of Biopolymers.

Much recent research effort has been made on the synthesis, characterization, and property evaluation of core-shell structured Fe nanoparticles. Fundamental properties of these particles depend on both their external crystal faceting planes and the nature of a protective oxide layer. In this paper, the crystal faceting planes and oxide coating structures of core-shell structured iron/iron oxide nanoparticles synthesized by a sputter-gas-aggregation process were studied using transmission electron microscopy (TEM), electron diffraction and Wulff shape construction. The particles grown by this process and deposited on a support at room temperature process have been compared with particles grown and deposited at high temperature as reported in literature. Most synthesis processes produce round particles for particles less than 20 nm in diameter. For larger particles crystallographic facets are observed. It has been found that the Fe nanoparticles formed at RT are invariantly faceted on the {100} lattice planes and truncated by the {110} planes at different degrees. Substantial fraction of particles are confined only by the 6 {100} planes (not truncated by the {110} planes), this contrasts with the Fe particles formed at high temperature (HT) for which a predominance of {110} planes has been reported. Furthermore, at RT no particle was identified to be only confined by the 12 {110} planes which is relatively common for the particles formed at HT. The Fe cubes defined by the 6 {100} planes show a characteristic inward relaxation along the <100> and <110> directions and the reason for this behavior is not fully understood. The oxide shell on the Fe {100} plane maintains an orientation relationship: Fe(001)// Fe_3O_4(001) and Fe[100]//Fe_3O_4[110], which is same as the oxide formed on a bulk Fe(001) through thermal oxidation. Orientation of the oxide that forms on the Fe{110} facets differs from that on Fe{001}, therefore, properties of core-shell structured Fe nanoparticle faceted primarily with one type of lattice plane may be fully different from that faceted with another type of lattice planes.

The research of C Wang, D Baer, J Amonette, M Engelhard, Y Qiang, and J Antony was featured on the cover of the June 27, 2007, issue of Nanotechnology.

The effects of level of hydration and temperature on the nanostructure of an atomistic model of a Nafion^{TM} (Du Pont) membrane and the vehicular transport of hydronium ions and water molecules were examined using classical molecular dynamics simulations. Through the determination and analysis of structural and dynamical parameters such as density, radial distribution functions, coordination numbers, means square deviations, and diffusion coefficients, the researchers identified that hydronium ions themselves play a role in modifying the interfacial structure in the membrane at the sulfonate pendants. In the regime of low level of hydration, short hydrogen bonded linkages made of water molecules and also hydronium ions give a more constrained structure to the sulfonate pendants. The diffusion coefficient for water was found to be in good accord with experimental data. The diffusion coefficient for hydronium ions was determined to be much smaller (6 to 10 times) than for water. Temperature was found to have a significant effect on the absolute value of the diffusion coefficients for both water and hydroniums.

The research of A Venkatnathan, R Devanathan, and M Dupuis was featured on the cover of the June 28, 2007, issue of Journal of Physical Chemistry B.

Patents

EMSL staff and their collaborators received two patents in Fiscal Year 2007

U.S. Patent 7,136,759, "Method for Enhanced Accuracy in Predicting Peptides using Liquid Separations or Chromatography." Anderson, GA, KJ Auberry, LJ Kangas, and RD Smith. November 14, 2006.

U.S. Patent 7,176,784, "Multi-Mode Radio Frequency Device." Gilbert RW, CL Carrender, GA Anderson, and KD Steele. February 13, 2007.

Outreach Activities

The following outreach activities were conducted by EMSL staff in Fiscal Year 2007:

- EMSL hosted an intensive 2-week college course, "Nanoclusters, Nanomaterials, and Nanotechnologies," in May 2007. This course provided an introduction to nanoscience and nanotechnology and included lectures and small hands-on projects using EMSL capabilities, providing the 18 participants with an introduction for using EMSL. The participants mostly consisted of graduate students who, through this course, could obtain college graduate-level credit from Washington State University or the University of Washington. This approach provides these young researchers with an introduction to user facilities and provides linkages from their home research institutions to appropriate EMSL capabilities.

- A January 2007 workshop on the future of NWChem brought 65 scientists to EMSL, half who were new to the facility. To date, more than 1750 researchers worldwide have signed an EMSL software agreement to use the software. In October 2006, a brochure entitled "NWChem: Delivering High-Performance Computational Chemistry to Science" was developed and has been distributed to enthusiastic scientists at large national and international meetings.

- At the suggestion of EMSL's User Advisory Committee, EMSL conducted a user outreach exercise at the 49th Rocky Mountain Conference in Analytical Chemistry, chaired by committee member Sarah Larsen. This major solid-state NMR meeting focused on materials development, catalysis/materials chemistry, computational simulations, solid-state biological systems, and novel NMR methods as the primary scientific topics. EMSL presented a poster at two poster sessions and contributed literature that highlighted the unique capabilities EMSL has to offer in biological/and materials research in the solid state. New users as well as some active and past EMSL users were brought up to speed on recent developments in solid-state NMR, NWChem, and surface science capabilities at EMSL. About 250 to 300 people attended each poster session.

- A symposium entitled "EMSL User Research" was organized and chaired by EMSL outreach staff at the 62nd Annual Meeting of the Northwest Region of the American Chemical Society. Fourteen presentations were given by EMSL users describing how EMSL has contributed to their research, and these presentations were attended by many potential users throughout the 10-state region.

- EMSL staff members have provided overview presentations of EMSL capabilities and research during several university seminars and professional society meetings. Some examples of this type of outreach:
    - The EMSL Director gave EMSL-focused presentations at universities such as Whitworth College, the University of California-Irvine, and Ohio State University.
    - A poster summarizing EMSL capabilities was presented at the April 2007 Environmental Sciences Research Program workshop.
    - An EMSL-established database related to characterization of oxide films was highlighted in posters at meetings in Japan, Belgium, and Seattle.


Nancy Foster-Mills (second from left), EMSL User Administration Manager, represented EMSL and user outreach at the 62nd Annual Meeting of the Northwest Region of the American Chemical Society. From left to right: Janet Bryant, PNNL and active ACS member; Foster-Mills, Ann Nalley, 2006 ACS President; Katie Hunt, 2007 ACS President; Bruce Bursten, incoming 2008 ACS President; Amber Hinkle, ACS Women Chemists Committee Chair; and Novella Bridges, PNNL and active ACS member.

User Surveys

In Fiscal Year 2007, EMSL conducted two user surveys to determine satisfaction with availability and performance of facilities and equipment, assistance of technical and administrative staff, training and safety procedures, and the user proposal process.

- In October 2006 (http://www.emsl.pnl.gov/homes/survey_oct2006.shtml), 290 responses (58.1%) were received out of 499 surveys sent out. Overall, 157 scientific users were very satisfied, 117 satisfied, 7 remained neutral, 8 were dissatisfied, and 1 felt the question was not applicable. This constitutes a 90.7% satisfaction rate.

- In April 2007 (http://www.emsl.pnl.gov/homes/survey_april_2007.shtml), 331 responses (60.7%) were received out of 545 surveys sent out. Overall, 158 scientific users were very satisfied, 141 satisfied, 15 remained neutral, 11 were dissatisfied, 2 were very dissatisfied, and 4 felt the question was not applicable. This constitutes an 88.8% satisfaction rate.

Specific comments from users and responses by EMSL to those comments are available at the web addresses listed above.

Director's Office Staff

The following individuals served as Director's Office staff in Fiscal Year 2007:

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We would also like to acknowledge the contributions of Shirley A. Alderson, Justin Almquist, Tyler I. Borders, Courtney Carpenter, Linda M. Connell, Cary A. Counts, Christopher G. DeGraaf, Brittney H. Drollinger, Geoffrey R. Elliott, Becky Ford, Matthew D. Elliott, Cara Giancola, Zoe Graddy, Loel Kathmann, Eileen Kuch, Tim Lawson, Kristin Manke, Amy Selch, and Pam Stevens.

Chemistry and Physics of Complex Systems Facility

The Chemistry and Physics of Complex Systems (CPCS) Facility supports the U.S. Department of Energy (DOE) mission of fostering fundamental research in the natural sciences to provide the basis for new and improved energy technologies and for understanding and mitigating the environmental impacts of energy use and contaminant releases. This research provides a foundation for understanding interactions of atoms, molecules, and ions with materials and with photons and electrons. Particular emphasis is on interfacial processes.

A distinguishing feature of research at national laboratories is their approach to problem solving. Significant scientific issues are addressed using focused and multidisciplinary investigative teams with each team member bringing a particular skill and capability to bear on the problem. This approach accelerates progress. The same approach—involving groups of scientists within the program as well as collaborators from throughout Pacific Northwest National Laboratory and the external scientific community—is inherent in how the CPCS Facility is managed.

The CPCS Facility and its staff have particular capabilities and expertise that support user research involving preparation and spectroscopic analysis of molecular clusters; high-resolution imaging of biological samples and studies of cellular processes, including DNA damage and repair and low-dose radiation processes; ultra-fast and non-linear optical spectroscopies; ultrahigh-resolution spectroscopy for measurements of electronic and geometric structures and dynamics; surface and interface structure; chemical reaction dynamics and kinetics; ion-molecule traps and storage technology; and specialized chambers, instruments, and models for studying chemical reactivity and analyzing atmospheric species including aerosols.

Our research underpins the fundamental understanding of chemical transport and reactivity in the condensed phase. It addresses the underlying uncertainties in thermal and non-thermal (i.e., radiation) chemistry, interfacial molecular and ionic transport, and other processes in complex natural and human-made systems related to energy use, environmental remediation, waste management, and understanding biological responses to environmental stresses. One focus is on structures and processes of molecular and nanoscale systems in complex environments such as condensed phases and interfaces. Research guides the development of new materials and approaches for clean and efficient energy use.

Instrumentation & Capabilities

- reaction mechanisms at solid, liquid, and gas interfaces
- high-energy processes at environmental interfaces
- cluster models of the condensed phase
- single-molecule spectroscopy and biomolecular sciences
- ultra-sensitive and environmental analysis.

Another central feature is the development of innovative experimental methods with broad applications to research in the natural sciences. Two examples of innovative methods developed in the CPCS Facility include 1) detecting and monitoring trace atmospheric species, including gaseous and particulate matter, and 2) studying biological processes important in the environment and health, including imaging of live cells to observe the reaction dynamics of functioning biological systems in real time, advancing our understanding of protein-protein interactions and DNA damage and repair using single-molecule spectroscopy, and studying cellular responses to low-dose radiation using novel instrumentation.

Capabilities

The capabilities of the CPCS Facility support research in five general areas, which are described below.

Reaction Mechanisms at Solid, Liquid, and Gas Interfaces. Research in this area focuses on developing fundamental molecular information about processes occurring at the interfaces between environmentally important liquids, solids, and gases. For example, a common element in environmental restoration is the need to understand molecular processes 1) in aqueous solutions and at the interface between aqueous and organic solutions and 2) at the interface between aqueous solutions and environmentally important solid materials. Examples of instruments that enable this research are shown in Figures 1 and 2.

Molecular processes occurring at liquid-liquid interfaces also play an important role in the subsurface transport of contaminants such as organic solvents (e.g., chlorinated hydrocarbons) released into soil and groundwater. Processes at the gas-liquid interface are critical in atmospheric transport processes.

Model systems such as amorphous solid water permit detailed studies of solvation and the effects of solvation on chemical reactivity. These studies provide information about intermolecular interactions that lay the foundation for accurate modeling of solution processes. Studies provide information about factors that control the rates of reactions in solution. This

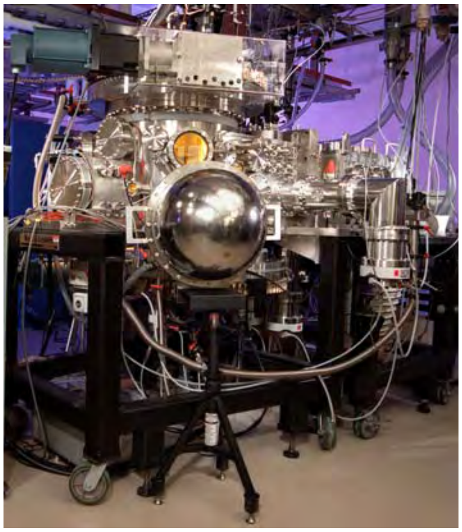

***Figure 1**. State-of-the-art molecular beam surface-scattering and kinetics instrument.*

***Figure 2**. Combined instrument that allows fluorescent optical microscopes and magnetic resonance microscopes to focus on the same samples at the same time.*

information is essential to both predicting the fate of contaminants in aqueous environments and influencing the selectivity of ligands for specific ions important in developing separations agents for waste treatment processes.

It is also crucial to understand molecular processes at the interface between aqueous solutions and environmentally important materials, such as aerosol particles, minerals, and glasses. This addresses fundamental science questions about contaminant fate and transport and waste immobilization. Because most environmental materials are in an oxidized form, we emphasize the structure and chemistry of oxide materials, especially naturally occurring oxides of silicon, aluminum, and iron. The adsorption of species on and their incorporation in soil minerals affect their transport through soil. Mineral interfaces can enhance or retard reactivity as well as transform contaminants. Knowledge of molecular processes at solid-liquid interfaces is also important to understanding the stability of glasses proposed for encapsulating high-level radioactive wastes that must be stored for long periods of time. Over the long half-lives of radionuclides, water can degrade these waste-encapsulating glasses, thus leading to higher-than-expected releases of radionuclides.

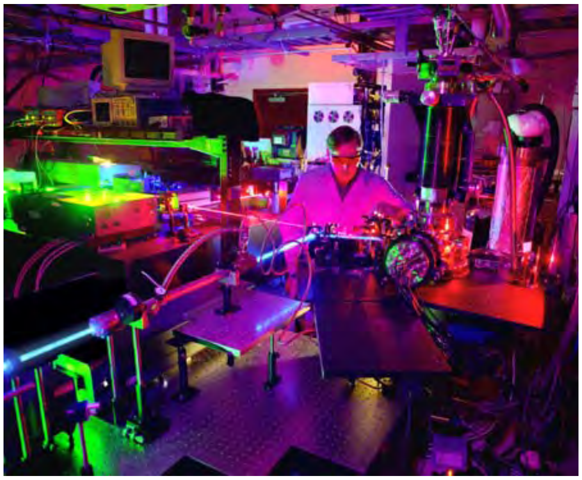

***Figure 3**. Laser desorption experiments investigate the effects of electronic excitation on crystalline materials.*

High-Energy Processes at Environmental Interfaces. Research in this area focuses on obtaining a mechanistic understanding of chemical transformations resulting from electronic excitation in condensed-phase materials relevant to the DOE environmental cleanup mission. Examples of capabilities that enable this research are shown in Figures 3 and 4. Energetic processes are important in the degradation of mixed wastes because of the radiolytic decay-driven chemistry that occurs in the solid and liquid phases of stored radioactive waste and in final waste storage forms. Reactions occurring at interfaces are of particular interest for characterizing material composition and response to electronic excitation. We use pulsed femtosecond and nanosecond laser sources to study laser-solid interactions in a combined experimental and theoretical program. Our goal is to

***Figure 4**. Electron-stimulated surface reaction apparatus is used to study non-thermal reactions that occur on surfaces or at interfaces.*

continue development of models for excited-state reactions by measuring ultra-fast dynamic processes and by demonstrating laser control of solid-state chemistry.

Cluster Models of the Condensed Phase. This research is aimed at providing a molecular-level understanding of solvation and subsequent reactions in simple and complex systems as they relate to the chemistry of complex wastes, contaminated solids and groundwater, and other systems found in nature. A major experimental and theoretical effort is devoted to understanding surface and interface properties using cluster models to study structure and bonding. Small and controllable cluster systems provide atomic-level models that enable us to understand bulk surfaces and defect sites. They are also an excellent testing ground to benchmark theories intended for large and real-world systems.

Single-Molecule Spectroscopy and Biomolecular Sciences. This research emphasizes single-molecule spectroscopy and high-resolution biological imaging techniques for studying biological systems. Recent advances in fluorescence microscopy, at both the EMSL and elsewhere, make it possible to detect single molecules at room temperature and to conduct spectroscopic measurements to monitor their dynamic processes. We have demonstrated fluorescence imaging of single molecules by two-photon excitation with a femtosecond laser. This approach has several advantages—the excitation volume is small, the penetration is deep, and photo-damage is reduced for biological samples—thus offering the opportunity of viewing chemical reactions in a living cell in real time. Structures are known for many proteins that perform vital cell functions, including DNA damage repair, reaction catalysis, and cell signaling. Nanoscale-structure materials will affect their properties; Figure 5 provides an example. However, how they perform these functions is generally not understood. Single-molecule and single-cell measurements provide real-time data on the molecular motions involved during these functions and how the timing of these reactions is correlated with other cellular biological activities. These data are likely to produce new information that is otherwise hidden, and will open up exciting possibilities for probing cellular processes.

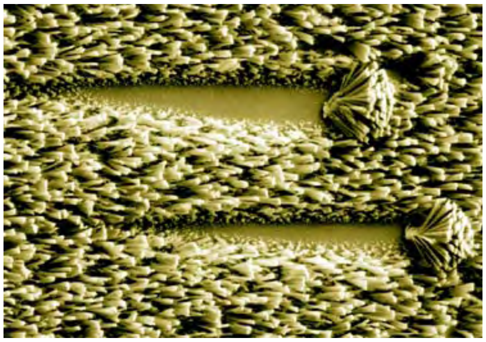

***Figure 5**. Nanostructures could be used to control and enhance chemical reactivity. Researchers at the CPCS Facility are trying to determine how molecules enter pores, are captured, and eventually released.*

Ultra-Sensitive Trace Gas Analysis. Research in this area focuses on developing a suite of instrumentation for fast, accurate, highly sensitive, and discriminatory real-time analyses of chemical and biological natural or human-made agents. Such instruments are ideally suited for identifying and quantifying many gases and pollutants, trace isotopic species, metabolic products in the breath, and chemical precursors and products from industrial processes. Some of these techniques can be developed for remote probing over long optical paths for remote interrogation of trace absorption features. Our infrared methods are supported by a state-of-the-art, high-resolution infrared spectroscopy laboratory that also is used for studies of the structures and dynamics of molecular species important in contaminant chemistry, photochemistry, and atmospheric processes. The high-resolution infrared spectroscopy laboratory is shown in Figure 6.

***Figure 6**. The high-resolution infrared spectroscopy laboratory is used by numerous users and U.S. government agencies to obtain high-resolution infrared spectra for applications in remote sensing, atmospheric science, space and planetary research, and infrared databases.*

Analyses of Environmental Aerosols Characterization of particulate matter in the atmosphere represents a unique challenge. Several approaches for both bulk and single particle analyses are employed that, in combination, are designed to understand the evolving inventory of atmospheric particulate matter and how particulates are changed by reactions with gas-phase species, photochemistry, and condensation and evaporation processes.

CPCS Facility capabilities relevant to aerosol characterization and aerosol chemistry research include single-particle mass spectrometry that provides real-time sampling and analysis of aerosol particles in laboratory and field studies, a variety of electron microscopy and microanalysis techniques for in-depth analysis of individual particles, and high resolution mass spectrometry for analysis of high molecular weight organic species (oligomers) in bulk aerosol samples. Figure 7 shows a unique, high-precision time-of-flight spectrometer used to study fundamental processes that govern the chemistry and physics of particles on the nano and micro scales.

***Figure 7.** The second-generation single particle laser ablation time-of-flight mass spectrometer offers users the versatility of laboratory studies and field campaigns.*

In conjunction with these analytical techniques, an array of special devices is being developed and deployed to collect and preserve aerosol samples for later analysis of in the laboratory. For example, in 2006 CPCS Facility researchers took part in a four-week field study in Mexico City (Figure 8), with the goal to characterize aerosol formation and changes

Figure 8. *EMSL staff have studied aerosols and aerosol transformations in many locations such as in Mexico City, Mexico.*

in aerosol composition, size distribution, light scattering coefficient, absorption coefficient, optical depth, soot-specific absorption, and radiative fluxes at selected vertical and horizontal locations in the outflow downwind of Mexico City. During June 2007, EMSL staff also worked with scientists from across the country on the Cumulus Humilis Aerosol Processing Study (CHAPS). This field campaign conducted near Oklahoma City, Oklahoma, is funded by DOE's Atmospheric Science Program to study the interactions of aerosols on clouds and of clouds on aerosols.

Together these analytical and sampling approaches and sampling techniques provide information over a broad range of particle types, chemistry, size, and morphology, leading to a more comprehensive understanding of the relationship between particles composition and their climate-related effects. In field studies, information is also correlated with meteorology data to understand possible sources and transport patterns of aerosols.

Instrument Upgrades

In Fiscal Year 2007, the CPCS Facility made several upgrades and procurements:

- **FT-ICR (Fourier-transform Ion Cyclotron Resonance Mass Spec) Data Acquisition System.** An old system no longer serviced by the National High-Field Magnet Laboratory was replaced to better support structural and thermodynamic studies of molecules.

- **Zeiss Incubator and QuadView System.** This system is used for cell growth control and protein imaging.

- **Photo-Emission Electron Microscope (PEEM) Cooling and Sample Transport Mechanism.** This mechanism is being used for studying catalytic and photocatalytic processes.

- **High-Sensitivity Interface for Photon Transfer Reaction-Mass Spectrometer (PTR-MS).** This interface extends detection limits for volatile organic compounds and allows real-time measurement of trace organic gases.

- **High-Resolution Time-of-Flight Mass Spectrometer and Light Scattering Module.** This instrument is used for rapid single-particle measurements of complex organic species.

- **High-Resolution Mass Spectrometer LTQ-Orbitrap.** The Orbitrap and support instrumentation are being used for chemical characterization of organic aerosols.

- **TSI Powder/Dry and Liquid Aerosol Generation Devices.** This device is used to generate aerosols for laboratory studies.

- **Optical Portable Experimental Station.** This system is used for *in-situ* characterization of novel surfaces prepared by soft-landing of ions.

- **Large-Chip Cooled CCD Camera (Princeton Instruments).** This system is relied upon for identifying membrane protein interaction/function.

- **Residual Gas Analyzer.** This system provides detection capability for trace amounts of water or other contaminants using PEEM.

- **X-Y-Z-theta Manipulator.** This system replaced smaller manipulator on an electron stimulated desorption system, allowing use of the cryostat at lower base temps (~20K).

- **Automated Pre-Concentration System for Gas Chromatography-Mass Spectrometry.** This automated system for sample analysis is used to calibrate PTR-MS response for field measurements of volatile organic compounds.

- **Particle Counters.** One optical and one condensation particle counter were purchased for real-time concentration and size distribution measurements of particles.

Particokinetics *In Vitro*: Dosimetry Considerations for *In Vitro* Nanoparticle Toxicity

JG Teeguarden,[(a)] PM Hinderliter,[(a)] G Orr,[(a)] BD Thrall,[(a)] and JG Pounds[(a)]

(a) Pacific Northwest National Laboratory, Richland, Washington

The purpose of this work is to improve the basis for in vitro assessment of nanoparticle toxicity by advancing the understanding of particle solution dynamics in cell culture media as they relate to dosimetry and dose-response assessment. These results begin to address the urgent need for rapid hazard assessment of emerging nanoparticles through development of suitable high-throughput in vitro assays.

Developing testing strategies that can meet the burgeoning demand to characterize the hazard potential of the considerable number of nanomaterials that have been or will be produced is one of the most significant challenges faced by the regulatory, research, and producer communities. *In vitro* studies, which have become an essential component of risk assessment-directed research paradigms for chemicals, pharmaceuticals, consumer products, and fine and ultrafine particulates, are an essential element of all tiered approaches for toxicity assessment of nanomaterials that have been proposed.

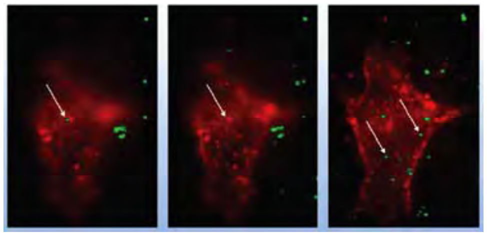

***Figure 1.** Images of an alveolar epithelial cell (C10), grown in culture and exposed to fluorescence-tagged 500-nm amorphous silica particles. The three panels show the uptake of the nanoparticles in time.*

Despite the considerable attention that *in vitro* systems have received and their growing application to nanomaterial toxicity assessment, little attention has been devoted to a critical examination of their suitability, particularly when it comes to particle solution dynamics and dosimetry. In contrast to soluble chemicals, nanoparticles can settle, diffuse, and aggregate differentially according to their size, density, and surface physicochemistry. These processes are expected to significantly affect the cellular dose. The definition of dose for nanoparticles in an *in vitro* system is, therefore, more dynamic, more complicated, and less comparable across particle types than it is for soluble chemicals. Before adequate dose-response assessments for nanomaterials can be conducted, there is a need to develop a better understanding of these processes, how particle and media characteristics affect them, and their potential impact on cellular dose *in vitro*.

The purpose of this research is to improve the basis for *in vitro* assessment of nanoparticle toxicity by advancing the understanding of particle solution dynamics in cell culture media as they relate to dosimetry and dose-response assessment. Particles in general and nanoparticles specifically, diffuse, settle, and agglomerate in cell culture media as a function of systemic and particle properties: for example, media density and viscosity, and particle size, shape, charge, and density. Cellular dose then is also a function of these factors as they determine the transport rate of nanoparticles to cells in culture.

Dose amount and time (i.e., both the time of dose and the duration of dose) are two key elements that must be considered for *in vitro* chemical dosimetry. Dose for nanoparticles *in vitro* can be defined at various levels of specificity with regard to the site and mode of action: administered dose is the most nonspecific level, while apparent exposure is a more specific level, and cellular dose is the most specific level. This concept is illustrated in Figure 1, which shows time-resolved images of an alveolar epithelial cell (C10) grown in culture and exposed to fluorescence-tagged, 500-nm amorphous silica particles. The three panels show the uptake of the nanoparticles in time. Panel 1 illustrates delivered dose, a silica particle (the green at the tip of the arrow) on the apical surface of the cell. In time, the particle is no longer visible as the focal plane moves into the interior of the cell (Panel 2). In Panel 3, the silica particle has been taken up into the cell and is observed as the focal plane moves farther into the interior of the cell.

As illustrated in Figure 1, the delivered dose also has the advantage of being directly scaleable and comparable to metrics of dose commonly used for particulates *in vivo*; for example, the delivered dose per surface area of cells in culture can be compared with the dose delivered/surface area of respiratory tract tissues. Intracellular sites of action such as the endosome, lysosome, or phagolysozome are best represented by more specific metrics of dose such as internalized mass, surface area, or number of particles or their amounts in specific intracellular compartments. These dose metrics have the advantage of accounting for size or other particle-dependent differences in cellular uptake and can also be tailored to a mode of action, although in practice, they are difficult to measure.

In this research, we develop and apply the principles of dosimetry *in vitro* and outline an approach for simulating nanoparticle particokinetics in cell culture systems. We also illustrate that where equal mass concentrations (mg/ml) imply equal doses for dissimilar materials, the corresponding particle number or surface area concentration doses differ by orders of magnitude. More importantly, when rates of diffusional and gravitational particle delivery are accounted for, trends and magnitude of the cellular dose as a function of particle size and density differ significantly from those implied by "concentration" doses. For example, 15-nm silver nanoparticles appear ~4000 times more potent than micron-sized cadmium oxide particles on a cm^2/ml media basis, but are only ~50 times more potent when differences in delivery to adherent cells are considered.


TOXICOLOGICAL SCIENCES

The Official Journal of the Society of Toxicology

Figure 2. *Cover of the February 2, 2007, issue of Toxicological Sciences.*

Often, simple surrogates of dose can cause significant misinterpretation of response and uptake data for nanoparticles *in vitro*. Incorporating particokinetics and principles of dosimetry would significantly improve the basis for nanoparticle toxicity assessment, thus increasing the predictive power and scalability of such assays. This work was featured on the cover of the February 2, 2007, issue of *Toxicological Sciences* (Figure 2).

Citation

Teeguarden JG, PM Hinderliter, G Orr, BD Thrall, and JG Pounds. 2007. "Particokinetics *In Vitro*: Dosimetry Consideration for *In Vitro* Nanoparticle Toxicity Assessments." *Toxicological Sciences* 95(2):300-312.

Imaging Water Dissociation on TiO_2(110): Evidence for Inequivalent Geminate OH Groups

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Titania (TiO_2) is widely used as a catalyst and may provide a pathway for the use of solar radiation as a viable source of clean energy. Understanding the chemical activity of this material has become the focus of a number of model catalytic studies, and these results are a major step towards that direction.

The TiO_2-H_2O system is of great interest for many areas of both fundamental and applied science, including the areas of photo-catalysis, electrochemistry, active coatings, and corrosion. For example, the discovery of photochemical water dissociation on TiO_2, with potential applications in solar cells, has stimulated extensive research on reactions of water on TiO2 surfaces. In particular, the detailed understanding of water adsorption, diffusion, and dissociation on prototypical rutile TiO_2(110) has become one of the leading topics in the area of oxide surface chemistry. The reactivity of rutile TiO_2(110) is believed to be dominated by missing oxygen ion defect sites, generally called bridge-bonded oxygen vacancies (BBO_V). There is good evidence that dissociative adsorption is limited to BBO_V sites. Understanding the chemical activity of this particular surface site has become the focus of a number of model catalytic studies.

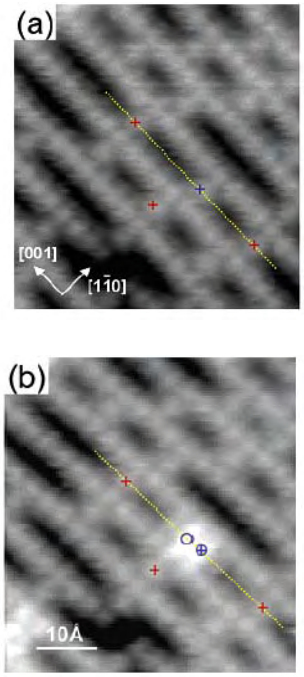


Figure 1. *Two STM images obtained from the same area of TiO_2(110) before (a) and after (b) background adsorption of H_2O at room temperature. The + signs mark the positions of several BBO_Vs. Two circles mark the positions of two OH groups formed after H_2O adsorption and dissociation on the BBO_V site.*

Scanning tunneling microscopy (STM) makes it possible to image the adsorption, dissociation, and diffusion of atoms and molecules on surfaces. We used STM to image and characterize the time evolution of hydroxyl (OH)

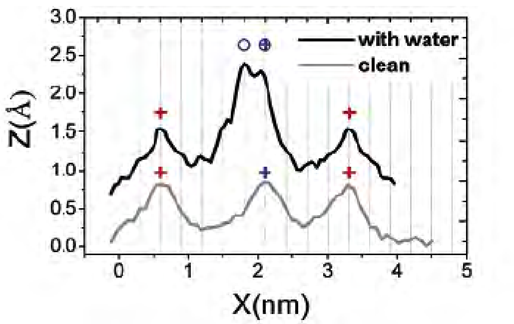
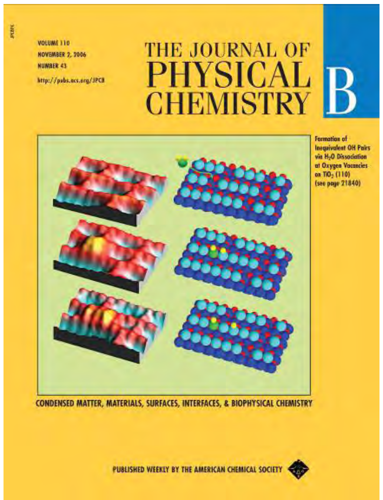


Figure 2. *Line profiles indicated in Figure 1 panels (a) and (b) before and after water adsorption along the [001] direction. Vertical lines represent the bridge-bonded oxygen atom positions.*

groups formed upon H_2O dissociation on TiO_2(110) BBO_V sites at very low coverage. Figure 1 shows STM images of the same surface area before (a) and after (b) background adsorption of H_2O at room temperature. The bright rows in Figure 1 are identified as the fivefold coordinated Ti^{4+} ions; the dark rows are the BBO ions. The bright spots along the BBO rows are assigned to BBO_Vs. Figure 2 shows line scans along dark rows in the images in Figures 1a and 1b. In Figure 2, the vertical dashed gridlines correspond to the positions of the BBO atoms. The two curves in Figure 2 are line scans of identical segments along the [001] direction before and after dosing water from the background. Two of the three vacancies on the dotted line in Figure 1(a) remain unoccupied in Figure 1(b), while the third vacancy is replaced by a broader, higher-intensity region with two local maximas. The positions of the two local maxima provide direct evidence that water molecules dissociate upon adsorption on BBO_Vs at 300 K. Our results confirm that paired hydroxyl groups are the direct product of water dissociation on oxygen vacancies.

In subsequent images, we tracked the OH groups as a function of time. This experiment provides valuable insight because the positions of the original BBO_Vs are known. For the first time, the hydrogens of these hydroxyl pairs are found spontaneously separated along the (001) direction, indicating hydrogen hopping without the assistance of water molecules. Surprisingly, we found that the hydrogens of the hydroxyl pair are not identical; the first hydrogen hop is much less likely for the hydrogen located at the original vacancy. That is, the first hop associated with the nearest-neighbor hydroxyl pair formed from H_2O dissociative adsorption strongly favors motion of the hydrogen on OH_B. This observation is rather puzzling considering the generally accepted view of equivalent OH groups formed by water dissociation. Therefore, we would expect that, upon OH pair formation, the charge should redistribute and lead to formation of a symmetric OH pair. Our experiments clearly indicate that this is not the case, and that the electronic environment of these two OH groups is likely different.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CHEMISTRY B

Formation of Inequivalent OH Pairs via H_2O Dissociation at Oxygen Vacancies on TiO_2 (110) (see page 21840)

CONDENSED MATTER, MATERIALS, SURFACES, INTERFACES, & BIOPHYSICAL CHEMISTRY

PUBLISHED WEEKLY BY THE AMERICAN CHEMICAL SOCIETY

Figure 3. *November 2, 2006, issue of The* Journal of Physical Chemistry B.

This exciting work was featured on the cover of the August 31, 2006, issue of *The Journal of Physical Chemistry B* (Figure 3) (Zhang et al. 2006).

Citation

Zhang Z, O Bondarchuk, BD Kay, JM White, and Z Dohnalek. 2006. "Imaging Water Dissociation on TiO_2(110): Evidence for Inequivalent Geminate OH Groups." *Journal of Physical Chemistry B* 110(43):21840-21845.

Study of Martensitic Phase Transformation in a NiTiCu Thin-Film Shape-Memory Alloy Using Photoelectron Emission Microscopy

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This work describes a unique imaging instrument for characterizing the spatial and temporal changes in the phases and microstructures on the surfaces of a wide variety of materials, including shape-memory alloys. Understanding how changes in microstructure affects the electronic properties of a material may enable creation of novel materials with unique electrical and optical properties.

Shape-memory alloys (SMAs) are an important class of intelligent materials, with properties that can be programmed to achieve specific mechanical responses. When mechanically or thermally cycled, SMAs exhibit reversible shape changes that are associated with a solid-state, martensitic phase transformation. The development of new SMAs is being driven by market demands, especially in micro-electromechanical systems. Recently, SMA thin films have been investigated for applications in microsensors and microactuators. Phase transformations in SMA thin films are often accompanied by significant changes in mechanical, physical, chemical, electrical, and optical properties, including yield stress, elastic modulus, damping modulus, hardness, electrical resistivity, thermal conductivity, thermal expansion, and surface roughness.

Martensitic phase transformations are diffusionless, first-order transformations that involve shear deformation. The thermal responses of bulk SMAs typically are studied using differential scanning calorimetry, which exploits the exothermic/endothermic character of the phase transformation. This technique does not provide information on the associated microstructure. On the other hand, photoelectron emission microscopy (PEEM) exploits photoelectron emission to image the surface. Photoelectron emission depends strongly on the work function of the imaged surface, which in turn depends strongly on a materials microstructure. Thus, martensitic phase transformations can significantly alter the electronic and optical properties of SMAs. For this reason, we employed *in situ* PEEM to characterize the transformation of a thin film of NiTiCu SMA in real time.

PEEM images of the SMA film at 25°C (martensite phase) and at 100°C (austenite phase) are shown in Figure 1. The most prominent difference between the images is the presence of wrinkle-like features on the surface of the low-temperature phase in Figure 1a, and the absence of these features on the surface of the high-temperature phase in Figure 1b. Sequences of PEEM images acquired while cycling the temperature indicate that the wrinkles disappear at 73.1°C during heating and reappear at 52.4°C during cooling under the conditions of this work.

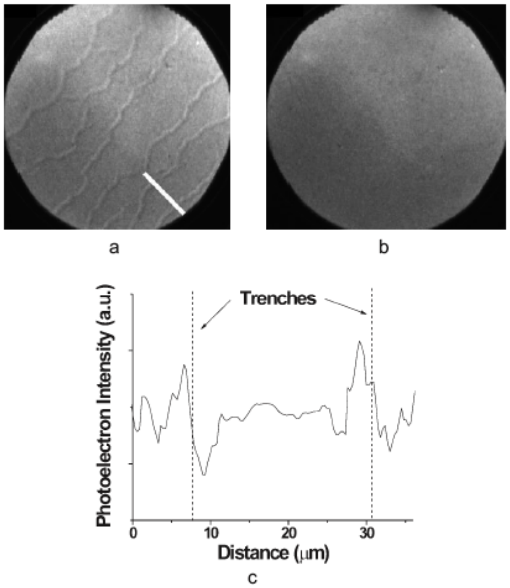

Figure 1. *In situ PEEM images of the NiTiCu thin film at 25°C (a) and 100°C (b). The PEEM intensity along the white line in (a) is shown in (c). The dotted lines in (c) mark the approximate positions of the trenches.*

The wrinkles in the PEEM image of Figure 1a show consistent variation in brightness. In general, the wrinkles are brighter along one edge and darker along the other. The wrinkles in the field of view run predominately from the lower left to the upper right, with the bright edge on the upper left. The magnitude of this variation is indicated in Figure 1c, which displays the PEEM intensity as a function of position along the white line in Figure 1a. These intensity variations are typically interpreted in terms of variations in the sample work function or topography.

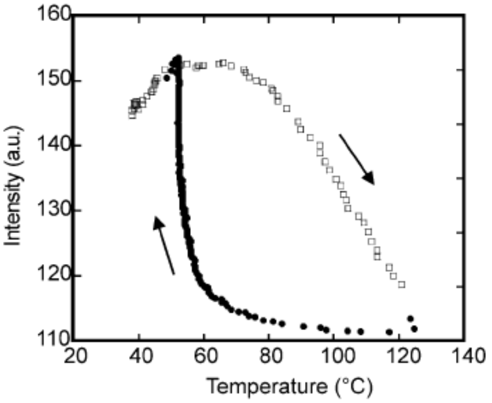

Figure 2. *Integrated photoelectron intensities versus temperature during heating and cooling of the NiTiCu thin film: solid black dots are for heating, open squares are for cooling, and open circles are for cooling.*

Significantly, the PEEM image of the high-temperature phase in Figure 1b is darker than the image of the low-temperature phase in Figure 1a. Quantitative measurements of the integrated image intensities during heating and cooling are plotted in Figure 2. The PEEM intensity is nearly constant from 45 to 70°C, and then decreases monotonically from 70 to 120°C. This decrease corresponds roughly to the temperature range of the phase transformation during heating. During cooling from 120 to 55°C, the photo-electron intensity increases slowly, and then rises rapidly to levels associated with the early stages of heating between 50 and 55°C.

The real-time PEEM images of a NiTiCu SMA film show distinct trenches near room temperature that disappear as the temperature is raised above 73°C. During heating, the image intensities decrease gradually because of a corresponding gradual increase in surface work function. When the film is subsequently cooled, these trenches reappear between 52 and 53°C; near this same temperature, the PEEM image intensi-ties increase suddenly, in concert with a sharp drop in work function. The magnitude of the effective work-function change during thermal cycling is about 0.16 eV. We attribute the sharp change in work function and PEEM intensity during cooling to the rapid transformation of surface material from austenite to martensite.

The surface sensitivity of PEEM measurements reveal correlations between changes in microstructure and electronic structure on time scales of seconds or less with sub-micrometer spatial resolution. These capabilities make PEEM an important tool for characterizing the spatial and temporal changes in phase and microstructure in a wide variety of materials, including SMAs. A paper describing this exciting work was published in the January issue of the *Journal of Advanced Functional Materials*.

Citation

Cai M, SC Langford, MJ Wu, WM Huang, G Ziong, TC Droubay, AG Joly, KM Beck, WP Hess, and JT Dickinson. 2007. "Use of Martensitic Phase Transmission in a NiTiCu Thin Film Shape Memory Alloy Using Photoelectron Emission Microscopy." *Journal of Advanced Functional Materials* 17(1):161-167.

Reactive Ballistic Deposition of Porous TiO_2 Films: Growth and Characterization

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(c) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington

Titania (TiO_2) is widely used as a catalyst and may provide a pathway for the use of solar radiation as a viable source of clean energy. This work describes a method to create nanoporous TiO_2 films with a combination of high surface area and thermal stability that could serve as supports for applications in heterogeneous catalysis.

As a material, titania (TiO_2) has attracted much attention because of its uses in a wide range of applications such as heterogeneous catalysts, gas sensors, photocatalysts, optical coatings, and pigments. Correspondingly, it is the most studied metal oxide in surface science. Recently, there has been great interest in the growth and chemical characterization of metal-oxide-supported metal particles and thin films as model systems for industrial catalytic systems. These films are of interest from the aspect of fundamental chemistry and for the study of surfaces that better emulate those employed in industrial catalytic systems.

In this study, we explored high-surface-area, porous TiO_2 thin films grown using reactive ballistic deposition (RBD) and glancing angle deposition techniques. In prior work, we showed that these techniques can produce highly porous, high-surface-area metals, metal oxides, and other materials. The techniques are based on a simple shadowing model. At glancing angles, random height differences that arise during the initial film growth can block incoming flux, essentially creating shadows that result in void regions in the shadowed region. If surface and/or bulk diffusion are slow compared to the incident flux (i.e., if the molecules "hit and stick"), then the voids remain unfilled. Continued deposition results in porous films with filamentous columnar morphologies. Varying degrees of film porosity can be achieved by varying the deposition angle and substrate temperature.

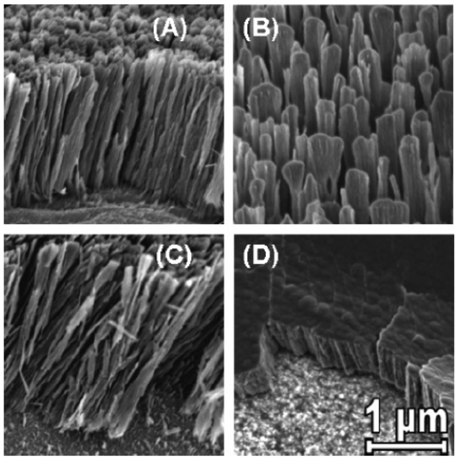

Figure 1. *SEM images of TiO_2 films deposited via RBD. (A) Top and (B) side views of a film grown at 300 K and at a deposition angle of 85°. (C) Side view of a film grown at 100 K and 85°, (similar in appearance to the film grown at 300 K). (D) Side view of a film grown at 300 K and at 70°.*

Figure 1 shows scanning electron microscopy (SEM) images for a 750 ML thick TiO_2 film deposited 85° from substrate normal and at a sample temperature of 300 K. The images confirm that the film consists of an array of separated filaments that grow toward the physical vapor deposition source. Figure 1C shows a film deposited at 85° and 100 K; the image of this film appears to be very similar to the film grown at 300 K. The images indicate that an increase in temperature from 100 to 300 K does not increase the mobility of ad-atoms enough to affect the morphology of the film. Figure 1D is a SEM image of a film deposited at 70° and 300 K. Decreasing the deposition angle from 85° to 70° has a dramatic effect on film structure as seen in Figure 1D. On this length scale, a film deposited at 70° appears dense, but films deposited at this angle actually prove to have the greatest surface area as was confirmed using nitrogen adsorption.

Transmission electron microscopy (TEM) of filaments scraped from the tantalum plate and placed on amorphous carbon grids was performed. The filaments grown at both 100 and 300 K reveal nanoscale features within the filaments when viewed under high magnification (Figure 2A). Selected area diffraction (SAD) analysis of individual filaments indicates that the filaments are predominantly amorphous; however, in some cases randomly oriented groups of filaments display the well-defined diffraction patterns seen in insets (B) and (C) of Figure 2. D-spacing values extracted from these SAD patterns are indicative of the rutile phase.

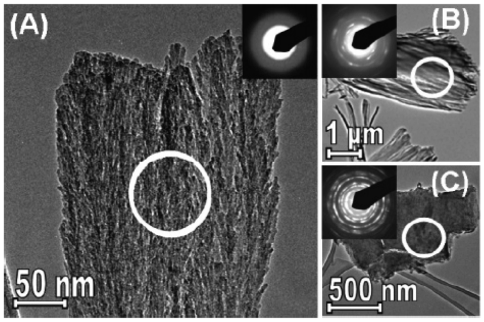

Figure 2. *TEM images of TiO_2 films accompanied by insets with SAD. (A) A single amorphous filament from a film deposited at 85° and 300 K. (B) A cluster of filaments from the same film as (A) displaying a SAC pattern corresponding to polycrystalline rutile TiO_2. (C) A portion of a film grown at 70° and 300 K with a high degree of crystallinity.*

This work confirms that nanoporous, high-surface area films of TiO_2 can be synthesized by reactive ballistic deposition of titanium metal in under oxygen ambient conditions. The SEM and TEM results show that the films consist of arrays of separated filaments. The surface area and the distribution of binding site energies of the films were measured as functions of growth temperature, deposition angle, and annealing conditions using temperature programmed desorption of nitrogen. We found that TiO_2 films deposited at 70° and 50 K exhibited the greatest specific surface area (i.e., 100 m^2/g). In addition, the films retain greater than 70 percent of their original surface area after annealing to 600 K. The combination of high surface area and thermal stability suggests that these films could serve as supports for applications in heterogeneous catalysis. This exciting work was recently published in the *Journal of Physical Chemistry C.*

Citation

Flaherty, DW, Z Dohnálek, A Dohnálkova, BW Arey,DE McCready, N Ponnusamy, CB Mullins, and BD Kay. 2007. “Reactive Ballistic Deposition of Porous TiO_2 Films: Growth and Characterization.” *Journal of Physical Chemistry C* 111(12):4765-4773. Available at http://pubs.acs.org/cgi-bin/article.cgi/jpccck/2007/111/i12/html/jp067641m.html

Doping Golden Buckyballs: $Cu@Au_{16}^-$ and $Cu@Au_{17}^-$ Cluster Anions

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Clusters are groups of a small number of atoms that often have chemical and physical properties that are different than the corresponding bulk materials. Understanding the underlying physical and structural reasons for these unique properties may allow for improved materials for electronics, sensors, and catalysis.

The discovery of the unique catalytic effects of gold nanoparticles on oxide substrates has stimulated a flurry of research into the structures and properties of free gold nanoclusters, which may hold the key to elucidating the catalytic mechanisms of supported gold clusters. One of the most remarkable results has been the discovery of planar gold cluster anions (Au_n^-) of up to 12 gold atoms and the two- to three-dimensional transition for clusters with n larger than 12. Among larger gold clusters, Au_{20} has been found to be a perfect

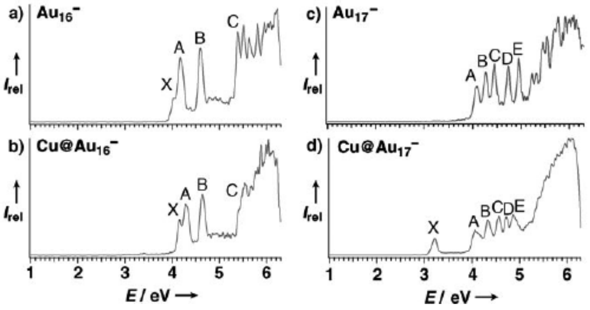

Figure 1. *Photoelectron spectra of the cluster anions $CuAu_{16}^-$ and $CuAu_{17}^-$ (Figures 1b and 1d), compared to the parent gold clusters Au_{16}^- and Au_{17}^- (Figures 1a and 1c).*

tetrahedron. A more recent study of the structures of Au_n^- cluster anions in the medium size range (n=15-19) has shown that clusters with n=16-18 possess unprecedented empty cage structures. In particular, the Au_{16}^- cluster anion has an interesting tetrahedral structure with an inner diameter of about 5.5 Å and can be compared to the fullerenes (buckyballs). The cage structures of the cluster anions Au_{16}^- and Au_{17}^- have recently been confirmed by electron diffraction, and thus, they are the first experimentally confirmed and the smallest possible gold cages. The large empty space inside these cage clusters immediately suggested that they can be doped with a foreign atom to produce a new class of endohedral gold cages that are analogous to endohedral fullerenes.

A gold cage containing a central atom first was predicted for a series of icosahedral clustersM@Au_{12} (M=W, Ta^-, Re^+) based on the 18-electron rule and subsequently was confirmed experimentally. However, because Au_{12} itself does not possess a cage structure, the dopant atom with the appropriate electron count must play an essential role in maintaining the integrity of the cage. Bimetallic gold clusters have been studied experimentally as they offer new opportunities to fine tune the electronic and structural properties of gold nano-clusters. Following the discovery of the hollow gold cages, two recent theoretical studies that focused on doping the cages with a foreign atom have appeared. Because the parent Au_{16}^- and Au_{17}^- cluster anions are empty cages, many different types of atoms could be used as dopants to form new endohedral gold clusters. In this highlight, we report the first use of photoelectron spectroscopy (PES) analysis and density functional theory (DFT) calculations to observe and characterize Au_{16}^- and Au_{17}^- doped with a Cu atom ($Cu@Au_{16}^-$ and $Cu@Au_{17}^-$).

Figure 1 shows the spectra of $CuAu_{16}^-$ and $CuAu_{17}^-$ ions along with the of the parent gold clusters. First, we focus on the $CuAu_{16}^-$ ion (Figure 1b), whose PE spectrum is remarkably similar to that of its parent gold cluster Au_{16}^- (Figure 1a). The similarity between the spectra of these two species suggests that Cu doping does not alter the geometric and electronic structures of the Au_{16}^- cluster anion significantly, which is only possible if the Cu is trapped inside the Au_{16}^- cage.

The spectrum of the doped cluster anion $CuAu_{17}^-$ is also very similar to that of the parent gold cluster Au_{17}^-, except that there is one low-binding-energy peak followed by a large energy gap in the spectrum of the Cu-doped cluster (Figures1 c and d). This spectral similarity again suggests that the Cu dopant induces very little structural change in the Au_{17}^- cage except that it donates one electron. Au_{17}^- is a closed-shell species with 18 valence electrons; therefore, the extra electron is expected to enter its lowest occupied molecular orbital and give rise to the low-binding-energy peak (X) in the PE spectrum of the $CuAu_{17}^-$

cluster anion (Figure 1d). All these observations again imply that Cu stays in the center of the Au_{17}^- ion cage ($Cu^+@Au_{17}^{2-}$) and does not perturb the electronic and geometric structures of the cage significantly.

We carried out theoretical studies to confirm these observations. The results revealed that the endohedral $Cu@Au_{16}^-$ and $Cu@ Au_{17}^-$ cluster anions are overwhelmingly favored over any other structure with the Cu atom on the outside of the cage. Figure 2 shows the simulated PE spectra for two endohedral structures each for the $Cu@Au_{16}^-$ and $Cu@Au_{17}^-$ cluster anions along with those of the parent clusters. In one structure, the Cu atom is located in the center of the cages, and in the other structure, it is displaced slightly from the center. The energy differences between the two isomers are very small, and their simulated PE spectra are also very similar to each other. The calculated vertical detachment energies for the $Cu@Au_{16}^-$ and $Cu@Au_{17}^-$ cluster anions also are in good agreement with the experimental values. Overall, the excellent agreement between theory and experiment unequivocally confirms the endohedral structures of these Cu-doped gold cages.

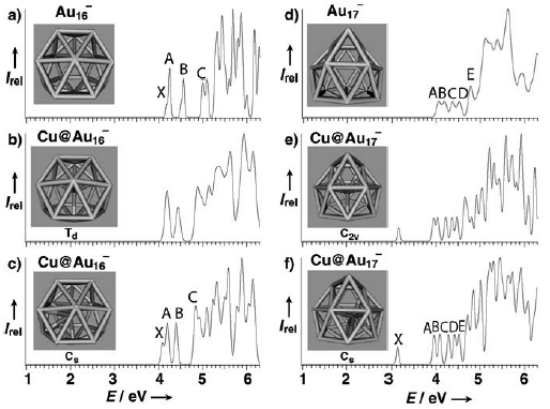

Figure 2. *Simulated photoelectron spectra for two endohedral structures, each for* $Cu@Au_{16}^-$ *and* $Cu@Au_{17}^-$ *along with those for* Au_{16}^- *and* Au_{17}^-*.*

Doping gold clusters could be a powerful way to tune their chemical and physical properties, and the results reported in this highlight suggest that a new class of endohedral gold cages is indeed viable. In these examples, the cage structures of Au_{16}^- and Au_{17}^- cluster anions are maintained simply by changing the dopants, which is reminiscent of the behavior of endohedral fullerenes. It would be particularly interesting to dope transition-metal atoms inside these gold cages to create magnetic gold clusters as the resulting material may exhibit new, physical, chemical, and catalytic properties that are distinct from the pure gold clusters. This exciting work was published online in the April 13, 2007, edition of the journal *Angewandte Chemie* (Wang et al. 2007).

Citation

Wang LM, S Bulusu, HJ Zhai, XC Zeng, and LS Wang. 2007. "Doping Golden Buckyballs: $Cu@Au_{16}^-$ and $Cu@Au_{17}^-$ Cluster Anions." *Angewandte Chemie* 46(16):2915-2918.

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.

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 fragmentation 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.

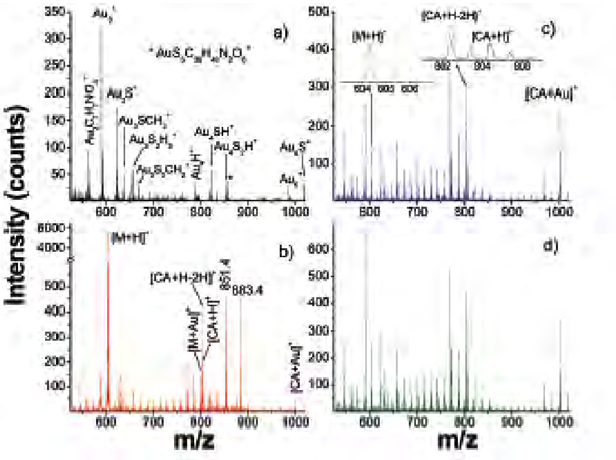

Figure 1. *TOF-SIMS spectra of unmodified NHS-SAM (a); NHS-SAM with 1 ng soft-landed c(-RGDfK-) before (b) and after (c) rinsing; and NHSSAM following 2 h solution-phase reaction (d).*

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}.

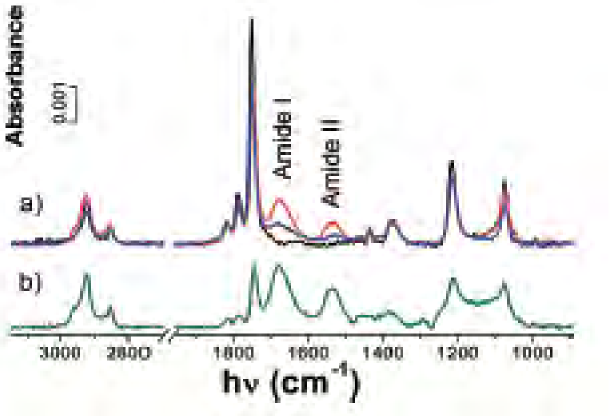

Figure 2. *IRRAS spectra of unmodified NHS-SAM (a, black); NHS-SAM with 18 ng soft-landed c(-RGDfK-) before (a, red) and after (a, blue) rinsing; and NHS-SAM following 2 h solution-phase reaction (b, green).*

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.

User Projects

Low-Coordinated Oxygen Sites on MgO Surfaces

O Diwald, E Knozinger, Vienna University of Technology, Wien, Austria

High-Resolution Gas-phase UV- and IR-Absorption Cross-Sections of Naphthalene to Calibrate the First DOAS Detection of Naphthalene in Mexico City

MJ Molina, Massachusetts Institute of Technology, La Jolla, California

RM Volkamer, University of California, San Diego, La Jolla, California

Study of Martensitic Transformations in Shape Memory Alloys by Real-time Measurement of Surface Work Function Change

M Cai, JT Dickinson, Washington State University, PUllman, Washington

AG Joly, WP Hess, Pacific Northwest National Laboratory, Richland, Washington

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

G Xiong, unknown, Washington

Properties of Ice and Liquid Interfaces (Kay's BES-Surface Kinetics, PNNL Scope #16248)

JP Cowin, HM Ali, Pacific Northwest National Laboratory, Richland, Washington

Y Lilach, Hebrew University of Jerusalem, Jerusalem, Israel

M Iedema, Environmental Molecular Sciences Laboratory, Richland, Washington

Mechanisms of Fragmentation of Post Translationally Modified Peptides

H Lioe, RA O'Hair, University of Melbourne, Melbourne, Victoria, Australia

J Laskin, Pacific Northwest National Laboratory, Richland, Washington

Probing the Electronic Structure of Metal Clusters

L Cui, L Wang, X Li, L Wang, H Zhai, J Yang, W Huang, Washington State University, Richland, Washington

Energetics of Dissociation of Peptide Radical Cations

J Laskin, JH Futrell, Z Yang, Pacific Northwest National Laboratory, Richland, Washington

IK Chu, N Lam, The University of Hong Kong, Pokfulam, Hong Kong

Photoelectron Emission Microscopy (PEEM) Study of Cu Nanoparticles on TiO_2(110)

WP Hess, Pacific Northwest National Laboratory, Richland, Washington

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

JM White, W Wei, University of Texas at Austin, Austin, Texas

Atomically Resolved Studies of Adsorbates on TiO_2(110)(Kay's BES/Chemical Physics-Catalysis WBS0502 of Peden's BES-Chemical Transformations at Complex Interfaces, PNNL Scope #47319)

Z Dohnalek, Z Zhang, Pacific Northwest National Laboratory, Richland, Washington

O Bondarchuk, JM White, S Li, Y Kim, University of Texas at Austin, Austin, Texas

Infrared and CARS Spectroscopy of Cyclopropane

JW Nibler, Oregon State University, Corvallis, Oregon

J Kelly, Pacific Northwest National Laboratory, Richland, Washington

A Masiello, National Institute of Standards and Technology, Gaithersburg, Maryland

Determination of DNAPL Mass Flux Reduction as a Function of Source Zone Mass Removal

EL Difilippo, ML Brusseau, University of Arizona, Tucson, Arizona

Aerosol and Organic Precursor Measurements at Ground-Based Sites during the Megacity Aerosol Experiment in Mexico City 2006 (MAX-Mex 2006)

JS Gaffney, University of Arkansas, Little Rock, Little Rock, Arkansas

NA Marley, Argonne National Laboratory, Argonne, Illinois

MJ Molina, LT Molina, Massachusetts Institute of Technology, Cambridge, Massachusetts

V Shutthanandan, Environmental Molecular Sciences Laboratory, Richland, Washington

RJ Hopkins, Lawrence Berkeley National Laboratory, Berkeley, California

PW Lunn, RC Petty, DOE BER Climate Change Research ASP, Washington DC,

R Gonzalez, Molina Center for Strategic Studies in Energy and the Environment, La Jolla, California

Aerosol Composition and Hydrocarbon Measurements from the DOE G-1 Aircraft during the Megacity Aerosol Experiment in Mexico City (Max-Mex)(Alexander's ASP, PNNL Scope #47789)

LN Kleinman, Brookhaven National Laboratory, Upton, New York

JV Ortega, Environmental Molecular Sciences Laboratory, Richland, Washington

Chemical Ionization Mass Spectrometry of Organic Aerosols (Alexander's STTR, PNNL Scope #48597)

PN Irving, Innovatek, Inc., Richland, Washington

VB Mikheev, Battelle Columbus, Columbus, Ohio

High Resolution Infrared Spectroscopy of Trans-Hexatriene

RL Sams, Pacific Northwest National Laboratory, Richland, Washington

A Masiello, National Institute of Standards and Technology, Gaithersburg, Maryland

NC Craig, Oberlin College, Oberlin, Ohio

High and Moderate Resolution Infrared Spectroscopy of Diiodomethane

TJ Johnson, Pacific Northwest National Laboratory, Richland, Washington

A Masiello, National Institute of Standards and Technology, Gaithersburg, Maryland

Dynamic Changes in Molecular Interactions Along the Circadian Rhythm (Orr-LDRD Membrane Biology GC, PNNL Scope #90001)

G Orr, DJ Panther, KJ Cassens, Pacific Northwest National Laboratory, Richland, Washington

HB Pakrasi, Washington University in St. Louis, St. Louis, Missouri

T Ogawa, Shanghai Institute of Plant Physiology and Ecology, Shanghai, China

AFM Imaging of Photo System Protein in Photosynthetic Membranes (Lu's LDRD-EMSL GC Biomembranes, PNNL Scope #90001)

D Pan, D Hu, Pacific Northwest National Laboratory, Richland, Washington

HP Lu, Bowling Green State University, Bowling Green, Ohio

Reactive and Non-Reactive Deposition of Hyperthermal (1-100 eV) Peptide Ions Surfaces (J Laskin's joint BES/LDRD, PNNL Scope #49904)

J Laskin, O Hadjar, P Wang, Pacific Northwest National Laboratory, Richland, Washington

PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

Mechanisms of Organic Ions Release from Water Droplets

GB Ellison, LA Cuadra-Rodriguez, University of Colorado, Boulder, Colorado

High Resolution Infrared Spectroscopy of Cis-Cis and Trans-Trans Difluorobutadiene

NC Craig, Oberlin College, Oberlin, Ohio

High Resolution Infrared Spectroscopy of the 360 cm-1 Band of Acetonitrile

L Brown, Jet Propulsion Laboratory, Pasadena, California

Comparative Analysis of Growth and Morphology among Citric Acid Producing and Non-Producing Strains of *Aspergillus niger*

KS Bruno, Z Dai, LL Lasure, Pacific Northwest National Laboratory, Richland, Washington

Morphology and Composition of Encoded Segmented Metal Oxide Nanowires

A Kolmakov, Southern Illinois University, Carbondale, Illinois

Y Lilach, Hebrew University of Jerusalem, Jerusalem, Israel

A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

Environmental Effects of Aircraft Engine Exhaust Particles (A. Laskin's DOD-ILA, PNNL Scope #49510)

Y Dessiaterik, Pacific Northwest National Laboratory, Richland, Washington

A Laskin, ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

CW Spicer, MW Holdren, Battelle Columbus, Columbus, Ohio

Oxidation of Atmospheric Organic Particulate Matter

AK Bertram, DA Knopf, University of British Columbia, Vancouver, British Columbia, Canada

A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

Visualization of Gamma H2AX Foci

MB Sowa, DL Springer, JS Peters, Pacific Northwest National Laboratory, Richland, Washington

WF Morgan, University of Maryland, Baltimore, Maryland

Chemical Characterization of Arrays of TiO_2 Nanocolumns

Z Dohnalek, Pacific Northwest National Laboratory, Richland, Washington

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

C Mullins, DW Flaherty, University of Texas at Austin, Austin, Texas

Measurement of Ambient Concentrations of Aerosols to Support the Analysis of MIRAGE Urban Plume Transport and Chemistry

BK Lamb, Washington State University, Pullman, Washington

Chemistry and Microphysics of the Small Particles (Zelenyuk's BES-Particles, PNNL Scope #47327)

BJ Finlayson-Pitts, Y Yu, M Ezell, University of California, Irvine, Ivine, California

A Zelenyuk, J Yang, Pacific Northwest National Laboratory, Richland, Washington

JV Ortega, ML Alexander, MK Newburn, Environmental Molecular Sciences Laboratory, Richland, Washington

K Mueller, State University of New York at Stony Brook, Stony Brook, New York

Y Han, Y Cai, unknown, Richland, Washington

Nanoscale Insight into the Living Cell Membrane Responses to Ultrafine PM (Orr LDRD-EBI, PNNL Scope #49989)

C Rodriguez, Washington State University, Richland, Washington

G Orr, BJ Tarasevich, JG Teeguarden, JG Pounds, JL Phillips, DJ Panther, Pacific Northwest National Laboratory, Richland, Washington

FRET Screening of Protein-Protein Interactions in *Shewanella* (Orr GTL-Imaging, PNNL/ORNL Scope #43930)

G Orr, MF Romine, DJ Panther, B Hooker, Pacific Northwest National Laboratory, Richland, Washington

HS Wiley, Environmental Molecular Sciences Laboratory, Richland, Washington

Regulation of Cell Surface Ligand Dynamics (Orr LDRD-BSI, PNNL Scope #90001)

G Orr, DJ Panther, L Opresko, Pacific Northwest National Laboratory, Richland, Washington

HS Wiley, Environmental Molecular Sciences Laboratory, Richland, Washington

SPLAT: Real-Time Characterization of Individual Exhaust Particles (Zelenyuk's EE proposal: PNNL scope #48932)

A Zelenyuk, Pacific Northwest National Laboratory, Richland, Washington

Y Cai, unknown, Richland, Washington

Aerosol Aging and Climate Change (Cowin's NOAA, PNNL Scope #47840)

JP Cowin, Y Liu, Pacific Northwest National Laboratory, Richland, Washington

M Iedema, A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

X Yang, Fudan University, Shanghai, China

Optical and Hygroscopic Properties of Atmospheric Aerosols (A Laskin's ASP, PNNL Scope #47767)

S Nizkorodov, ML Walser, University of California, Irvine, Irvine, California

ER Gibson, University of Iowa, Iowa City, Iowa

Y Liu, Y Dessiaterik, Pacific Northwest National Laboratory, Richland, Washington

A Laskin, PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

L Alvarez-Aviles, University of Alaska Fairbanks, Fairbanks, Alaska

Use of SEM/EDX Analysis to Study the Oxidation of Aerosol by Hydroxyl Radical

BJ Finlayson-Pitts, LM Wingen, AC Moskun, University of California, Irvine, Irvine, California

DJ Gaspar, Y Dessiaterik, JP Cowin, Pacific Northwest National Laboratory, Richland, Washington

A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

Transition Metal Oxide Clusters - Electronic Structure and Chemical Bonding Using Photoelectron Spectroscopy (Wang's BES/Chemical Physics-Catalysis WBS0505 of Peden's BES-Chemical Transformations at Complex Interfaces, PNNL Scope #47319)

H Zhai, L Wang, L Wang, X Wang, Washington State University, Richland, Washington

Spectral Library (Sharpe's NNSA, PNNL Scope #28727)

SW Sharpe, T Blake, TJ Johnson, RL Sams, DC Scott, RG Tonkyn, Pacific Northwest National Laboratory, Richland, Washington

Infrared Reflectance Spectroscopy of Soils (Blake's NNSA, PNNL Scope #43865)

T Blake, Pacific Northwest National Laboratory, Richland, Washington

PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

Infrared Spectroscopy of Methyl Halides (Blake's LDRD, PNNL Scope #49961)

T Blake, TJ Johnson, Pacific Northwest National Laboratory, Richland, Washington

Personal Samplers for Traffic-Related Particle Exposures in NYC

SR Chillrud, Columbia University, palisades, New York

JP Cowin, Pacific Northwest National Laboratory, Richland, Washington

M Iedema, TA Seim, Environmental Molecular Sciences Laboratory, Richland, Washington

Electronic Properties of the Metal and Thin Film Oxide Insulator Junction

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

PTR-ITMS: Next Generation Aircraft Instrumentation (Alexander's ASP, PNNL Scope #47789)

SP Garland, University of California, Davis, Redding, California

CM Berkowitz, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, MK Newburn, Environmental Molecular Sciences Laboratory, Richland, Washington

Innovative Aerosol Collector (Alexander's SBIR, PNNL Scope #48595)

ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

D Worsnop, JT Jayne, Aerodyne Research Inc, Billerica, Massachusetts

Infrared Absorption Cross Sections of Acetone and Acetic Acid

A Weber, National Institute of Standards and Technology, Gaithersburg, Maryland

Fundamental Investigations of Water Splitting on Model TiO_2 (Kimmel's BES WBS04 of Henderson's BES-Hydrogen, PNNL Scope #48526)

GA Kimmel, NG Petrik, Z Dohnalek, Pacific Northwest National Laboratory, Richland, Washington

CD Lane, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

The Non-Covalent Interaction of Some Aromatic Molecules with H2O Studied with Photoelectron Energy Spectroscopy and Quantum Chemical Calculation (Summer Research Institute, PNNL Scope #16248)

L Wang, Washington State University, Richland, Washington

G Wang, M Zhou, Fudan University, Shanghai, China

Development and Testing of a New Ion Trap Assembly (Summer Research Institute, PNNL Scope #16248)

JA Lloyd, MV Johnston, University of Delaware, Newark, Delaware

ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

TA Smith, Genesee Community College, Arlington, Virginia

Laboratory Studies of Gas-Particle Reaction Kinetics of Particulates Emitted from Aircraft (Summer Research Institute, PNNL Scope #16248)

JP Cain, H Wang, University of Southern California, Los Angeles, California

A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

Exploratory Synthesis of Novel Cluster-Based Nanomaterials

L Wang, Z Sun, Washington State University, Richland, Washington

TL Hubler, Pacific Northwest National Laboratory, Richland, Washington

MF Bertino, University of Missouri, Rolla, Rolla, Missouri

Infrared Spectra of HCN at Low Temperatures

MA Smith, NASA Langley Research Center, Hampton, Virginia

Infrared Spectral Library of Bacterial Spores (Sharpe's NNSA, PNNL Scope #28727)

TJ Johnson, NB Valentine, Pacific Northwest National Laboratory, Richland, Washington

Soft-Landing of Complex Ions on Surfaces

JR Green, RG Cooks, W Peng, MP Goodwin, Purdue University, West Lafayette, Indiana

J Laskin, O Hadjar, P Wang, JH Futrell, Z Yang, Pacific Northwest National Laboratory, Richland, Washington

Z Zhu, PL Gassman, AS Lea, Environmental Molecular Sciences Laboratory, Richland, Washington

Chemistry of Aerosols in Mexico City: MILAGRO 2006 Study

Y Dessiaterik, Pacific Northwest National Laboratory, Richland, Washington

KS Johnson, LT Molina, Massachusetts Institute of Technology, Cambridge, Massachusetts

V Shutthanandan, Cn Wang, Z Zhu, A Laskin, TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

MK Gilles, RJ Hopkins, A Tivanski, Lawrence Berkeley National Laboratory, Berkeley, California

Chemical and Physical Properties of Biomass Burning Aerosol

Y Dessiaterik, J Laskin, Pacific Northwest National Laboratory, Richland, Washington

JL Hand, JL Collett, SM Kreidenweis, Colorado State University, Fort Collins, Colorado

A Laskin, CN Wang, Environmental Molecular Sciences Laboratory, Richland, Washington

Energy and Entropy Effects in Dissociation of Non-Covalent Complexes: A Combined Experimental and Theoretical Investigation

J Laskin, Z Yang, Pacific Northwest National Laboratory, Richland, Washington

Open Ocean Ship-Board Study of Atmospheric Aerosols at the Equatorial Pacific: Characterizing Iron in Marine Aerosol

Y Dessiaterik, Pacific Northwest National Laboratory, Richland, Washington

V Shutthanandan, CN Wang, Z Zhu, A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

AM Johansen, LS Shank, Central Washington University, Ellensburg, Washington

JW Murray, University of Washington, Seattle, Washington

The Formation and Structure of Tropical Organic/Water Aerosols

GB Ellison, LA Cuadra-Rodriguez, University of Colorado, Boulder, Colorado

A Zelenyuk, J Laskin, Y Dessiaterik, J Yang, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

Development of Novel Microchip CE-MS Platform for Organic Aerosol Characterization

X Yu, Y Lin, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, L Saraf, Environmental Molecular Sciences Laboratory, Richland, Washington

Integrated Experimental and Modeling Studies on Secondary Organic Aerosol Formation

R Zaveri, SM Kathmann, A Zelenyuk, DA Maughan, JC Birnbaum, J Yang, C Song, Pacific Northwest National Laboratory, Richland, Washington

SN Madronich, National Center for Atmospheric Research, Boulder, Colorado

A Laskin, ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

JA Thornton, University of Washington, Seattle, Washington

Characterization of Organic Aerosols throughout the Depth of an Urban Planetary Boundary Layer: Proposed Field Deployment of EMSL Mass Spectrometers

JP Stutz, University of California, Los Angeles, Los Angeles, California

CM Berkowitz, R Zaveri, Pacific Northwest National Laboratory, Richland, Washington

R Zhang, Texas A&M University, College Station, Texas

ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

D Worsnop, JT Jayne, Aerodyne Research Inc, Billerica, Massachusetts

Secondary Organic Aerosol Formation

R Zaveri, X Yu, CM Berkowitz, C Song, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, MK Newburn, JV Ortega, Environmental Molecular Sciences Laboratory, Richland, Washington

High Resolution Infrared and Coherent Raman Studies of Propellane

RW Kirkpatrick, JW Nibler, Oregon State University, Corvallis, Oregon

A Masiello, A Weber, National Institute of Standards and Technology, Gaithersburg, Maryland

Infrared Spectra of the Fundamental Bands of $^{34}SO_2$

RL Sams, T Blake, Pacific Northwest National Laboratory, Richland, Washington

WJ Lafferty, National Institute of Standards and Technology, Gaithersburg, Maryland

JH Flaud, University of Paris-7, Creteil CEDEX, France

High Resolution Spectra of Phosphine in the 1370-800 Wavenumber Region

RL Sams, Pacific Northwest National Laboratory, Richland, Washington

A Masiello, National Institute of Standards and Technology, Gaithersburg, Maryland

L Brown, Jet Propulsion Laboratory, Pasadena, California

Excitation of Surface Excitons in the Nanoscale Calcium Oxide Surface

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

O Diwald, Vienna University of Technology, Wien, Austria

Combinatorial *Operando* Catalyst Research

D Hu, ZC Zhang, G Xia, C Windisch, Pacific Northwest National Laboratory, Richland, Washington

Surface Plasmon Polariton Dependence on Metal Surface Morphology

RE Peale, University of Central Florida, Orlando, Florida

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

Study of Martensitic Transformations in Shape Memory Alloys by Real-time Measurement of Surface Work Function Change

M Cai, JT Dickinson, Washington State University, Pullman, Washington

WP Hess, AG Joly, Pacific Northwest National Laboratory, Richland, Washington

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

G Xiong, unknown, Washington

Large-Scale Synthesis of Monodisperse and Ultra-Small Metal Clusters

L Wang, Z Sun, J Yang, X Wang, NS Parmar, Washington State University, Pullman, Washington

H Woo, Scripps Research Institute, La Jolla, California

TL Hubler, Pacific Northwest National Laboratory, Richland, Washington

A Gupta, Battelle Columbus, Columbus, Ohio

MF Bertino, University of Missouri, Rolla, Rolla, Missouri

Probing and Manipulating Protein Conformation Changes by Time-Resolved Single-Molecule Spectroscopy and Site-Specific Ultramicroscopy (Hu's DARPA, PNNL Scope #52021)

D Hu, Pacific Northwest National Laboratory, Richland, Washington

HP Lu, Bowling Green State University, Bowling Green, Ohio

Characterization of the Local Order of Organic Thin Film Material by Combined Atomic Force Microscopy and Optical Microscopy

D Hu, AB Padmaperuma, H Qiao, PE Burrows, Pacific Northwest National Laboratory, Richland, Washington

PF Barbara, University of Texas at Austin, Austin, Texas

Laser Desorption from Metal Oxides (Kay's BES-Surface Kinetics, PNNL Scope #16248)

AL Shluger, PV Sushko, London, University College, London, United Kingdom

AG Joly, WP Hess, Pacific Northwest National Laboratory, Richland, Washington

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

Non-Thermal Reactions in Thin Aqueous Films (Kay's BES-Surface Kinetics, PNNL Scope #16248)

GA Kimmel, NG Petrik, Pacific Northwest National Laboratory, Richland, Washington

MC Akin, University of Texas at Austin, Austin, Texas

Chemical Kinetics and Dynamics at Interfaces: Structure and Reactivity of Ices, Amorphous Solids, and Supercooled Liquid Solutions (Kay's BES-Surface Kinetics, PNNL Scope #16248)

RS Smith, BD Kay, Z Dohnalek, T Zubkov, Pacific Northwest National Laboratory, Richland, Washington

Inelastic Electron Scattering Cross Section Measurements in Liquid Water

NG Petrik, GA Kimmel, RG Tonkyn, Pacific Northwest National Laboratory, Richland, Washington

CM Brown, Wadsworth Center, Albany, New York

Automated Image Analysis of Low Frequency Radiation Induced Genomic Instability in Human Colon Carcinoma Cells

MB Sowa, Pacific Northwest National Laboratory, Richland, Washington

GR Holtom, Harvard University, Cambridge, Massachusetts

WF Morgan, University of Maryland, Baltimore, Maryland

BL Lamarche, DF Hopkins, Environmental Molecular Sciences Laboratory, Richland, Washington

Structure and Catalytic Activity of Supported Early Transition Metal Oxide Clusters (Kay's BES/Chemical Physics-Catalysis WBS0502 of Peden's BES-Chemical Transformations at Complex Interfaces, PNNL Scope #47319)

Z Dohnalek, BD Kay, RS Smith, Z Wang, Z Zhang, Pacific Northwest National Laboratory, Richland, Washington

JM White, Y Kim, S Li, J Gong, University of Texas at Austin, Austin, Texas

Roles for Membrane Receptors in Cellular Responses to External Cues; The Case of ErbB4 and Morphology Dynamics

CN Lai, Scripps Research Institute, La Jolla, California

G Orr, DJ Panther, JL Phillips, Pacific Northwest National Laboratory, Richland, Washington

SN Vicini, Georgetown University, Washington DC, Wash DC

Nanoparticle Fluorescence

K Yu, National Research Council of Canada, Ottawa, Ontario, Canada

W Chen, University of Texas at Arlington, Arlington, Texas

Real Time Study of Phase Transformation of In_2Se_3 Thin Films by PEEM

F Ohuchi, MA Olmstead, C Lu, E Yitamben, University of Washington, Seattle, Washington

Carbon Nanotube Tips for High Aspect Ratio Scanning Tunneling Microscopy

Z Dohnalek, Pacific Northwest National Laboratory, Richland, Washington

KJ Stevenson, University of Texas at Austin, Austin, Texas

Investigation of Hydrogen Tunneling in Tropolone

RL Redington, Texas Tech University, Lubbock, Texas

Site-Specific Surface Excitation of Calcium Oxide "Nanocubes"

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

O Diwald, Vienna University of Technology, Wien, Austria

Photochemical Processing of Organic Aerosol Particles Studied with High-Resolution Mass Spectrometry

S Nizkorodov, AP Bateman, ML Walser, University of California, Irvine, Irvine, California

Y Dessiaterik, J Laskin, Pacific Northwest National Laboratory, Richland, Washington

A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

Time-Resolved Study of Phase Transformation of In_2Se_3 Thin Films by PEEM

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

F Ohuchi, MA Olmstead, C Lu, E Yitamben, University of Washington, Seattle, Washington

Surface Plasmon Polariton Dependence on Metal Surface Nano-Structure

RE Peale, JW Cleary, University of Central Florida, Orlando, Florida

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

Jet Spectrum of Nitromethane

DS Perry, University of Akron, Akron, Ohio

Activation and Dissociation of Large Molecules in Mass Spectrometry

J Laskin, Z Yang, Pacific Northwest National Laboratory, Richland, Washington

JS Smith, University of Washington, Seattle, Washington

Energetics, Dynamics and Mechanisms of Dissociation of Peptide Radical Cations

J Laskin, Z Yang, Pacific Northwest National Laboratory, Richland, Washington

IK Chu, N Lam, The University of Hong Kong, Pokfulam, Hong Kong

C Siu, York University, Toronto, Ontario, Canada

Secondary Organic Aerosol Formation from Nitrate Photochemistry

BJ Finlayson-Pitts, University of California, Irvine, Irvine, California

A Zelenyuk, J Yang, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

High Resolution Infrared Spectroscopy of Boron Trifluoride

AG Maki, Private (Maki), Mill Creek, Washington

Chemical Kinetics and Dynamics at Interfaces: Structure and Reactivity of Ices, Amorphous Solids, and Supercooled Liquid Solutions

J Matthiesen, RS Smith, BD Kay, Z Dohnalek, T Zubkov, Pacific Northwest National Laboratory, Richland, Washington

Instrument Testing and Deployment for the DOE CHAPS Field Campaign

CM Berkowitz, Pacific Northwest National Laboratory, Richland, Washington

ML Alexander, Environmental Molecular Sciences Laboratory, Richland, Washington

JA Ogren, National Oceanic and Atmospheric Administration (NOAA), Boulder, Colorado

Fluorescence Imaging of Tobacco Cells

D Hu, Z Dai, Pacific Northwest National Laboratory, Richland, Washington

Structure and Catalytic Activity of Supported Early Transition Metal Oxide Clusters

Z Dohnalek, BD Kay, Z Zhang, Pacific Northwest National Laboratory, Richland, Washington

JM White, S Li, Y Kim, J Gong, University of Texas at Austin, Austin, Texas

Laser Desorption from Metal Oxides

AL Shluger, London, University College, London, United Kingdom

WP Hess, AG Joly, Pacific Northwest National Laboratory, Richland, Washington

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

Interfacial Excited State Dynamics on TiO_2

WP Hess, Pacific Northwest National Laboratory, Richland, Washington

K Tanimura, Osaka University, Osaka, Japan

KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

Non-Thermal Reactions in Thin Aqueous Films

GA Kimmel, NG Petrik, Pacific Northwest National Laboratory, Richland, Washington

MC Akin, University of Texas at Austin, Austin, Texas

Non-Thermal Reactions in Water Adsorbed on Anion-Doped $TiO_2(110)$

GA Kimmel, NG Petrik, Pacific Northwest National Laboratory, Richland, Washington

Inelastic Electron Scattering Cross Section Measurements in Liquid Water

NG Petrik, RG Tonkyn, GA Kimmel, Pacific Northwest National Laboratory, Richland, Washington

CM Brown, Wadsworth Center, Albany, New York

Understanding and Development of Novel NanoMaterials for Frequency Upconversion

AG Joly, Pacific Northwest National Laboratory, Richland, Washington

K Yu, National Research Council of Canada, Ottawa, Ontario, Canada

W Chen, University of Texas at Arlington, Arlington, Texas

Understanding the Mechanisms and Enhancement of Photostimulated Luminescence by Nanoscale Design and Fabrication

AG Joly, Pacific Northwest National Laboratory, Richland, Washington

W Chen, University of Texas at Arlington, Arlington, Texas

Experimental Studies of Fundamental Molecule-Particle Interactions and Reactions on Iron Metal and Oxide Surfaces

RS Smith, BD Kay, Z Dohnalek, GS Parkinson, Pacific Northwest National Laboratory, Richland, Washington

The Binding Energetics of Methane on Water Ice Surfaces

RS Smith, BD Kay, Pacific Northwest National Laboratory, Richland, Washington

CD Neish, University of Arizona, Tucson, Arizona

The Interaction of HCl on Water Ice Nanoscale Films

RS Smith, BD Kay, Pacific Northwest National Laboratory, Richland, Washington

P Ayotte, Universite de Sherbrooke/Concordia University (University of Sherbrooke), Sherbrooke, Quebec, Canada

Semi-Experimental Equilibrium Structures for Molecules of Biological Significance

NC Craig, Oberlin College, Oberlin, Ohio

Roles for Membrane Receptors in Cellular Responses to External Cues; The Case of ErbB4 and Morphology Dynamics

CN Lai, Scripps Research Institute, La Jolla, California

G Orr, KJ Cassens, Pacific Northwest National Laboratory, Richland, Washington

SN Vicini, Georgetown University, Washington DC

Fundamental Studies on Biomolecule Ions Desorbed from Open-Air Surfaces

J Laskin, Z Yang, O Hadjar, Pacific Northwest National Laboratory, Richland, Washington

FM Fernandez, L Nyadong, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

From Gas Phase Clusters to Nanomaterials

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Nanoscale Characterization of Nanomaterial - Cell Interactions

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Probing the Electronic Structures of Atomic Clusters and Solution Phase Species in the Gas Phase

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Synthesis of Nanostructured Materials and Cluster-Assembled Materials

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Cluster Model Studies of Condensed Phase Phenomena

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Oxide Clusters - Electronic Structure and Chemical Bonding Using Photoelectron Spectroscopy

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Ultrafast Laser Interactions with Wide Bandgap Materials

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WP Hess, AG Joly, Pacific Northwest National Laboratory, Richland, Washington

Active Standoff Detection of Low-Volatility Chemicals on Soils Using Infrared Reflection-Absorption Spectroscopy (NNSA, PNNL Scope #25399)

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FRET-Based Molecular Dynamics Simulation of Membrane-Receptor Activation

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Combinatorial Operando Catalyst Research

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Real-Time Imaging of Lignocellulosic Biomass Degradation by Fluorescence Microscopy and Atomic Force Microscopy

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Characterization of the Local Order of Organic Thin Film Material by Combined Atomic Force Microscopy and Optical Microscopy

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Heterogeneous Photochemistry of Organic-Coated Mineral Dust Aerosol

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J Laskin, Pacific Northwest National Laboratory, Richland, Washington

A Laskin, Environmental Molecular Sciences Laboratory, Richland, Washington

Kinetic Study of Heterogeneous Reaction of Soot with Reactive Oxidants

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CN Wang, A Laskin, PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

Hydronium Hydroxide at Platinum Interfaces

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Ice Nucleation on Aged Field Aerosols

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Automated Image Analysis of Low Frequency Radiation Induced Genomic Instability in Human Colon Carcinoma Cells

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Heterogeneous Uptake of HNO_3 on $CaCO_3$: Determination of the Gas-Particle Reaction Probability as Function of Relative Humidity

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Characterization of Bio-inspired Photonic Crystals for Enhancing Solar Energy Conversion by Single-Molecule Spectroscopy

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Impact of Reactive Halogen Species on the Air Quality in Southern California Coastal Areas

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Analysis of Organic Oligomers Forming Secondary Aerosol from Wood Combustion-Derived Phenols

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High Resolution Fourier Transform Infrared Spectroscopy Studies of Multidimensional H Transfer in Tropolone/Tropolonoid Molecules-a Bridge to the Behavior in Biological Systems

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Atomically Resolved Studies of Catalytic and Photocatalytic Processes on TiO_2(110)

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JM White, S Li, University of Texas at Austin, Austin, Texas

The Relationship between Particle Properties and Ice Nucleation: Laboratory and Field Investigation and Parameterization Development

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The Role of Ice and Aerosol Surfaces in Halogen Activation in the Arctic Springtime Boundary Layer

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Chemistry and Microphysics of Small Particles

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Hygroscopic Properties of Aerosol Organics

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The Effect of Surface Active Organic Molecules on the Water Uptake, Shape and Density of Hygroscopic Particles of Atmospheric Importance

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The Characterization of Diesel Exhaust Particle Matter and its Atmospheric Lifecycle: The Size, Shape and Composition of Soot Particles in the Atmosphere

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The Cloud Nucleating Properties of Aerosols at a Continental Site: CHAPS Study

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ClusterSculptor: An Expert Driven Visual Analytics Tool for the Classification of Single Particle Mass Spectra

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Measurement and Optimization of the Redox Properties of Enzymes Using Single-Molecule Imaging, Controlled Electrochemical Potential, and Nanoscale Confinement

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Integrated Experimental and Modeling Studies on Aerosol Evolution and Aging

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Ionic Transport of Hydrogen in Structured Soft Materials

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Temperature Dependent High-Resolution UV- and IR-Absorption-Cross-Section Spectra of Low-Volatility SOA Precursor Hydrocarbons in the Gas-Phase

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Laboratory Spectroscopy of CO_2 for Earth Observations

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Measurement of Ambient Concentrations of Aerosols to Support the Analysis of MIRAGE Urban Plume Transport and Chemistry

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Innovative Aerosol Collector (Alexander's SBIR, PNNL Scope #48595)

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Pulsed Multiple Laser Deposition Facility for the Growth of Thin Films in Interfacial Combinatorial Material Exploration

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F Ohuchi, E Venkatasubramanian, University of Washington, Seattle, Washington

High Resolution Infrared Spectroscopy of Metyl Nitrite

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Pd Nanoclusters Supported on MgO(100): Effects of Cluster Size on Chemisorption Properties

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Infrared (IR) Versus Terahertz (THz) Absorption Strengths for Chemical Species Associated with Homeland Security

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Evaluation of Newly Developed Multiuse Affinity Probes for Subdiffraction Imaging

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Single Molecule Studies of Multi-Chromophoric Foldamers

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Development of an Electrospray Photoelectron Spectroscopy Apparatus with a Low Temperature Ion Trap (Kay's BES-Surface Kinetics, PNNL Scope #16248)

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Investigation of Aromatic and Other Novel Gas Phase Atomic Clusters and Molecules

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Computational Chemistry Modeling of Main-Group and Transition-Metal Cluster Systems

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Development of Data Analysis and Visualization Software - SpectraMiner

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Laser-Materials Interactions: Theory and Experiment (Kay's BES-Surface Kinetics, PNNL Scope #16248)

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Single Particle Analysis of Smoke Aerosols during the Summer 2002 Yosemite Aerosol Characterization Study

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Surface Induced Dissociation of Polyatomic Ions (J Laskin's BES, PNNL Scope #40457)

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Single Molecule Approach for Understanding EGFR Molecular Interactions (Orr LDRD-FRET, PNNL Scope #48287)

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Electron Stimulated Reactions in Thin Water Films (Kay's BES-Surface Kinetics, PNNL Scope #16248)

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Condensed Phase Chemical Physics of Low Temperature Amorphous Solids and Gas Surface Interactions (Kay's BES-Surface Kinetics, PNNL Scope #16248)

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Single Molecule Electron Transfer Dynamics (Lu's BES-Single-Molecule/Ultrafast Spec, PNNL Scope #16248)

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Microbial Cell Analysis and Imaging
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Ion Channel Protein Dynamics in Lipid Bilayer

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HP Lu, Bowling Green State University, Bowling Green, Ohio

Chemical Characterization of Heterogeneous Inclusions in Soot Particles

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Temperature-Dependent Yield of Frenkel Pairs Generated by Valence Excitation in NaCl

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EMSL CAT in Analytical Mass Spectrometry

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Early Transition Metal Oxides as Catalysts (Kay's BES/Chemical Physics-Catalysis WBS0502 of Peden's BES-Chemical Transformations at Complex Interfaces, PNNL Scope #47319)

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High Resolution Infrared Spectroscopy of BF2OH

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JH Flaud, University of Paris-7, Creteil CEDEX, France

High Resolution Infrared Spectroscopy of Peroxynitric Acid

J Kelly, Pacific Northwest National Laboratory, Richland, Washington

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Metal Sulfide Clusters in the Environment

MV Johnston, JM Spraggins, University of Delaware, Newark, Delaware

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Photoelectron Spectroscopic Studies of Complex Anion Solvation in the Gas Phase (Kay's BES-Surface Kinetics, PNNL Scope #16248)

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Environmental Spectroscopy and Biogeochemistry Facility

The Environmental Spectroscopy and Biogeochemistry (ES&B) Facility supports experimental and modeling studies of chemical phenomena and mechanisms on mineral and microbe surfaces and on complex heterogeneous environmental materials from soils, sediments, and groundwater zones. ES&B Facility staff members, along with other Pacific Northwest National Laboratory staff, form a multidisciplinary research team with expertise in chemistry, mineral physics, geochemistry, soil chemistry, microbiology, and hydrology and advanced computational methods.

Capabilities

Capabilities are available for materials characterization, aqueous- and solid-phase speciation and reaction/kinetic measurements, analytical environmental chemistry, molecular and thermodynamic geochemical process modeling, and intermediate-scale, reactive-transport studies. Research includes studies on:

- surface chemistry of Fe, Mn, and Al oxides; carbonates; and layer silicates
- redox reactions of organic and metal contaminants with Fe- and Mn-containing mineral solids
- biogeochemistry of Fe(III) and Mn(IV) oxide reduction by bacteria and associated bio-mineralization processes
- mineral surface structure and dynamics by modeling and microscopy
- sorbate surface structure and dynamics on mineral surfaces by spectroscopy
- reactivity and thermodynamics of contaminants at high ionic strengths
- intermediate scale subsurface flow and transport
- molecular, thermodynamic and kinetic modeling.

The ES&B Facility consists of seven laboratories that are proximally located to facilitate multi-technique studies. For example, environmental chambers are available with spectroscopic access to allow

Instrumentation & Capabilities

- Cryogenic laser fluorescence microscopy
- Laser spectroscopy and kinetic systems
- Mössbauer spectroscopy
- Atomic Force/Scanning Tunneling microscopies
- Dynamic force scanning probe microscopy
- Computational geochemical molecular modeling software and hardware
- Subsurface flow and transport experimental laboratory
- Hydro- and biogeochemical modeling and software
- Thermodynamics measurements of aqueous and adsorption reactions
- Micro and special applications X-ray powder diffraction
- Single crystal diffraction
- Controlled atmosphere chambers
- Analytical chemistry instrumentation

controlled-atmosphere experiments. These laboratories are located near other instruments that are integral to environmental molecular science, including high-resolution scanning and transmission electron microscopies and a variety of ultrahigh vacuum microprobe techniques for surface analyses. The seven ES&B Facility laboratories are described below.


Figure 1. *The ES&B Facility offers users an array of instruments, including fluorescence microscopies.*

Optical Spectroscopy Laboratory. Laser-based-fluorescence, breakdown, nonlinear, and Raman spectroscopies and microscopies (Figure 1) are available to use in investigations of aqueous and interfacial reactions. Kinetic studies ranging from stopped-flow to ultra-fast optical pump-probe methods can be performed. Cryogenic capabilities and time-resolved detection methods from pico-second to millisecond for enhanced spectroscopic studies of solution and heterogeneous materials are available. State-of-science Fourier transform infrared (FTIR) spectrometers enable the study of various mineral-chemistry topics as well as sorbate binding mechanisms at mineral, biotic, and organic interfaces. The modular design of the spectrometers in this laboratory enables rapid changing of detector and beam-splitter combinations so researchers can readily change from the visible to the near-, mid-, or far-infrared wavelength ranges. A vacuum bench equipped with a helium-cooled bolometer and step-scanning capabilities is optimized for far-infrared measurements as well as time-resolved spectroscopy. A nitrogen-purged system equipped with a microscope and temperature-controlled mapping stage (-200 to 600°C) allows spatially resolved infrared measurements at the 60-μm level. A variety of cells are available for analyzing gas, liquid, solid, and slurry samples using a variety of techniques. Raman vibrational analyses can be obtained using the FT-Raman module and Raman confocal microscope.

Mössbauer Spectroscopy Laboratory. Five Mössbauer spectrometers with cryogenic capabilities allow studies of Fe structure and redox chemistry in oxides, clays, sediments and biogeochemical systems. A new applied magnetic field Mossbauer spectrometer is available for magnetic properties of Fe minerals. Software incorporating Voigt-line fitting and quadrupole-splitting distributions enable state-of-science spectral deconvolution and fitting.

Imaging Microscopy Laboratory. Optical and scanning-probe microscopies are available for particle imaging from millimeter to nanometer scales. An inverted optical microscope is available for time-resolved fluorescence imaging in a broad temperature range. Expertise is also available in the characterization of processes of microbial reduction and biogenic mineral formation by high-resolution transmission electron microscopy, involving lattice imaging, selected area diffraction, and energy dispersive spectrometer analysis. A state-of-science scanning-probe microscopy facility has been developed for imaging water-wet samples and microbe-water and mineral-microbe interfaces, and for characterizing a wide variety of environmental materials. A bio-atomic force microscope (AFM) scanning probe is available for protein imaging and force measurements. This new instrument will help researchers meet the special requirements of life sciences microscopy (e.g., studies of delicate biological samples under physiological conditions) and provide detailed observations of molecular structures with unprecedented resolution and without the need for rigorous sample preparation and labeling. The system can be used for studying cellular membrane structures, drug-receptor and virus-cell binding, as well as single-molecule recognition of molecular complexes (e.g., antibody-antigen, ligand-receptor, DNA-protein, DNA-DNA, and protein-protein interactions).

Environmental Analytical Chemistry Laboratory. A wide variety of instrumentation is available for quantification of inorganic and organic contaminants and their reaction, transformation, or degradation products. State-of-science separation instruments, including gas and high-performance liquid chromatographs coupled with mass spectrometry, are available to users engaged in diverse research activities. An inductively coupled plasma mass spectrometer with laser ablation for solids analysis and a collision cell for improved detection of oxide-interfering elements (e.g., Fe) is available for broad-spectrum, high-sensitivity inorganic analyses.

Computational Geochemistry. Multiple workstations linked to the computational infrastructure of the EMSL are available for molecular-level simulations and modeling to support research in the ES&B Facility. Experts are available to perform first-principles molecular dynamics calculations of molecular liquids and solid state systems as well as electronic structure calculations either as stand-alone activity or in support of experimental or spectroscopic measurements. Thermodynamic and kinetic geochemical codes also are available to users, as are multidimensional geochemical reaction/transport codes for numerical experiments or simulations of the intermediate-scale flow and transport experiments described below.

Subsurface Flow and Transport Experimental Laboratory (SFTEL). This laboratory (Figure 2) is uniquely equipped for intermediate-scale (i.e., meter-scale) experimentation in single-fluid and multifluid (air-water, air-nonaqueous-phase liquid [NAPL]-water, NAPL-water) porous media systems. These distinctive experimental systems allow testing of basic theories of flow and transport; studies of coupled processes involved with microbial, reactive chemical, or colloid transport; and experimental

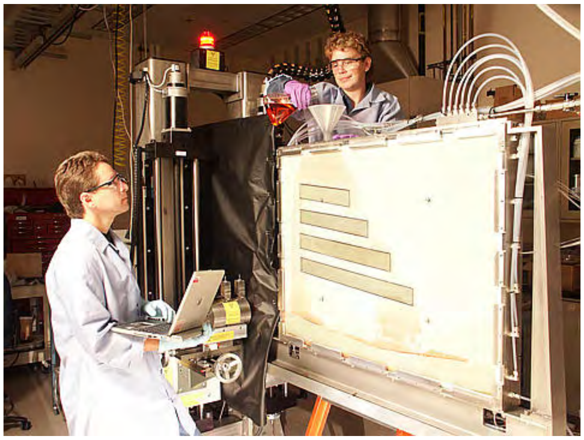

Figure 2. *EMSL's Subsurface Flow and Transport Laboratory.*

simulation of subsurface remediation scenarios. Close linkages exist between this center and the modeling facility, as both pre- and post-experiment modeling efforts are key to experimental design and interpretation. The main focus of the SFTEL is on intermediate-scale experimentation. The laboratory offers several meter-scale flow cells and columns for research in saturated and unsaturated porous media. Some of the flow cells and columns can be used in conjunction with a dual-energy gamma radiation system. The SFTEL also offers a fully automated saturation-pressure apparatus, as well as an automated system to measure fundamental hydraulic properties of soil.

Instrument Upgrades

In Fiscal Year 2007, the ES&B Facility made the following upgrades.

- A **micro-x-ray diffraction capability** was installed, with an x-ray beam that can be focused to a 10-micron spot size and capability for investigating 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 that 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, allows rapid data acquisition on even minute samples. Both copper and chromium x-ray wavelengths are available (see Figure 3).

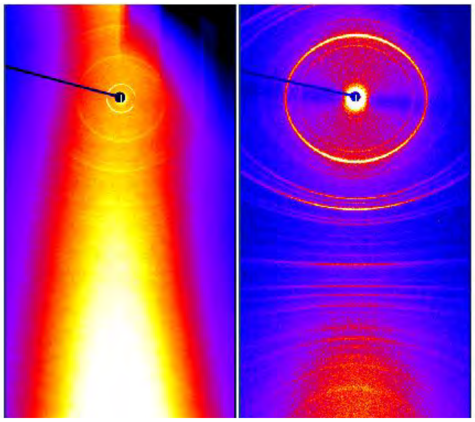

Figure 3. *Comparison of the micro-diffaction curved image plate exposures from a sample containing Fe minerals using Cu (left) and Cr x-ray excitation.*

- **Gas purification systems** used on the four anaerobic environmental glove boxes in the ES&B Facility were replaced by enhanced two-column gas purification systems. The new dual-column system will allow the low oxygen/moisture atmosphere to be maintained while regenerating the purification system by switching between the two catalyst columns. This eliminated the need to take the chamber out of use and the attendant exposure of samples to high-oxygen conditions for at least 24 hours while the catalyst is regenerated. The new systems are controlled by a user-friendly touch screen.

- **The X-band electron paramagnetic resonance spectrometer** was returned to service after upgrading the microwave source and the source control. EMSL user S Miller used the upgraded system to analyze borosilicate glass samples for radiation-generated free radicals and reported excellent results.

Kinetics of Microbial Reduction of Solid Phase U(VI)

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Using state-of-the-art experimental techniques and geochemical modeling, the dissolution, diffusion, and microbial reduction processes of U(VI) in soils and sediments were studied. The results predicted slow U(VI) reduction in contaminated Hanford Site sediments because of high concentrations of dissolved calcium.

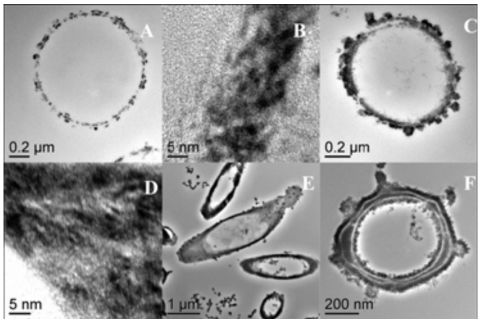

Figure 1. *TEM images showing UO_2 accumulation on cell surfaces and in periplasms. Samples for images A (a sectioned cell) and B (part of a cell periplasm) were collected at 2 days, samples for images C (a sectioned cell) and D (part of a cell periplasm) were collected at 7 days, and samples for images E and F were collected at 100 days after cell spike.*

Microbial reduction of U(VI) by dissimilatory metal-reducing bacteria and subsequent precipitation of U(IV) has been proposed as a technology that could be used to immobilize U(VI) in uranium contaminated sediments. However, microscopic and spectroscopic analysis of uranium-contaminated sediments from the U.S. Department of Energy's Hanford Site has revealed that uranium often exists as U(VI) precipitates associated with small fractures and pores within sediment particle grains that exhibit pore sizes of a few micrometers or less. This multifacility study of microbial reduction of U(VI) solids used cryogenetic time-resolved fluorescence and geochemical modeling capabilities available in the EMSL Environmental Spectroscopy and Biogeochemistry (ESB) Facility as well as transmission electron microscope (TEM) instrumentation available in the Interfacial and Nanoscale Science Facility. The insights derived from the microscopic and spectroscopic analyses were used to establish a coupled model of dissolution, intragrain diffusion, and microbial reduction processes that lead to the ultimate formation of UO_2 precipi-tates on cell surfaces and periplasms (see Figure 1). The developed model was then applied to describe the experimental kinetic data of microbial reduction of solid phase U(VI). Of relevance to the Hanford Site, this study predicts that microbial reduction of U(VI) in contaminated sediments would proceed at two orders of magnitude slower than expected because of the high concentration of dissolved calcium in the environment (Liu et al. 2006).

Citation

C Liu, Byong-Hunjeon, JM Zachara, Z Wang, A Dohnalkova, and JK Fredrickson. 2006. "Kinetics of Microbial Reduction of Solid Phase U(VI)." *Environmental Science & Technology* 40:6290-6296.

Correlation between Fundamental Binding Forces and Clinical Prognosis of *Staphylococcus aureus* Infections of Medical Implants

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In this study, we used atomic force microscopy to show that pathogenic strains of Staphylococcus aureus are able to attach to substrates simulating an implant device much more efficiently than nonpathogenic control strains of S. aureus. These results suggest that pathogenic strains express specific surface-exposed proteins that allow the bacteria to bind to the surface of an implant. They also suggest that one way to prevent S. aureus-related device infections is to prohibit the initial binding reaction itself.

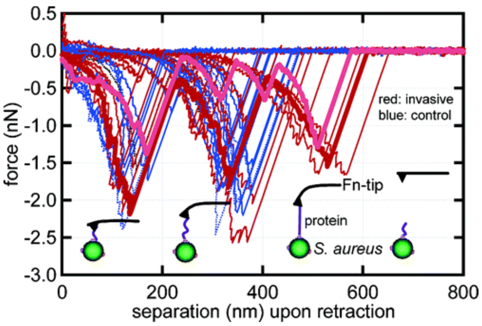

Figure 1. *Retraction force profiles (i.e., force spectra) collected as an Fn-coated probe was pulled from contact with the cell wall of S. aureus. Shown are randomly selected curves from the eight control isolates (blue) and seven invasive isolates (red). The lighter red curve was collected on a mutant strain of S. aureus that overproduces FnBP on its cell wall. The phenotype of this mutant strain is described in Greene et al. (1995).*

In the United States, surgical implants (e.g., prosthetic heart valves or pacemakers) significantly improve the quality of life for many people but, paradoxically, place these same patients at risk for life-threatening infections. These infections are frequently caused by pathogenic strains of S. aureus that adhere to the surface of the implant allowing the bacteria to form a biofilm that is difficult to combat with host defenses or antibiotics. SK Lower of Ohio State University and co-workers from Duke University Medical Center and EMSL had a manuscript accepted by the American Chemical Society journal *Langmuir* in January 2007. This article describes the work that Lower conducted in collaboration with BH Lower (EMSL) as part of their EMSL Science Theme Project, Substrate-Specific Binding of Staphylococcus Adhesins to Solid Surfaces. This project is managed by NJ Hess

(EMSL) and also includes collaborations with Dr. VG Fowler's group from Duke University Medical Center. The title of their article is "Correlation between Fundamental Binding Forces and Clinical Prognosis of *Staphylococcus aureus* Infections of Medical Implants" and their results suggest that S. aureus' "force taxonomy" may provide a fundamental and practical indicator of the pathogen-related risk that infections pose to patients with implanted medical devices (Figure 1). The note can viewed early in published form at http://pubs3.acs.org/acs/journals/doilookup?in_doi=10.1021/la063117v.

Citation

Greene C, D McDevitt, P Francois, PE Vaudaux, DP Lew, and TJ Foster. 1995. "Adhesion Properties of Mutants of *Staphylococcus aureus* Defective in Fibronectin-binding Proteins and Studies on the Expression of fnb Genes." *Molecular Microbiology* 17(6):1143-1152.

Yongsunthon R, VG Fowler, Jr., BH Lower, FP Vellano III, E Alexander, LB Reller, GR Corey, and SK Lower . 2007. "Correlation between Fundamental Binding Forces and Clinical Prognosis of *Staphylococcus aureus* Infections of Medical Implants." *Langmuir* ASAP Web Release Date: 03-Feb-2007; (Letter) DOI: 10.1021/la063117v.

Relative Raman Intensities in C_6H_6, C_6D_6, and C_6F_6: A Comparison of Different Computational Methods

SD Williams,(a) TJ Johnson,(b) TP Gibbons,(a) CL Kitchens(a)

(a) Appalachian State University, Boone, North Carolina

(b) Pacific Northwest National Laboratory, Richland, Washington

As supercomputers allow molecular modeling to better model and predict what is observed by experimental scientists, it is important to "reality check" whether the models are in fact true to the data. In this study, various theoretical models were vetted against careful analytical work to determine which programs could best (and how well) model experimental data for a method useful not only to basic science, but also to real-world applications such as environmental monitoring/restoration.

In this project we compared the accuracy of various computational methods (Hartree-Fock, MP2, CCSD, CAS-SCF, and several types of density functional theory) for predicting relative intensities in Raman spectra for C_6H_6, C_6D_6, and C_6F_6. The predicted relative intensities for ν1 and ν2 were compared with relative intensities measured by a Fourier Transform-Raman spectrometer. While none of these methods excelled at this prediction, the Hartree-Fock method using a large basis set was most successful for predictions of C_6H_6 and C_6D_6, while the PW91PW91 method was the most successful for C_6F_6. The degree of success can be seen in Figures 1 and 2, where the experimental points are displayed as circles and the solid lines are the fit to the data. A paper based on this work was published in the February issue of *Theoretical Chemistry Accounts*.

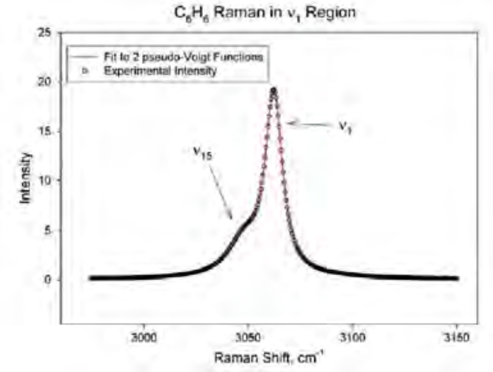

Figure 1. *Experimental Raman intensities (corrected for spectrometer response) for liquid benzene in the CH stretch region, 2 cm^{-1} resolution. The solid line is a fit to two pseudo-Voigt lineshapes. R2 for the fit was 0.9998, and the area for υ1 was 279 ± 1.*

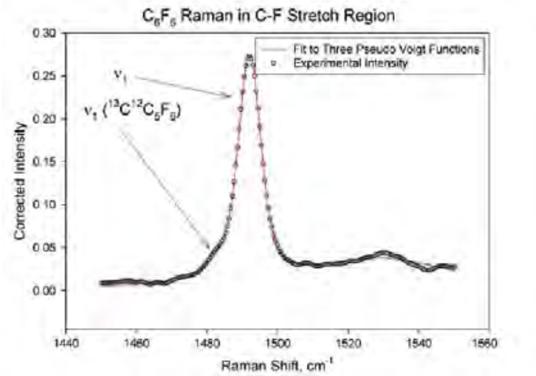

Figure 2. *Experimental Raman intensities (corrected for spectrometer response) for liquid C6F6 in the CF stretch region, 2 cm^{-1} resolution. The solid line is a fit to three pseudo-Voigt lineshapes. R2 for the fit was 0.998, and the area for υ1 was 2.7 ± 0.5.*

Citation

Williams SD, TJ Johnson, TP Gibbons, and CLKitchens. 2007. "Relative Raman Intensities in C_6H_6, C_6D_6, and C_6F_6: A Comparison of Different Computational Methods." *Theoretical Chemistry Accounts* 117(2):283-290.

Specific Bonds between Iron Oxide Surface and Outer Membrane Cytochromes MtrC and OmcA from *Shewanella oneidensis* MR-1

***BH Lower,*[a] *L Shi,*[a] *R Yongsunthon,*[b] *TC Droubay,*[a] *DE McCready,*[c] *and SK Lower*[b]**

(a) Pacific Northwest National Laboratory, Richland, Washington
(b) Ohio State University, Columbus, Ohio
(c) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington

In this study, we used atomic force microscopy to show that membrane cytochromes MtrC and OmcA purified from Shewanella oneidensis MR-1are able to form a stable bond with the surface of the iron oxide hematite (Fe_2O_3).

Dissimilatory iron-reducing microorganisms (DIRMs) have evolved the ability to reduce iron oxide minerals, thereby coupling Fe(III) reduction to the oxidation of energy-rich carbon compounds. The mechanism of dissimilatory iron reduction is not known because of the complexity of the biogeochemical reactions that occur at the mineral-microbe interface.

Because most iron oxides exist as solids in the environment (e.g., hematite), particular challenges exist for DIRMs with regard to transferring electrons from inside the cell where they are generated, across the cellular membrane, and then to the exterior of the cell where the Fe(III) in iron oxides serves as the terminal electron acceptor. *S. oneidensis* MR-1 is a DIRM that is purported to use the outer membrane cytochromes MtrC and OmcA to catalyze the transfer of electrons directly to Fe(III) in iron-bearing minerals during anaerobic respiration. A prerequisite for this type of reaction is the formation of a stable bond between the cytochrome and the iron oxide surface.

In our study, the force spectra obtained between pure cytochromes and Fe_2O_3 exhibited a strong correlation with those obtained between living *S. oneidensis* MR-1 cells and Fe_2O_3. This finding is shown in Figure 1, which compares force spectra obtained between MtrC-hematite (blue), OmcA-hematite (red), and *S. oneidensis* MR-1-hematite (green). These results suggest that *S. oneidensis* MR-1 expresses MtrC and OmcA on the cell surface where the cytochromes make direct contact with an iron oxide surface and play a prominent role in the terminal electron transfer reaction that occurs between *S. oneidensis* MR-1 and a Fe(III)-bearing mineral during anaerobic respiration. Figure 2 is a schematic showing the proposed mechanism of dissimilatory Fe(III) reduction in *S. oneidensis* MR-1.

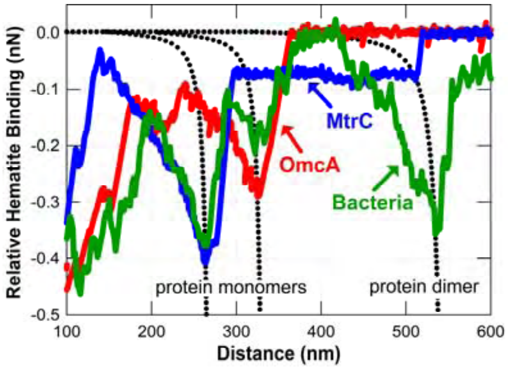

Figure 1. *Comparison of force spectra obtained between MtrC-hematite (blue), OmcA-hematite (red), and S. oneidensis MR-1-hematite (green).*

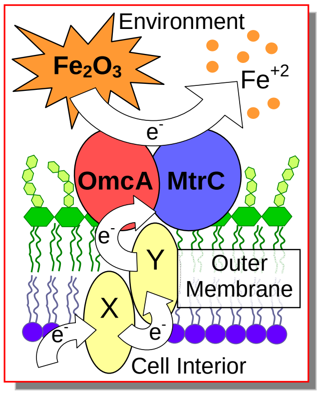

Figure 2. *Schematic showing the proposed mechanism of dissimilatory Fe(III) reduction in S. oneidensis MR-1.*

Citation

Lower BH, L Shi, R Yongsunthon, TC Droubay, DE McCready, and SK Lower. 2007. "Specific Bonds between an Iron Oxide Surface and Outer Membrane Cytochromes MtrC and OmcA from *Shewanella oneidensis* MR-1." *Journal of Bacteriology 189*: In press.

Bio-Stimulation of Iron Reduction and Subsequent Oxidation of Sediment Containing Fe-Silicates and Fe-Oxides: Effects of Redox Cycling on Fe(III) Bio-Reduction

J Komlos,[(a)] *RK Kukkadapu,*[(b)]*, JM Zachara,*[(c)] *and PR Jaffé*[(a)]

(a) Princeton University, Princeton, New Jersey
(b) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington
(c) Pacific Northwest National Laboratory, Richland, Washington

Effective bio-remediation depends on the durability of bio-reduced sediments to trap contaminants. This study determined that iron silicates in sediments can be repeatedly bio-reduced and re-oxdized, thus forming a cyclical means of sequestering contaminants in the environment.

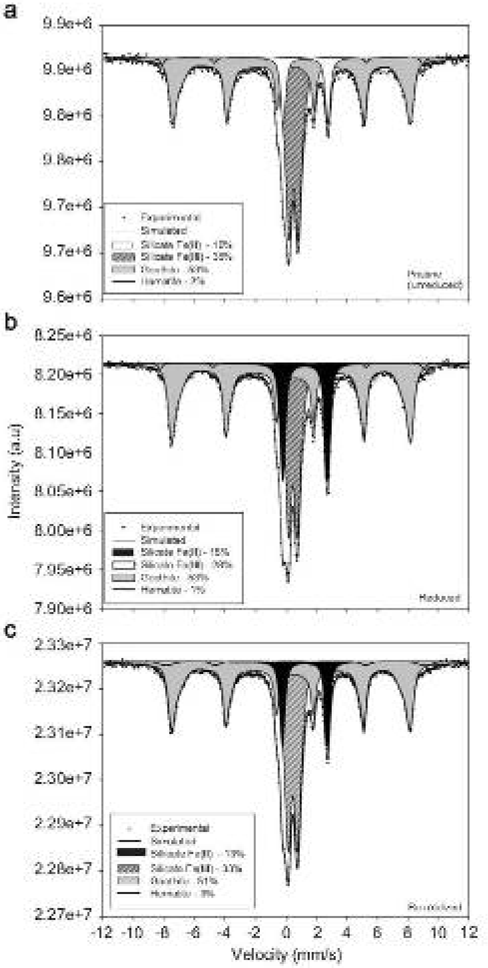

***Figure 1.** Mössbauer spectra (12K) of the (a) pristine sediment, (b) bio-reduced sediment, and (c) re-oxidized sediment.*

Sediment containing a mixture of iron(Fe)-phases, including Fe-oxides and Fe-silicates, was bio-reduced in a long-term flow-through column experiment followed by re-oxidation with dissolved oxygen. This study de-termined the nature of the re-oxidized Fe(III) and how redox cycling of Fe would affect subsequent Fe(III) bio-availability. In addition, the effect of manganese (Mn) on Fe(III) reduction was explored. ^{57}Fe-Mössbauer spectroscopy measurements showed that bio-stimulation resulted in partial reduction (20 percent) of silicate Fe(III) to silicateFe(II), while the reduction of Fe-oxides was negligible. Furthermore, the reduction of Fe in the sediment was uniform throughout the column, suggesting that Fe is not mobilized. As shown in Figure 1, the Mössbauer spectra of the re-oxidized sample were similar to that of pristine sediment implying that Fe-mineralogy of the re-oxidized sediment was mineralogically similar to that of the pristine sediment. Batch experiments showed that Fe(III) reduction occurred at a similar rate although the time required for Fe(II) accumulation to begin was longer in the pristine sediment than the re-oxidized sediment under identical seeding conditions. This rate change was attributed to oxidized Mn that acted as a temporary redox buffer in the pristine sediment. The oxidized Mn was transformed to Mn(II) during bio-reduction but, unlike silicate Fe(II), the Mn(II) was not re-oxidized when exposed to oxygen. A paper describing the results of this research was published in the July 2007 edition of the journal *Water Research* (Komlos et al. 2007).

Citation

Komlos J, RK Kukkadapu, JM Zachara, and PR Jaffé. 2007. "Biostimulation of Iron Reduction and Subsequent Oxidation of Sediment Containing Fe-Silicates and Fe-Oxides: Effect of Redox Cycling of Fe(III) Bioreduction." *Water Research* 41(13):2996-3004.

User Projects

Lab Studies of Phytoremediation & Apatite Sequestration (PNNL Scope #46524)

JL Phillips, JE Szecsody, CA Burns, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

Formation of Iron(II) Secondary Minerals after Iron(III) Bioreduction in humid Tropical Forest Soils

T Peretyazhko, G Sposito, University of California, Berkeley, Berkeley, California

Environmental Sensing, Metabolic Response, Regulatory Network (PNNL 42654, BES)

JK Fredrickson, DW Kennedy, Pacific Northwest National Laboratory, Richland, Washington

Demonstration of the Capability of Mobility-Controlled-Flooding Technology to Overcome Heterogeneity Induced Bypassing in Subsurface Remediation (PNNL LDRD #90001, Overcoming Heterogeneity Induced Bypassing)

L Zhong, KJ Cantrell, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

Mechanisms and Dynamics of Abiotic and Biotic Interations at Environmental Interfaces (Rosso EMSI-Stanford, PNNL Scope # 47286)

GE Brown, Stanford University, Stanford, California

KM Rosso, S Yanina, SN Kerisit, Pacific Northwest National Laboratory, Richland, Washington

CS Lo, Washington University in St. Louis, St. Louis, Missouri

The Reduction of Uranyl and Chromate to Insoluble Species by Green Rust and Other Ferrous Hydroxides Surfaces

MC Wander, MA Schoonen, RJ Reeder, State University of New York at Stony Brook, Stony Brook, New York

Scintillator Research (PNNL Scope #30932: Ambient Temperature Radiation Detectors)

M Bliss, Z Wang, JE Amonette, SD Miller, Pacific Northwest National Laboratory, Richland, Washington

Thrust 3,4: Molecular Forces in Bacterial Adhesion at the Oxide-Water Interface

MF Hochella, NS Wigginton, Virginia Polytechnic Institute, Blacksburg, Virginia

TC Droubay, Pacific Northwest National Laboratory, Richland, Washington

Establish a Penn State Center for Environmental Kinetics - as part of the Environmental Molecular Science Institute (EMSI) program (NSF/DOE-OBER) [PNNL Scope #47287, Zachara EMSI)

T Peretyazhko, University of California, Berkeley, Berkeley, California

J Zachara, Z Wang, Pacific Northwest National Laboratory, Richland, Washington

A Dohnalkova, PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

WD Burgos, ML Minyard, SL Brantley, DR Hummer, DE Ross, MC Davis, H Tan, J Senko, Pennsylvania State University, University Park, Pennsylvania

Characterization of Synthesised Mixed Valent Natuarlly Occuring Fe-Films

GH Grathoff, Portland State University, Portland, Oregon

Thrust 4: Whole Cell and Cytochrome Biological Force Microscopy (LDRD: Cytochrome and Whole Cell Interactions with Iron Oxides)

BH Lower, Pacific Northwest National Laboratory, Richland, Washington

Probing the Structural Network of Buried Water Molecules in the Hydrophobic core of Staphlococcal Nuclease

RL Reynald, EE Lattman, Johns Hopkins University, Baltimore, Maryland

Thrust Area 4: How Redox Proteins on the Exterior of the Outer Membrane of *Shewanella* Accomplish Interfacial Electron Transfer to the Fe(III) Oxide Surface

CM Eggleston, University of Wyoming, Laramie, Wyoming

AM Spormann, J Ha, Stanford University, Stanford, California

TC Droubay, Pacific Northwest National Laboratory, Richland, Washington

Thrust Area 1: The Surface Structure of *Shewanella* and the Localization of Outer Membrane-Associated Proteins Hypothesized to be Involved in Electron Transfer from Metal-Reducing Bacteria to Metal Oxide Surfaces

TJ Beveridge, JR Dutcher, University of Guelph, Guelph, Ontario, Canada

TC Droubay, Pacific Northwest National Laboratory, Richland, Washington

Thrust Area 3: Mutagenesis and Functional Characterization of *Shewanella oneidensis* Genes Involved in Fe(III) and Mn(IV) Oxide Reduction (LDRD #3)

TJ Beveridge, University of Guelph, Guelph, Ontario, Canada

AS Beliaev, MF Romine, JK Fredrickson, Pacific Northwest National Laboratory, Richland, Washington

T Dichristina, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

Simulating Mineral Interfaces (also related to Bylaska BES PNNL#42859: First Principles Simulation of the Supercritical Behavior)

WH Casey, University of California, Davis, Davis, California

EJ Bylaska, Pacific Northwest National Laboratory, Richland, Washington

JH Weare, SA Bogatko, University of California, San Diego, La Jolla, California

The Interaction between Uranium(VI) and Magnetite Surfaces: A Combined STM and Electron Transfer Calculation Approach

FN Skomurski, RC Ewing, U Becker, University of Michigan, Ann Arbor, Michigan

Strait Science - Biosensor Task 1.1 of the Coastal and Environmental Effects Program (PNNL Scope #46754)

DW Ewert, M Pinza, JR Adamec, Pacific Northwest National Laboratory, Sequim, Washington

Evaluate Injection of Zero Valent Iron (PNNL Scope# 488994: Oostrom Fluor Daniel Hanford)

M Oostrom, Pacific Northwest National Laboratory, Richland, Washington

Laser Fluorescence Analysis of Natural Isotopic Abundance Uranium Oxide Samples (Nuclear Noncompliance Verification, PNNL Scope #48379)

JE Amonette, Pacific Northwest National Laboratory, Richland, Washington

Time-Revolved Laser Spectroscopy of Europium Adsorbed on Gibbsite and Silica

GV Korshin, University of Washington, Seattle, Washington

Foldable Polymers

JJ Han, AD Li, Washington State University, Pullman, Washington

Characterization of Novel Arsenic-Iron Precipitates Formed during Biological Iron Reduction

BD Kocar, S Fendorf, Stanford University, Stanford, California

T Borch, Colorado State University, Fort Collins, Colorado

A Dohnalkova, RK Kukkadapu, Environmental Molecular Sciences Laboratory, Richland, Washington

Determining the Effects of Gamma Irradiation on the Oxidation State of Iron using Mossbauer Spectroscopy

PM Jardine, Oak Ridge National Laboratory, Oak Ridge, Tennessee

TL Bank, State University of New York at Buffalo(SUNY), Buffalo, New York

Investigation of Metals Corrosion in SOFCs Using Raman Spectroscopy (PNNL Scope # 40552 SOFC Interconnects)

G Xia, Pacific Northwest National Laboratory, Richland, Washington

PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

Effect of NAPL Dissolution on NAPL-Water Interfacial Area

M Oostrom, MA Covert, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

M Schroth, Swiss Federal Institute of Technology, Zurich, Switzerland

Couple Proton-Electon Dynamics in Iron-Containing Phyllosilicates: Annite, $KFe_3AlSi_2O_{10}(OH)_2$ - Mössbauer Determination of Fe^{2+}/Fe^{3+} ratio (N.Hess LDRD, PNNL SCOPE # 90001)

NJ Hess, ES Ilton, Pacific Northwest National Laboratory, Richland, Washington

RK Kukkadapu, Environmental Molecular Sciences Laboratory, Richland, Washington

Transformations in Iron Mineralogy Induced by Microbial Processes in Natural Sediments

RG Ford, Environmental Protection Agency, Ada, Oklahoma

Characterization of Synthetic Mixed Valence U Compounds

NJ Hess, ES Ilton, Z Wang, Pacific Northwest National Laboratory, Richland, Washington

CL Cahill, George Washington University, Washington DC

Determination of Hydrolysis Rate for CCl4 under Ambient Groundwater Conditions (PNNL Scope #46431, Amonette's Fluor Hanford)

JE Amonette, CK Russell, OS Qafoku, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

Zero Emission Research & Technology (ZERT) CO_2 Sequestration Leakage Evaluation Task: Parameterization of Leakage from Geologically Sequestered CO_2 (PNNL Scope # 46379)

CJ Thompson, Z Wang, Pacific Northwest National Laboratory, Richland, Washington

Microscopic Visualization of Membrane Pores and Bacterial Foulants

S Yanina, Pacific Northwest National Laboratory, Richland, Washington

S Chellam, S Cheethirala, AR Badireddy, University of Houston, Houston, Texas

A Dohnalkova, PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

Evaluation of Pore Scale Porous Media Effects on Reactive Transport in Groundwater

C Werth, T Willingham, University of Illinois, Urbana, Illinois

Z Wang, Pacific Northwest National Laboratory, Richland, Washington

Development of Microscopically-Based Models for Prediction of the Impact of Surface Grain Coating on Mineral Dissolution and Leaching Rates

J Boily, KM Rosso, ES Ilton, OS Qafoku, Pacific Northwest National Laboratory, Richland, Washington

AR Felmy, Environmental Molecular Sciences Laboratory, Richland, Washington

Multiscale Design of Advanced Materials based on Hybrid *ab-initio* and Quasicontinuum Methods

EB Tadmor, University of Minnesota, Minneapolis, Minnesota

EJ Bylaska, Pacific Northwest National Laboratory, Richland, Washington

S Sorkin, Technion -- Israel Institute of Technology, Haifa, Israel

Substrate-Specific Binding of *Staphylococcus adhesins* to Solid Surfaces

SK Lower, Z Oestreicher, Ohio State University, Columbus, Ohio

C Gassman, Columbia Basin College, Pasco, Washington

BH Lower, Pacific Northwest National Laboratory, Richland, Washington

Quorum Sensing in a Dissimilatory Metal Reducing Bacterium

MF Hochella, DR Learman, Virginia Polytechnic Institute, Blacksburg, Virginia

BH Lower, Pacific Northwest National Laboratory, Richland, Washington

Raman Capability for EMSL Users

NJ Hess, Pacific Northwest National Laboratory, Richland, Washington

Protein Adsorption at the Metal Oxide/Water Interface by Second Harmonic Generation

CM Eggleston, University of Wyoming, Laramie, Wyoming

J Boily, L Shi, AG Joly, Pacific Northwest National Laboratory, Richland, Washington

Development of an Integrated Atomic Force/Fluorescence Microscope at EMSL

BH Lower, Z Wang, Pacific Northwest National Laboratory, Richland, Washington

Specificity of *Shewanella oneidensis* Outer Membrane Cytochromes OmcA and OmcB towards Iron- and Manganese-Oxide Surfaces

BH Lower, TC Droubay, L Shi, Pacific Northwest National Laboratory, Richland, Washington

The Role of U(V) during Heterogeneous Reduction of Aqueous U(VI) to U(IV).

ES Ilton, J Boily, Pacific Northwest National Laboratory, Richland, Washington

MH Englehard, Environmental Molecular Sciences Laboratory, Richland, Washington

The Impact of Carbonate on Surface Protonation, Electron Transfer and Crystallization Reactions in Iron Oxide Nanoparticles and Colloids

JR Rustad, University of California, Davis, Davis, California

J Boily, Pacific Northwest National Laboratory, Richland, Washington

DA Dixon, M Hernandez Matus, MT Nguyen, VE Jackson, University of Alabama, Tuscaloosa, Tuscaloosa, Alabama

Basis of Microbial Membrane Attachment to Mineral Surfaces and Ionic Contaminants Uptake

BH Lower, RD Lins, Pacific Northwest National Laboratory, Richland, Washington

M Valiev, Environmental Molecular Sciences Laboratory, Richland, Washington

Mössbauer Analysis of Microbial Redox Transformations of Naturally Occurring Fe(III)-bearing Phyllosilicates

EE Roden, University of Wisconsin, Madison, Wisconsin

ES Shelobolina, University of Wisconsin-Madison, Madison, Wisconsin

RK Kukkadapu, Environmental Molecular Sciences Laboratory, Richland, Washington

Nondestructive Surface-Spectroscopy of Oxidized Metallic Gas Samples

JE Amonette, Pacific Northwest National Laboratory, Richland, Washington

PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

Determination of Hydraulic Conductivity and Soil Moisture Retention Relations with the EMSL Hydraulic Properties Apparatus

MJ Fayer, M Oostrom, MA Covert, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

IR and RAMAN Analysis of Water Diffusion in the Surface of Glasses for Nuclear Waste Immobilization

A Fluegel, DM Strachan, TJ Johnson, Pacific Northwest National Laboratory, Richland, Washington

Determination of Fluorescence Lifetime of Natural Organic Matter

T Ohno, University of Maine, Orono, Maine

Column and Flow Cell Experiments to Study Influence of Wetting and Mass Transfer Properties of Organic Chemical Mixtures in Vadose Zone Materials

H Yoon, GP Prescod, AJ Valocchi, SR Nellis, University of Illinois, Urbana-Champaign, Illinois

M Oostrom, MA Covert, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

Intermediate-Scale Experiments to Investigate Subsurface Flow and Transport of an apataite Solution in Support of Sr-90 Sequestration at the Hanford 100N Area

JE Szecsody, M Oostrom, MA Covert, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

Enhancing C Sequestration in Terrestrial Ecosystems: Linking C and N Cycling in Soils (Part of Center for Research on Carbon Sequestration in the Terrestrial...., PNNL SCOPE # 30929)

VL Bailey, SJ Fansler, DW Kennedy, Pacific Northwest National Laboratory, Richland, Washington

Demonstration of the Multiple-Location Saturation-Pressure Apparatus for Multiphase Porous Media Systems

MA Covert, M Oostrom, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

C Hofstee, Netherlands Organization for Applied Scientific Research TNO-NITG, Utrecht, Netherlands

Electron Donor Dependence of the Extent and Forms of Microbially Reducible Uranium from Contaminated Sediments

AS Madden, AV Palumbo, LA Fagan, TJ Phelps, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Detection of Gas Inclusion in Organic and Metal-Organic Solids

P Thallapally, Pacific Northwest National Laboratory, Richland, Washington

Influence of Speciation on the Transport of U(VI) through Hanford Sediments

Z Wang, Pacific Northwest National Laboratory, Richland, Washington

MA Mayes, XL Yin, W Dong, Oak Ridge National Laboratory, Oak Ridge, China

Mossbauer Spectroscopy of LaSrFerrites

PC Rieke, Pacific Northwest National Laboratory, Richland, Washington

RK Kukkadapu, Environmental Molecular Sciences Laboratory, Richland, Washington

Spectroelectrochemical Sensor for Pertechnetate, TcO^{4-}, Applicable to Hanford and Other DOE Sites

SA Bryan, WD Samuels, S Hightower, Pacific Northwest National Laboratory, Richland, Washington

WR Heineman, CJ Seliskar, University of Cincinnati, Cincinnati, Ohio

Mineralogical Analysis of Substrates and End-Products of Microbial Fe Redox Transformations

EE Roden, University of Wisconsin, Madison, Wisconsin

Distance-Dependent Electron Transfer to Mineral Surfaces Mediated by Bacterial Multiheme Cytochromes

NS Wigginton, MF Hochella, Virginia Polytechnic Institute, Blacksburg, Virginia

KM Rosso, Pacific Northwest National Laboratory, Richland, Washington

Desiccation of Porous Media to Limit Contaminant Migration

M Oostrom, MA Covert, Pacific Northwest National Laboratory, Richland, Washington

JH Dane, Auburn University, Auburn, Alabama

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

DNAPL-Water Interfacial Area Determinations During Entrapped DNAPL Dissolution Using Tracer Techniques

M Oostrom, MA Covert, Pacific Northwest National Laboratory, Richland, Washington

S Bottero, Utrecht University, Utrecht, Italy

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

M Schroth, Swiss Federal Institute of Technology, Zurich, Switzerland

Electrochemical Analyses of the Electron Transfer Rates of MtrC and OmcA to Hematite

L Shi, Pacific Northwest National Laboratory, Richland, Washington

Biogeochemistry of Oxidation-Reduction Cycling of Uranium and Iron

WD Burgos, Pennsylvania State University, University Park, Pennsylvania

Development of Single Molecule Force Microscopy Capability to Examine the Molecular Mechanism of Lignocellulosic Material Degradation

BH Lower, Z Dai, KM Rosso, Z Wang, G Orr, Pacific Northwest National Laboratory, Richland, Washington

Reduction of U^{6+} by Magnetite and the Rate of Electron Transfer

SN Kerisit, Pacific Northwest National Laboratory, Richland, Washington

RC Ewing, U Becker, FN Skomurski, University of Michigan, Ann Arbor, Michigan

Measurement of Saturation-Dependent Anisotropy in Hydraulic Conductivity of Hanford Vadose Zone Sediments

F Zhang, M Oostrom, MA Covert, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

The Characterization of Adsorbed Fe(II) and its Reactivity With Nitrite

CJ Matocha, University of Kentucky, Lexington, Kentucky

Determining the Effects of Organic Chemical Mixtures and Wastewater on DNAPL Migration

H Yoon, AJ Valocchi, C Werth, University of Illinois, Urbana, Illinois

M Oostrom, MA Covert, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

Wettability and Mass Transfer Effects on Flow and Transport of Mixed DNAPL in Hanford Site Sediments

C Werth, AJ Valocchi, University of Illinois, Urbana-Champaign, Illinois

M Oostrom, MA Covert, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

Product Analysis of Reactions of a Model System for Organics on Atmospheric Particles: Ozonolysis of Self-Assembled Monolayers on Silicon Surfaces

TM McIntire, University of California, Irvine, Irvine, California

The Effects of Gamma-Irradiation on the Fe(II)/Fe(III) Signatures in Iron Oxide and Iron Silicate Minerals

TL Bank, State University of New York at Buffalo (SUNY), Buffalo, New York

Microbiological, Geochemical and Hydrologic Processes Controlling Uranium Mobility: An Integrated Field-Scale Subsurface Research Challenge Site at Rifle, Colorado

RK Kukkadapu, C Wang, Environmental Molecular Sciences Laboratory, Richland, Washington

Reduction of Technetium by Fe(II) Associated with Reduced Clay Mineral Nontronite

H Dong, Miami University, Oxford, Ohio

RK Kukkadapu, Environmental Molecular Sciences Laboratory, Richland, Washington

Reductive Transformation of Iron Oxides: Coupled Solution and Solid-State Pathways

GV Gibbs, Virginia Polytechnic Institute, Blacksburg, Virginia

KM Rosso, S Yanina, SN Kerisit, TC Droubay, Pacific Northwest National Laboratory, Richland, Washington

P Meakin, Idaho National Engineering and Environmental Laboratory (INEEL), Idaho Falls, Idaho

C Wang, MH Englehard, B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

D McCready, unknown, Washington

Experimental Investigation of Sr-90 Subsurface Contamination Sequestration in Hanford 100N Area Sediments by Surface Infiltration of an Apatite Solution

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Subsurface Reductive Elimination of Trichloroethylene using Zero-Valent Iron Emplaced by Polymer Solutions

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Characterizing the Composition, Morphology and Reactivity of Bacterial Nanowires using Advanced Scanning Probe Microscopy, MS-Based Proteomics and Scanning Electron Microscopy

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Coupled Hydrological and Geochemical Studies on Uranium Plumes at Hanford Site: Reactions, Spatial Distributions, Speciation, and Future Mobility

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Coprecipitation of Aluminum Hydroxides and Calcium Carbonates during Denitrification: A Stabilization Strategy for Oxidized Metals and Radionuclides

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Validation of Whole-Core Determination of Soil Hydraulic Properties

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Mössbauer Spectroscopy and SEM/TEM Study of the Reductive Dissolution of Fe-Oxyhydroxides in Porous Media

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Development of a Microfluidics Flow and Transport Laboratory

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Chlorinated Methane Hydrolysis Rates

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Experimental Investigation of Strontium Mass Transfer in a Dynamic Vadose Zone - Aquifer - River System

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Terrestrial Carbon Sequestration Studies

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Studies on 1,2,3-trichloropropane (TCP) and its Derivatives

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Advances in Understanding Electron Transfer Kinetics at Environmental Interfaces

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Determination of Saturation-Capillary Pressure Relations of Crude Oil-Brine Systems to Estimate Oil-Water Interfacial Areas

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Development of Time-Dependent Quantum Reaction Dynamics for Surface Reactions

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Development of 1st Principles Dynamics with exact exchange and Spin-Orbit ZORA

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Characterizing the Effects of Iron- and sulfate-Reduction on Aquifer Mineralogy: Linking Geophysics and Geomicrobiology

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Photo-Luminescent Properties of Quantum Dots and Dye Molecules Imbedded in Ceramic and Polymer Materials

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Synthesis and Single-crystal X-ray Characterization of Cluster-Assembled Materials

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Screening Protein Crystals for XRD Data Collection at Synchrotrons

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A Theoretical and Experimental Investigation of Multiplet Splitting for Transition Metal and Uranium Spectra Generated by XPS and XANES

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Nanoscale Investigation of Microbial Role in Promoting the Smectite to Illite Transformation

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Multi-Resolution Structure and Reactivity of Kinetically Roughened Oxide Surfaces: Nanometric Scaling Behavior and Molecular-Scale Controls (Rosso BES, PNNL Scope #43862. Rosso BES)

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Center for Research on Carbon Sequestration (Amonette CSITE, PNNL SCOPE# 30929)

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Enhancing Carbon Sequestration and Reclamation of Degraded Lands and Sequester C in Soils (Amonette NETL, PNNL Scope #40265)

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Carbon Tetrachloride Degradation Reaction Mechanisms (Amonette/Bylaska EMSP-CCl4, PNNL Scope #44012)

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Interactions Between Fe(III) - Reducing Bacteria and Fe Oxides: Microbial and Geochemical Dissolution Controls (Zachara BES-oxide, PNNL Scope #28036)

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Coupling of Fe and Tc Speciation in Subsurface Sediments: Implications to Long-Term Tc Immobilization (Zachara NABIR-Fe/Tc, PNNL Scope # 40761)

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Mineralogic Residence and Desorption Rates of Sorbed ^{90}Sr in Contaminated Subsurface Sediments: Implications to Future Behavior and In-Ground Stability (Zachara EMSP-Sr, PNNL Scope #40896)

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Characterization of U(VI) Sorption-Desorption Processes and Model Upscaling (Zachara, EMSP-U, PNNL Scope #43914)

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Remediation & Closure Science Project/Subsurface Science Tasks (Zachara/Freshly, EM-Closure, PNNL Scope #47040) [was also known as S & T Road Mapping for Needs from All Sources (PNNL Scope #30998)]

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Influence of Mass Transfer on Bioavailablility and Kinetic Rate of U(VI) Biotransformation (Liu NABIR-U, PNNL Scope # 45386. Liu NABIR)

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Influence of Microscopic Mass Transfer on the Reactivity and Stability of Uranium

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Characterization of U(VI) Speciation in Samples from Laboratory Batch and Column Experiments

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Liquid Infrared Spectroscopy and Spill Phenomenology (Hylden FTIR-Liquids, PNNL Scope # 44568)

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Quantification and Chemical Analysis of Iron Oxidation in Microbially-Reduced Sediments

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Model Development on Using Clay Membranes for Arsenic Removal from Drinking Water

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Model Development on Using Clay Membranes for Arsenic Removal from Drinking Water

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Biogeochemical Heterogeneity in the Subsurface (Long, PNNL scope #16259)

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Enhance Plutonium Mobility during Long-Term Transport through an Unsaturated Subsurface Environment: Iron and Manganese Oxide Characterization

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Uranium Immobilization by Sulfate-Reducing Biofilms

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How Aluminum Substitution in Goethite Affects Iron Release

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Characterizing the Products of Field-Scale Biostimulation: Decoupling the Mineralogical Effects of Iron- and Sulfate-Reduction

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Photophysics of Organophosphorous Compounds (PNNL LDRD Project: Synchrontron X-ray Spectroscopy of Novel Organic Diphosphine, WP# F47177)

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Influence of Flow on Abiotic and Biotic Reactivity of CL--20 (Hexaanitrohexaazaiso-Wurtzitane) (PNNL Scope # 42095)

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Conductivity of Bacterial Nanowires

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Mossbauer Spectroscopic Investigations of Fe Doped SnO_2 Powders

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High-Field Magnetic Resonance Facility

The High-Field Magnetic Resonance Facility (HFMRF) brings a powerful synergy of creative scientific staff and unique instrumentation to bear on complex scientific problems. HFMRF is equipped with state-of-the-art nuclear magnetic resonance (NMR) and pulsed electron paramagnetic resonance (EPR) instruments, all of which play a role in determining molecular structures that are relevant to environmental remediation efforts, materials development for national energy needs, and biological health effects.

HFMRF offers unique tools and techniques designed in-house to enable novel research, including 1) *in situ* catalysis probes, 2) radionuclide NMR capabilities, 3) solid-state NMR cryogenic probes for direct observation of metals in macromolecules, 4) high-temperature probe technology, 5) laser-polarized gas for visualizing gas-filled spaces using magnetic resonance imaging (MRI), and 6) pulsed EPR techniques designed to follow conformational changes in membrane protein complexes containing metal clusters. In collaborative partnership with world-class scientists around the globe, we forge innovative approaches to some of the most pressing research needs in environmental molecular science and other national research priorities.

Staff and science consultants within this facility offer expertise in the areas of structural biology, solid-state materials characterization, and MRI techniques. Research activities include structure determination of large molecular assemblies such as protein-DNA (normal and damaged DNA) and protein-RNA complexes that model assemblies that may form as a cellular response to chemical or radiological insults; examination of conformational changes in membrane protein complexes involving metal clusters using pulsed EPR; NMR-based structural and functional genomics; multi-nuclear detection and catalyst and materials characterization using solid-state techniques; and non-invasive biological imaging, integrated magnetic resonance and confocal microscopy, and slow-spinning NMR to study cell systems.

Instrumentation & Capabilities

NMR and EPR

- 900-MHz NMR
- 800-MHz NMR
- 750-MHz NMR
- 600-MHz NMR (two systems)
- 500-MHz (two wide-bore systems and one narrow-bore system)
- 300-MHz wide-bore NMR (two systems – one radionuclide capable)
- Horizontal-bore 2-tesla NMR
- EPR spectrometer with electron nuclear double resonance (ENDOR)/electron-electron double resonance (ELDOR) capability

Additional Capabilities

- Combined optical and magnetic resonance microscope
- Low-temperature probes for metallo-protein chemistry and structure
- Virtual NMR capability enabling use and collaboration with EMSL scientists for remote users via secure shell over the internet

The research interests of staff and scientific users include some of the most exciting areas in modern molecular biology and biochemistry:

- **Structural/Functional Genomics**. Determination of three-dimensional structures of DNA, RNA, proteins, and enzymes and their intermolecular associations. Particular interests and collaborations exist relative to protein fold classification and sequence-structure-fold relationships.

- **Biomolecular Complexes**. Understanding the molecular interactions of larger complexes of biomolecules (proteins, DNA, RNA, and mimetic membranes) that are key regulators in cell signaling and growth (e.g., DNA damage recognition and repair processes).

- **Biological Imaging**. Acquisition of imaging and corresponding chemical information in biological samples, with particular interest in development of combined magnetic resonance and optical spectroscopy techniques to observe and elucidate biological processes.

- **Solid State**. Low-gamma nuclei detection, ultra-low-temperature NMR for sensitivity enhancement, and slow-magic-angle-spinning (MAS) methodologies for nondestructive research of cells, tissues, small animals, and bacterial colonies.

- **Measurement Science and Instrumentation Development**. Development and application of novel and unique NMR instrumentation techniques for biological and environmental problems.

Capabilities

Varian INOVA 900. The Varian 900 (Figure 1) is an INOVA-based spectrometer utilizing an Oxford 21.1-tesla (T) magnet with a 63-mm room-temperature bore. This system is capable of high-resolution liquid- and solid-state NMR. There are four radio frequency (RF) channels with waveform generators and triple-axis pulsed-field gradients. The wide-line analog digital converters (ADCs) run at 5 MHz and the narrow ADCs have a maximum rate of 500 kHz. This console also has a solids variable-temperature (VT) control capability. We currently have a 5-mm HCN probe with X, Y, and Z axis gradients for liquids, a 5-mm orthogonal HX powder probe optimized for low-gamma nuclides, a 5-mm orthogonal H-N-Zn triple-tuned probe for powders, and a 3.2-mm low-gamma HX MAS probe (24 kHz spinning).

***Figure 1**. 900-MHz NMR spectrometer.*

Figure 2. Varian INOVA 800-MHz NMR spectrometer.

Varian INOVA 800. The Varian 800 (Figure 2) is an INOVA-based spectrometer utilizing an Oxford 18.8-T magnet with a 63-mm, room-temperature bore. This system is capable of high-resolution liquid- and solid-state NMR. There are four RF channels with waveform generators and pulsed-field gradients. The wide-line ADCs run at 5 MHz, and the narrow-line ADCs run at a maximum rate of 500 kHz. This console also has a solids VT control capability. Available probes include a 5-mm HCN cryoprobe and two room-temperature 5-mm HCN probes with Z gradient for liquids, a 4-mm HXY MAS probe (25-kHz spinning, VT-capable), a 5-mm HX orthogonal powder probe optimized for low-gamma (38 to 65 MHz) nuclides, and a 5-mm HX static low-temperature probe (3.8 to 300 K). A 5-mm HX MAS probe (12-kHz spinning) is under construction.

Figure 3. Varian INOVA 750-MHz NMR spectrometer.

Varian INOVA 750. The Varian 750 (Figure 3) is an INOVA-based spectrometer utilizing an Oxford 17.6-T magnet with a 51-mm, room-temperature bore. This system is capable of high-resolution liquid- and solid-state NMR. There are four RF channels with waveform generators and pulsed-field gradients. The narrow ADCs have a maximum rate of 500 kHz. We currently have two 5-mm HCN probes (Z gradient), a 5-mm HCP probe (Z gradient), a 5-mm HX MAS probe (X tuning range is 321 to 130 MHz; the spinning speed is rated to 12 kHz), and two 5-mm HX MAS probes (15-kHz spinning) with X tuning ranges of 60 to 120 MHz and 30 to 50 MHz.

Figure 4. Varian INOVA 600- MHz NMR spectrometer with Cryoprobe.

Varian INOVA 600. The Varian 600 (Figure 4) is an INOVA-based spectrometer utilizing an Oxford 14.1-T magnet with a 51-mm, room-temperature bore. This system is capable of high-resolution liquid-state NMR. There are four RF channels with waveform generators and pulsed-field gradients. The narrow-line ADCs run at a maximum rate of

500 kHz. We currently have a cryogenically cooled and a room-temperature 5-mm HCN probe with Z gradient and a 5-mm HX probe (X tuning range is 242 to 60 MHz).

Figure 5. *Varian INOVA 600-MHz NMR spectrometer.*

Varian Unity 600. The Varian 600 (Figure 5) is an INOVA-based spectrometer utilizing an Oxford 14.1-T magnet with a 51-mm, room-temperature bore. This system is capable of high-resolution liquid-state NMR. There are three RF channels with waveform generators and pulsed-field gradients. The narrow-line ADCs run at a maximum rate of 500 kHz. We currently have a 5-mm pentaprobe (proton, phosphorus, carbon, nitrogen and deuterium) with Z-gradient, a 5-mm HCN probe with Z gradient and a 5-mm HX probe (X tuning range is 242 to 60 MHz).

Figure 6. *Varian NMR System 500-MHz wide-bore NMR spectrometer.*

Varian NMR System 500 Wide Bore. The Varian 500 Wide Bore (Figure 6) has a new VNS-based spectrometer console and utilizes an Oxford 11.7-T magnet with an 89-mm room-temperature bore. This system is capable of a full range of solid-state NMR, experiments, including windo-less sequences and PISEMA. There are three RF channels with waveform generators. The wide-line ADCs run at 5 MHz. We currently have a new 4-mm HXY MAS probe capable of bio-solids triple resonance experiments and a new 7.5-mm HX MAS probe (8-kHz spinning), an HX single-crystal probe, a ^{1}H CRAMPS probe, a micro-coil imaging probe, a 40-mm imaging probe, and a static HX low-temperature probe (2 to 300 K).

Bruker Avance 500 Wide Bore. The Bruker Avance 500 Wide Bore (Figure 7) is a micro-imaging system using an 89-mm vertical room-temperature bore. The system is capable of imaging mice and also has high-resolution liquid magnetic resonance capabilities with a Bruker 10-mm QNP probe. This liquid probe has a ^{1}H outer coil and an inner coil that is switchable among ^{13}C, ^{31}P, and ^{19}F with no gradients. The system is equipped with a combined confocal and magnetic resonance microscope capable of monitoring single layers of eukaryotic cells in a perfusion system simultaneously with both modalities.

Figure 7. *Bruker Avance 500-MHz NMR spectrometer.*

Varian/Chemagnetics Infinity 500. The Chemagnetics 500 (Figure 8) is an Infinity-based spectrometer utilizing an Oxford 11.7-T magnet with a 51-mm, room-temperature bore. This system is capable of high-resolution liquid- and solid-state NMR. It has three RF channels and is equipped with both 16- and 14-bit ADCs. The solution state probes for this instrument include a 5-mm HCN gradient probe, a 5-mm DB gradient probe (X tuning range is 208.1 to 49.5 MHz), and a 10-mm HX probe (X tuning range is 218.6 to 21.2 MHz). There are two solid-state probes, a 5-mm HX MAS probe (X tuning range is 206.6 to 47 MHz; the spinning speed is rated to 12 kHz) and a 6-mm HX MAS probe (X tuning range is 218.6 to 48.7 MHz, H/F tuning range is 510.6 to 459 MHz; the spinning speed is rated to 9 kHz).

***Figure 8**. Varian/Chemagnetics Infinity 500-MHz NMR spectrometer.*

Varian/Chemagnetics Infinity 300. The Chemagnetics 300 (Figure 9) is an Infinity-based spectrometer utilizing an Oxford 7.02-T magnet with an 89-mm room-temperature bore. This system is capable of high-resolution liquid- and solid-state NMR. It has three RF channels and is equipped with both 16- and 14-bit ADCs. The solution-state probes for this instrument include a 5-mm HX probe and a 10-mm HX probe. The solids probes are a 7.5-mm HX MAS probe (X tuning range is 136.7 MHz to 29.5 MHz; H tuning range is 274.7 to 349.1 MHz; spin rate is rated to 7 kHz) and a 5-mm HXY MAS probe (X tuning range is 129 to 57.4 MHz; Y tuning range is 85.1 to 21.2 MHz; spin speed is rated to 12 kHz). Further probes available are a 7-mm HX MAS probe (10-kHz spinning), an HX single-crystal probe, a ^{1}H CRAMPS probe, a single-tuned HX 5-mm, low-temperature MAS probe (35 to 300K, 12-kHz spinning), a 7-mm HX high-temperature probe (-100 to 500°C, 7-kHz spinning)

***Figure 9**. Varian/Chemagnetics Infinity 300-MHz NMR spectrometer.*

***Figure 10**. Horizontal-bore 2-T magnet.*

Horizontal-Bore 2-T Magnet. The 2-T magnet (Figure 10) provides unique capabilities for the HFMRF. It is connected to a Varian Unity+ console with two RF channels and wideline 5-MHz

ADCs. It has a 30-cm, room-temperature bore and is equipped with an imaging gradient set capable of 50 gauss/cm. It is suitable for small animal or large sample imaging and *in vivo* spectroscopy. Three homemade birdcage coil probes are available: 8-cm and 5-cm imaging/spectroscopy probes and a 5-cm ^{3}He probe.

Bruker Pulsed EPR/ENDOR/ELDOR Spectrometer. This multi-functional pulsed EPR spectrometer (Figure 11), operating in the X-band near 9.5 GHz, permits application of modern pulsed magnetic resonance techniques to systems containing unpaired electron spins. The system is based on the Bruker EleXsys console and SuperX-FT microwave bridge, which allow both ELDOR (electron-electron double resonance) and ENDOR (electron nuclear double resonance) measurements. A number of probes for both continuous-wave and pulsed spectroscopy are included, with an operating temperature ranging from room temperature to below liquid helium. System capabilities include measurement of g-tensors; hyperfine and nuclear quadrupole-coupling tensors for the study of electronic wavefunction of free radicals and metallo-proteins; and determination of small dipolar interactions by pulsed ELDOR and double electron-electron resonance methods for the measurement of distances between radicals in solids or between spin labels in proteins.

***Figure 11**. Bruker pulsed EPR/ ENDOR/ ELDOR spectrometer.*

Instrument Upgrades

In 2007, the HFMRF made the following upgrades.

- **500-MHz Wide-Bore NMR Console upgrade:** A new 500-MHz NMR console and three updated probes were acquired for scientific user support. This purchase fully replaces a 13-year old console that was fully subscribed with users. It enables execution of modern/technically challenging pulse sequences not possible on the previous console generation. This 3-RF channel system delivers state-of-the-art performance in phase, amplitude, and frequency stability and is capable of windowless sequences: DRAWS, CRAMPS, PISEMA, and REDOR. This instrument supports work in solid-state materials/catalysis (Science of Interfacial Phenomena science theme) that impact environmental- and energy-related science as well solid-state NMR of protein-surface interactions (mineral and membrane) that are relevant to the Biological Interactions and Dynamics science theme. This system supports the unique capability of several probes developed in-house that allow *in-situ* chemistry for catalysis projects. In addition to the console, the purchase included three updated probes for addressing user projects that could not be met with the existing set of probes.

Magnetic Resonance Imaging of Proton Exchange Membranes Dehydration and Gas Manifold Flooding During Continuous Fuel Cell Operation

KR Minard,[a] VV Vishwanathan,[a] PD Majors,[a] LQ Wang,[a] and PC Rieke[a]
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The President's Hydrogen Fuel Initiative aims to reverse America's dependence on foreign oil by developing fuel cells that use hydrogen to produce electricity. Fuel cells with proton exchange membranes (PEMs) are of particular interest because they offer high power density, are lightweight and compact, operate at relatively low temperatures, and yield water as the primary byproduct of power generation.

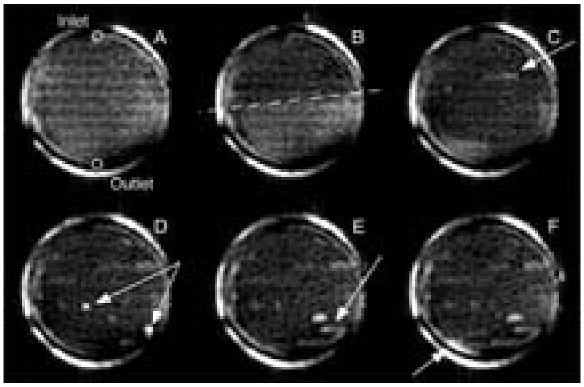

Figure 1. Selected ^1H water MRIs acquired at 128-second intervals over an 11-hour period. The dashed line highlights the position of the dehydration front, and the white arrows point to flooded regions.

The efficient operation of PEMs requires a delicate balance between water formation and removal because both membrane dehydration and/or flooding hinder mass transport to reactive catalytic sites. In recognition that few diagnostic tools are currently available for visualizing water distribution, EMSL users from PNNL recently described the use of magnetic resonance imaging (MRI) for this purpose (Minard et al. 2006). The work of this research team demonstrates the utility of MRI for visualizing water nonuniformity and understanding the effects on fuel cell performance. Representative images acquired over 11 hours of continuous fuel cell operation are shown in Figure 1. Briefly, they show: A, the initial water distribution within the PEM fuel cell; B and C, a dehydration front that was observed to propagate slowly over the surface of the fuel cell membrane, starting from gas inlets and progressing toward gas outlets; and C-F, the location of various flood zones within gas-delivery manifolds.

Citation

KR Minard, VV Vishwanathan, PD Majors, LQ Wang, and PC Rieke. 2006. "Magnetic Resonance Imaging (MRI) of PEM Dehydration and Gas Manifold Flooding During Continuous Fuel Cell Operation." *Journal of Power Sources* 16(2):856-863.

Quantification of Actinide [Alpha]-Radiation Damage in Minerals and Ceramics

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By using solid state nuclear magnetic resonance (NMR), we demonstrated that structural damage in plutonium (Pu)-doped zircon could be directly quantified. This finding is important to estimate the resistance to self-irradiation damage of materials incorporating actinides for long-term immobilization (i.e., over thousands of years).

One significant problem facing the world is safe disposal of unneeded, long-lived radioisotopes. It has been proposed to incorporate radioisotopes of elements, such as plutonium, americium, and curium, in a fixed, durable matrix until their radiation levels naturally decay to safe levels. While glass is favored by many scientists, crystalline solids such as zircon ($ZrSiO_4$) are also under consideration. However, prolonged exposure to the alpha-emissions of the encapsulated radioisotopes can cause crystalline structures to become amorphous over time. The relatively heavy and energetic alpha particle will break bonds and move atoms, and the main heavy atom recoils with a slower velocity, but equal energy, and also is able to disrupt the crystal structure (Figure 1). The result is a cumulative disruption of the crystal arrangement.

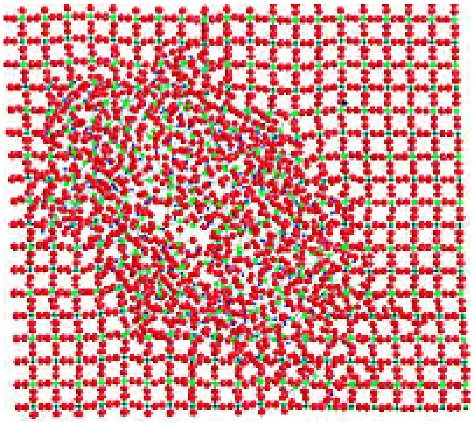

Figure 1. *Results of a calculation showing the disruption to a zircon crystal lattice caused by alpha particle emission from the decay of a single plutonium atom.*

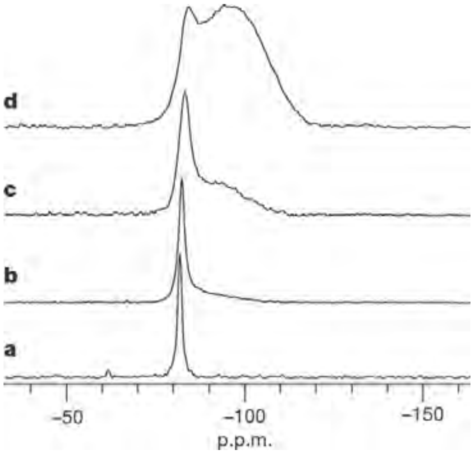

Figure 2. *^{29}Si NMR spectrum of zircon after accumulating the following doses of alpha particles. (a) no α decay, (b) 1.2 X1018 α /γ, (c) 2.9 X1018 α /γ, (d) 7.1 X1018 α /γ.*

Because zircon contains silicon, ^{29}Si NMR can be used to monitor the nature of the silicon sites in the zircon crystal. Initially, all of the sites will be identical and will give a single sharp line in the NMR spectrum. As the crystal is disrupted, the peak of atoms from damaged sites shifts and broadens, reflecting the disorganized state of the silicon at these sites. By comparing the area of the sharp peak and the broad peak, it is possible to estimate the extent of disruption of the crystal structure caused by exposure to alpha irradiation from the incorporation of plutonium (Figure 2).

Looking at samples with different levels of plutonium incorporation that have been aged for a number of years will give an estimate of the amount of damage that has accumulated over the time period. Based on this study, zircons with 10 wt.% plutonium incorporation will start to swell in 210 years and be completely amorphous in 1400 years. The time scale of this process compares unfavorably with the half-life of ^{239}Pu, which is 24,100 years.

Citation

Farnan I, HM Cho, WJ Weber, 2007. "Quantification of Actinide α-Radiation Damage in Minerals and Ceramics." *Nature* 445(7124):190-193.

Magnetic Resonance Studies of Proton Loss from Carotenoid Radical Cations

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An important protective process in photosynthetic organisms is the ability to cope with more light energy than can be used for photosynthesis. This excess energy must be dissipated or the chlorophyll (Ch1) will be damaged and cease to function. This protection of chlorophyll often involves carotenoids, but the chemical mechanism is not well known. In this study, we used electron paramagnetic resonance to study the reactive species to determine the pathway through which energy is dissipated.

Carotenoids are intrinsic components of reaction centers and pigment-protein complexes in photo-synthetic membranes and play a photoprotective role and serve as a secondary electron donor. The robust nature of carotenoids in living materials requires extensive characterization of their electron-transfer mechanism, radical-trapping ability, stability, structure in and on various hosts, and photochemical behavior before optimum use of them can be made in artificial photosynthetic systems.

In this project, we employed a combination of pulsed electron nuclear double resonance (ENDOR) spectrometry, two-dimensional hyperfine sublevel correlation spectroscopy (2D-HYSCORE) using the electron paramagnetic resonance (EPR) equipment available in EMSL, and density functional theory (DFT) calculations to study this system. This combined experimental/computational approach revealed that photo-oxidation of natural zeaxanthin (I) and violaxanthin (II) on silica-alumina produces not only the carotenoid radical cations ($\mathrm{Car}^{\bullet+}$) but also neutral radicals ($\#\mathrm{Car}^{\bullet}$) by proton loss from the methyl groups at positions 5 or 5′, and possibly positions 9 or 9′ and 13 or 13′. Notably, the proton loss favored in I at position 5 by DFT calculations, is unfavorable in II because of the epoxide at the 5, 6 position. Density function theory calculations predict the isotropic methyl proton couplings of 8 to 10 MHz for $Car^{\bullet +}$, which agree with the ENDOR data for carotenoid π-conjugated radical cations. Large α-proton hyperfine coupling constants (> 10 MHz) determined from HYSCORE are assigned from the DFT calculations to neutral carotenoid radicals. Proton loss upon photolysis was also examined as a function of carotenoid polarity [Lycopene (III) versus 8′-apo-β-caroten-8′-al (IV)]; hydrogen bonding [Lutein (V) versus III]; host [silica-alumina versus MCM-41 molecular sieve]; and substituted metal in MCM-41.

Loss of H^+ from the 5(5′), 9(9′), or 13(13′) methyl positions has importance in photoprotection. Photoprotection involves non-photochemical quenching in which $^{1}Ch1^{*}$ decays via 1) energy transfer to the carotenoid, which returns to the ground state by thermal dissipation, or 2) electron transfer to form a charge transfer state ($I^{\bullet +}\cdots Chl^{\bullet -}$) that is lower in energy than $^{1}Chl^{*}$. Formation of $I^{\bullet +}$ results in bond lengthening, which is a mechanism for nonradiative energy dissipation. Quenching requires zeaxanthin, a pigment-binding protein PsbS, and low pH in the thylalkoid lumen. A combination of low pH and excess light activates the xanthophyll cycle through the enzyme violaxanthin deepoxidase, which drives deep oxidation of violaxanthin to zeaxanthin. Also a low thylakoid lumen pH activates binding of zeaxanthin to PsbS by protonating carboxylate chains of violaxanthin deepoxidase and PsbS, thus facilitating attachment to the membrane and the conversion of violaxanthin to zeaxanthin. The low pH also drives adenosine triphosphate synthesis.

Solid-State NMR Characterization of CdS Nanoparticle/Polymer Interfaces

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Semiconducting nanopoarticles made from cadmium chalcogenide have unique optical, catalytic and energy transfer properties stemming from their size and morphology. To better understand the physical properties created during the processing of these nanopartical materials, nuclear magnetic resonance (NMR) spectrometry is one of the tools used to investigate atomic structure and substrate-surface interactions.

Cadmium chalcogenide (CdX; X = S, Se, Te) semiconducting (II-VI) nanoparticles are currently of significant interest because the properties of the nanoparticles are intermediate to those of molecular and bulk materials, which have a diverse number of realized and potential applications. Several of these applications include organic/inorganic light-emitting diodes, electroluminescence devices, nanoelectronics, quantum-dot LASERs, photovoltaic solar cells, catalysts, materials for imaging, and assaying bio-systems. In most of these systems, the critical property of the nanoparticle is its photoluminescence, for which the emission wavelength can be varied by varying the particle size. The photoluminescent properties are highly dependent on the surface structure of the nanoparticle, with high defect numbers producing more trapped-state luminescence. The surface defect sites can be electronically passivated by coating the CdX nanoparticle surfaces with capping agents, such as phosphine oxides, thiols, and amines. These passivated particles luminesce predominantly through band-edge emissions, resulting in longer excitation lifetimes and higher luminescent intensities.

Solid-state NMR is the ideal technique for the study of the structure of CdX nanomaterials as both the bulk and surface structures of the NMR active nuclei can be probed. In addition, the interaction between the nanoparticles and the surface passivation materials can be characterized. NMR studies of the CdX materials benefit from the presence of an array of ideal NMR active nuclei, including 113Cd (12.26 percent natural abundance [n.a.], spin=1/2), 77Se (7.6 percent n.a., spin=1/2), 125Te (7 percent n.a., spin=1/2), and 13C (1.1 percent n.a., spin=1/2).

The materials analyzed using capabilities in the EMSL High Field Magnetic Resonance Facility were cadmium sulfide (CdS) nanoparticles synthesized using two different capping agents: 1-thioglycerol and 4-bromophenylethenyl phosphonic acid (4BrEPPA). In summary, the cadmium chemical shift shows the successful formation of cadmium nanoparticles resulting from the resultant chemical shift and a wide line caused by structural heterogeneity. The lower spectrum shown in Figure 1 represents all the cadmium present in the sample, while the top spectrum of these represents that cadmium at the surface of the nanoparticles. The spectral editing was generated using a H-Cd cross polarization magic-angle spinning technique that uses protons on the surface to enhance the surface cadmium signal. There is a small fraction of cadmium at the surface compared to the whole sample.

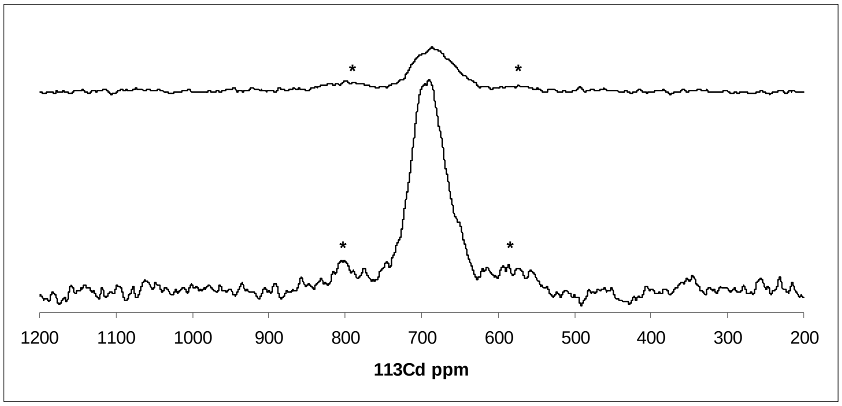

Figure 1. *Parts per million (ppm) 113Cd of CdS as synthesized, DP (bottom, d1=60 sec, ct=1146, lb=200, ss 5 KHz) and CP (top, d1=2sec, cp=1ms, ct=13660, lb=200, ss 5 KHz)*

A two-dimensional heteronuclear correlation experiment was performed on the CdS precipitated with ethanol. In that experiment, the correlation between the protons (F1 dimension) and the cadmium (F2 dimension) in the sample was observed (see Figure 2). The two protons were observed to have a strong correlation with the cadmium of the CdS nanoparticles, one at approxunately 4 ppm representing correlation with protons of CH_2 close to the sulfur and the CH and the other at about 8 ppm, possibly resulting from protons of the OH groups at the surface of the CdS.

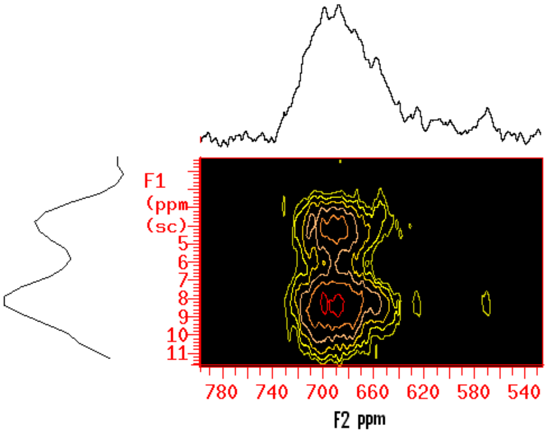

Figure 2. *1H-113Cd heteronuclear correlation experiment on CdS precipitated with ethanol.*

These and additional results, which discussed synthesis, further analysis, and the effects of hydration on the surface, were presented July 22, 2008, at the NMR Symposium during the Rocky Mountain Analytical Conference, in Breckenridge Colorado.

Structural Studies of Apo NosL, an Accessory Protein of the Nitrous Oxide Reductase System

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In this project, the researchers are seeking an understanding of proteins important for cleaning up groundwater, soils, and wetlands that have been contaminated by fertilizer run-off.

Denitrification, the process of reducing nitrate and nitrite to nitrogen gas, occurs under anaerobic conditions in both terrestrial and marine ecosystems. NosL is a 20-kDa copper binding lipo-protein needed for nitrous oxide reductase (N_2OR) assembly in denitrifying bacteria. This lipo-protein was discovered to have a very unique structure with a new configuration to bind and transport metal atoms in cells.

N_2OR performs the last step of denitrification, the conversion of nitrous oxide to dinitrogen (N_2), thus cycling nitrogen derived from biomass back to the atmosphere. To accomplish this energetically demanding reaction, N_2OR uses two functionally critical multi-nuclear copper clusters: 1) an electron donor site, Cu_A, and 2) a catalytic site, Cu_Z. Formation of this catalytic complex requires copper and sulfur, both of which can be toxic to the organism, thus necessitating dedicated uptake and transport systems to prevent undesirable side reactions and to ensure safe delivery of these species to the appropriate targets. The nosDFYL operon, located downstream of the N_2OR structural gene, nosZ, has been implicated in Cu_Z biogenesis. One gene in this operon, the nosL gene, is present in all denitrifying genomes sequenced thus far, suggesting an important function for this protein in N_2OR maturation. NosL has little sequence similarity with proteins that have a known function; therefore, the sequence reveals little about the NosL role in N_2OR assembly. NosL is known to bind copper and release it upon oxidation, so it likely functions as a metallochaperone to facilitate copper transport.

This research was led by V Copié of Montana State University with consultation from staff of the EMSL High-Field Magnetic Resonance Facility. Vital high-field nuclear magnetic resonance data (i.e., obtained at 800 MHz) enabled protein structure determination on the apo nosL protein (with no copper bound to the protein). The structure was discovered to consist of two flat planes connected by a short loop, with the planes oriented perpendicular to each other. As can be seen in Figure 1, each plane contains a ββαβ structure. Both the ββαβ structure and the planes oriented perpendicular to each other with a large cleft between them are unique structural motifs in NosL. Another surprising feature is that although the two planes have very different sequences, they have nearly identical structures. Only one other protein found in the protein data bank has a similar structure, the MerB protein, which is an organomercury lyase involved in a bacterial mercury resistance system. In the case of NosL and MerB, this conserved mechanistic feature would appear to require the presence of a large cleft between the two ββαβ domains contiguous with a mononuclear metal-binding site. NosL has the same highly conserved methionine in the cleft, which is likely to be involved in binding the copper ion. The most likely function for this protein is to chaperone copper atoms through the cell and deliver it to N_2OR for incorporation into the enzyme. Supporting experiments indicate the protein binds Cu(I) and then releases it upon oxidation.

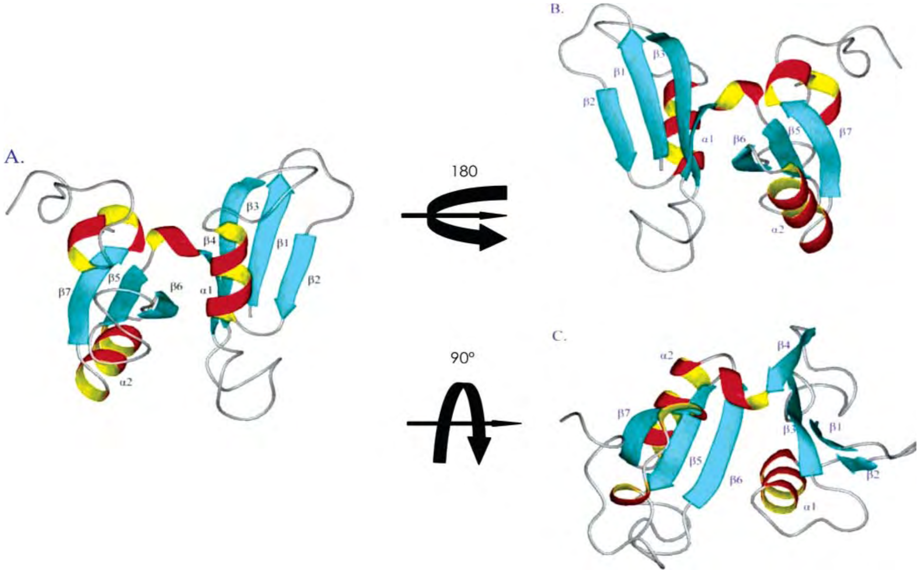

Figure 1. *Ribbon diagrams of a representative low-energy conformer of apo NosL viewed from various orientations: (A) The ß sheets are depicted in cyan, helices in red and yellow; (B) A view of the apo NosL structure rotated by 180° relative to the orientation in panel A; (C) The image rotated 90° relative to the orientation in panel A illustrates the perpendicular relationship of the two ß sheets.*

This structural work, published in the journal *Biochemistry* (Taubner et al. 2006), yielded the first detailed structure of an accessory protein from the nos cluster. It establishes the groundwork for understanding the role of the NosL protein in the bacterial N_2OR complex denitrification system.

Citation

Taubner LM, MA McGuirl, DM Dooley, and V Copié. 2006. "Structural Studies of Apo Nosl, an Accessory Protein of the Nitrous Oxide Reductase System: Insights from Structural Homology with MerB, a Mercury Resistance Protein." *Biochemistry* 45(40):12240-12252.

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

User Projects

Structure of Telomerase RNA and Telomeric Proteins

TC Leeper, G Varani, BM Lunde, DW Begley, University of Washington, Seattle, Washington

Slow MAS of Lipids in Mouse Fast and Slow Skeletal Muscle

MJ Kushmerick, KE Conley, EG Shankland, D Lee, University of Washington, Seattle, Washington

Solid State MAS NMR of High-Valent Cation Exchanged H-MFI

HS Lacheen, E Iglesia, University of California, Berkeley, Berkeley, California

Hydrogen Storage Materials

MR Hartman, Oregon State University, Corvallis, Oregon

WJ Shaw, T Autrey, J Linehan, A Karkamkar, CJ Howard, Pacific Northwest National Laboratory, Richland, Washington

AM Feaver, University of Washington, Seattle, Washington

ME Bowden, Industrial Research Ltd., Lower Hutt, New Zealand

Structural Genomics of Eukaryotic Model Organisms

JM Aramini, G Montelione, Rutgers University, New Brunswick, New Jersey

Routine ^{1}H and ^{13}C NMR Analysis of Functionalized Semiconductor and Metallic Nanoparticles Synthesized for Biodetection Studies

C Dutton. Washington State University, Richland, Washington

MG Warner, AM Pierson, Pacific Northwest National Laboratory, Richland, Washington

AM Shearrow, University of South Florida, Tampa, Florida

Investigating Molecular Recognition and Biological Function at Interfaces Using Antimicrobial Peptides

B Vollmar, ML Cotten, K Forseth, D Jacobsen, SM Jones, Pacific Lutheran University, Tacoma, Washington

Correlation of Structure and Function of Zinc Metalloproteins Via Solid-state NMR Methods

AS Lipton, PD Ellis, R Heck, Pacific Northwest National Laboratory, Richland, Washington

Magnetic Resonance Microscopy of Environmental Lung Injury

CG Plopper, University of California, Davis, Davis, California

KR Minard, R Jacob, Pacific Northwest National Laboratory, Richland, Washington

JR Harkema, Michigan State University, East Lansing, Michigan

Investigation of the Role of Mg^{2+} in DNA Repair Proteins APE1, Pol , and FEN1

AS Lipton, PD Ellis, R Heck, Pacific Northwest National Laboratory, Richland, Washington

GS Harbison, University of Nebraska, Lincoln, Nebraska

DM Wilson, National Institute on Aging, IRP, NIH, Baltimore, Maryland

SH Wilson, National Institute of Environmental Health Sciences, NIH, RTP, North Carolina

Slow-MAS NMR Methodology Developments

RA Wind, Pacific Northwest National Laboratory, Richland, Washington

Grand Challenge in Biogeochemistry

J Zachara, JK Fredrickson, Pacific Northwest National Laboratory, Richland, Washington

KH Nealson, University of Southern California, Los Angeles, California

AR Felmy, RK Kukkadapu, Environmental Molecular Sciences Laboratory, Richland, Washington

Draws Implementation

SD Burton, WJ Shaw, Pacific Northwest National Laboratory, Richland, Washington

J Sears, JJ Ford, Environmental Molecular Sciences Laboratory, Richland, Washington

Pulsed EPR of Membrane Proteins

MK Bowman, University of Alabama, Tuscaloosa, Tuscaloosa, Alabama

AG Mariassov, YD Tsvetkov, Institute of Chemical Kinetics and Combustion, Novosibirsk, Russian Federation

In-situ High Field, High Resolution NMR Spectroscopy

J Hu, CH Peden, Y Wang, J Kwak, Pacific Northwest National Laboratory, Richland, Washington

NMR Study of Effects and Mechanisms of Mechanical Activation on Hydrogen Sorption/Desorption of Nanoscale Lithium Nitrides

Z Yang, Jn Hu, J Kim, Pacific Northwest National Laboratory, Richland, Washington

NMR Study of Novel Hydrogen Storage Materials

Z Yang, J Hu, Pacific Northwest National Laboratory, Richland, Washington

Thrust Area 1: Purification and Biophysical Characterization of MR-1 Redox Proteins (LDRD 1: Specific Aims 5&6)

Y Xiong, Pacific Northwest National Laboratory, Richland, Washington

MK Bowman, University of Alabama, Tuscaloosa, Tuscaloosa, Alabama

Thrust Area 1: Metal-Reducing *Shewanella* Believed to be Involved in the Dissimilatory Reduction of Solid Phase Iron (III)

D Richardson, University of East Anglia, Norwich, United Kingdom

High-Resolution Imaging of the Passive Heart and Cardiac Valves for the Next Generation Cardiac Models

DR Einstein, KR Minard, Pacific Northwest National Laboratory, Richland, Washington

Investigation of Biodegradable and Nonbiodegradable Thermalreversible Gelling Polymers Using Slow Magic Angle Spinning NMR Spectroscopy

J Hu, BJ Tarasevich, Pacific Northwest National Laboratory, Richland, Washington

A Gutowska, Advanced Imaging Technologies, Richland, Washington

Grand Challenge in Membrane Biology

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N Koropatkin, Donald Danforth Plant Science Center, St. Louis, Missouri

T Ogawa, Shanghai Institute of Plant Physiology and Ecology, Shanghai, China

Dissolution of Borosilicate Waste Glass: Effect of Al and B Coordination on Alkali Ion Exchange

EM Pierce, WJ Shaw, Pacific Northwest National Laboratory, Richland, Washington

Structure of Trityls

H Halpern, C Mailer, University of Chicago, Chicago, Illinois

Interrogation of Glucose Metabolism by Oral Biofilms Using Combined NMR/Optical Spectroscopy and Stable Isotope Labeling

RA Wind, JC Scholten, MF Romine, J McLean, PD Majors, Pacific Northwest National Laboratory, Richland, Washington

Combined NMR/Optical Microscopy for Oral Biofilm Physiology Studies

RA Wind, J McLean, PD Majors, Pacific Northwest National Laboratory, Richland, Washington

PNNL Metabolomics Measurement and Validation Development for Renewable Energy Research

JC Scholten, J McLean, PD Majors, Pacific Northwest National Laboratory, Richland, Washington

MRI for Understanding Water Management in PEM Fuel Cells

PC Rieke, VV Viswanathan, L Wang, KR Minard, PD Majors, Pacific Northwest National Laboratory, Richland, Washington

***In vivo* and *ex vivo* High Resolution Slow-MAS MR Spectroscopy in Mice**

RA Wind, Pacific Northwest National Laboratory, Richland, Washington

MR Imaging of Respiratory Structure and Function

KR Minard, R Jacob, Pacific Northwest National Laboratory, Richland, Washington

A Multinuclear MAS NMR Investigation of Environmentally Relevant Materials: Lanthanum Strontium Gallium Magnesium Oxide and Magnesium Aluminum Layered Double Hydroxides

JL Palumbo, PJ Sideris, CP Grey, State University of New York at Stony Brook, stony brook, New York

Structural Investigation of alphaB-Crystallin Core Domains

P Rajagopal, R Klevit, University of Washington, Seattle, Washington

Structural Biology of the Human High Mobility Group A (HMGA) Proteins: Characterizing the Hub of Nuclear Function

RC Reeves, Washington State University, Pullman, Washington

MA Kennedy, Miami University, Oxford, Ohio

GW Buchko, Pacific Northwest National Laboratory, Richland, Washington

Structural Studies of Regulators of Histone Protein Synthesis

R Thapar. University of North Carolina, Chapel Hill, North Carolina

Analysis of Nitrogen in Humic Substances and Photochemical Degradation of TNT

KA Thorn, U.S. Geological Survey, Denver, Colorado

Structural Studies of a Novel Family of Manganese Uptake Proteins in Cyanothece Containing a Repeated Five-Residues Domain (RFR)

MA Kennedy, S Ni, Miami University, Oxford, Ohio

GW Buchko, Pacific Northwest National Laboratory, Richland, Washington

HB Pakrasi, Washington University in St. Louis, St. Louis, Missouri

Structural Studies of a Family of Proteins from the Diurnal Cyanobacteria Cyanothece 51142 that Contain an Unusual Repeated Five-Residues Domain (RFR)

S Ni, MA Kennedy, Miami University, Oxford, Ohio

GW Buchko, Pacific Northwest National Laboratory, Richland, Washington

HB Pakrasi, Washington University in St. Louis, St. Louis, Missouri

Investigation of Crystalline to Amorphous Phase of Cellulose by Using Slow Magic Angle Spinning NMR Spectroscopy

JE Holladay, J Kwak, J Hu, Pacific Northwest National Laboratory, Richland, Washington

Identifying Value Added Products from Biomass Conversion Reactions by NMR

H Zhao, JE Holladay, Pacific Northwest National Laboratory, Richland, Washington

Structure of Designer Proteins
G Varani, Dn Baker, University of Washington, Seattle, Washington

Determining *in vivo* Concentrations of Bacterial Autoinducers

KP Rumbaugh, Texas Tech University, Lubbock, Texas

Elucidation of the NAD Sensing Mechanism of Mitochondrial Apoptosis Inducing Factor

IF Sevrioukova, University of California, Irvine, Irvine, California

Solid State NMR to Investigate Protein Interactions at Interfaces

WJ Shaw, Pacific Northwest National Laboratory, Richland, Washington

The Iron Binding Environment of the Cyanobacterial Ferric Ion Transporter, FutA1

TJ Smith, Donald Danforth Plant Science Center, Saint Louis, Missouri

Non-Invasive Monitoring Of bFGF-Induced Signaling

TJ Weber, Pacific Northwest National Laboratory, Richland, Washington

Characterization of *in-vivo* ^{1}H-NMR Biomarkers for Pulmonary Phospholipidosis

K McAteer, Washington State University, Richland, Washington

J Hu, KR Minard, RA Wind, Pacific Northwest National Laboratory, Richland, Washington

D Rommereim, Environmental Molecular Sciences Laboratory, Richland, Washington

High Resolution ^{1}H NMR Metabolomics Using Slow and Ultra Slow Magic Angle Spinning

Q Zhang, TO Metz, Jn Hu, KR Minard, M Murphy, K Thrall, A Woodstock, GW Buchko, Pacific Northwest National Laboratory, Richland, Washington

D Rommereim, J Sears, Environmental Molecular Sciences Laboratory, Richland, Washington

J Caceres-Cortes, Bristol-Myers Squibb, Lawrenceville, New Jersey

Pulsed EPR Studies of Nanocrystalline Zeolites and Hollow Zeolite Structures

SC Larsen, University of Iowa, Iowa City, Iowa

High-resolution ^{27}Al MAS NMR of Weathered Clays and Hanford Sediments

GM Bowers, Michigan State University, East Lansing, Michigan

KT Mueller, CR Strepka, MC Davis, Pennsylvania State University, University Park, Pennsylvania

Binding Environment of Strontium-87 Nuclei in DOE Waste Remediation Materials

GM Bowers, Michigan State University, East Lansing, Michigan

KT Mueller, CR Strepka, MC Davis, Pennsylvania State University, University Park, Pennsylvania

Solid-State NMR Characterization of the Surface Sites of Alumina Nanofibers

JL Cross, MP Espe, University of Akron, Akron, Ohio

The Mechanism of Action of Carbonic Anhydrase and LpxC

AS Lipton, PD Ellis, R Heck, Pacific Northwest National Laboratory, Richland, Washington

CA Fierke, M Hernick, University of Michigan, Ann Arbor, Michigan

Conformational Dynamics of Pin1 Regulation of APP processing and Abeta Production

LK Nicholson, Cornell University, Ithaca, New York

Source Attribution of Biological Weapons (Ricin and Associated Metabolites) Using NMR Spectroscopy

GW Buchko, HM Cho, J Cort, HW Kreuzer, Pacific Northwest National Laboratory, Richland, Washington

Metabonomic Studies of Host Response to *Yersinia pestis* Exposure through Analysis of Plasma and Urine from Mice

K McAteer, Washington State University, Richland, Washington

MA Kennedy, Miami University, Oxford, Ohio

NMR Assignment & Structure of the C-Terminal Domains of Human Villin

CJ Mcknight, S Smirnov, Boston University School of Medicine, Boston, Massachusetts

^{99}Tc NMR Study of Tc(V) Solids

HM Cho, NJ Hess, Pacific Northwest National Laboratory, Richland, Washington

WA De Jong, Environmental Molecular Sciences Laboratory, Richland, Washington

Reversible Organic Derivatization of Silica: Development of New Methods for Creating Template Imprinted Surfaces

JP Deluca, RM Jorgensen, Central Washington University, Ellensburg, Washington

Solid State NMR Studies of Nano-Materials

L Wang, Pacific Northwest National Laboratory, Richland, Washington

NMR and Computational Studies of Chemical Transformations at Complex Interfaces

E Iglesia, A Bhan, B Temel, University of California, Berkeley, Berkeley, California

J Hu, CH Peden, Pacific Northwest National Laboratory, Richland, Washington

DA Dixon, R Craciun, S Li, M Hernandez Matus, University of Alabama, Tuscaloosa, Tuscaloosa, Alabama

H Zheng, Dalian Institute of Chemical Physics, CAS, Dalian, China

Clusters of Damage in Irradiated DNA

MD Sevilla, D Becker, Oakland University, Rochester, Michigan

JD Zimbrick, Colorado State University, Fort Collins, Colorado

MK Bowman, University of Alabama, Tuscaloosa, Tuscaloosa, Alabama

Free Radical Reactions in the Catalytic Cycle of Cytochrome bc Complexes

DM Kramer, JL Cape, IP Forquer, Washington State University, Pullman, Washington

TP Straatsma, Pacific Northwest National Laboratory, Richland, Washington

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Correlation of Structure and Function of Zinc Metalloproteins via a Combined NMR/Molecular Theory Approach

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CA Fierke, M Hernick, J Penner-Hahn, University of Michigan, Ann Arbor, Michigan

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Solution Structure of a 42 kDa "Metal Sensor" CzrA-DNA Complex

DP Giedroc, Indiana University - Bloomington, Bloomington, Indiana

AK Alphonse Ignatius, Texas A&M University, College Station, Texas

Protein Interactions and Interfaces

G Montelione, Rutgers University, New Brunswick, New Jersey

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J Cort, GW Buchko, Pacific Northwest National Laboratory, Richland, Washington

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Structural Engineering of the *de novo* Designed Protein Top7 as a Scaffold for Antigen-Binding

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Structure-Function Correlations of Proteins in Enamel Formation

WJ Shaw, BJ Tarasevich, GW Buchko, Pacific Northwest National Laboratory, Richland, Washington

ML Snead, University of Southern California, Los Angeles, California

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Solid-State NMR Spectroscopy on Radioactive Samples with Microcoils

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D Sakellariou, CEA Saclay, Gif-sur-Yvette, France

Local Structure in Zirconia-Based Nuclear Fuels and Transmutation Targets

I Farnan, University of Cambridge, Cambridge, United Kingdom

J Somers, European Commission Joint Research Centre, Karlsruhe, Germany,

NMR Studies of ^{207}Pb in Ferroelectric Powders

D Budker, AO Sushkov, LS Bouchard, C Qian, University of California, Berkeley, Berkeley, California

NMR Studies of Human Apolipoprotein-E

J Wang, S Shin, B Chen, J Chen, C Li, Y Zhang, Wayne State University, Detroit, Michigan

GM Bowers, RJ Kirkpatrick, Michigan State University, East Lansing, Michigan

Triple Resonance and Relaxation Dispersion Studies of the Enzyme Phosphomannomutase/Phosphoglucomutase

SR Van Doren, LJ Beamer, University of Missouri, Columbia, Columbia, Missouri

Analysis of Zinc Environments in Singlet Oxygen-Responsive Proteins

AS Lipton, Pacific Northwest National Laboratory, Richland, Washington

TJ Donohue, University of Wisconsin-Madison, MADISON, Wisconsin

Measuring Nanometer Distances in the Packaging RNA using Double Electron-Electron Resonance

PZ Qin, G Sowa, Q Cai, GG Grant, A Popova, University of Southern California, Los Angeles, California

MK Bowman, University of Alabama, Tuscaloosa, Tuscaloosa, Alabama

High-Field Static QCPMG ^{47}Ti and ^{49}Ti Studies of Nanoparticulate TiO_2

SE Hayes, Washington University in St. Louis, Saint Louis, Missouri

Thyroid Regulation of Cardiac Metabolism

OM Hyyti, University of Washington, Seattle, Washington

MA Portman, Children's Hospital and Regional Medical Center, Seattle, Washington

Cell Metabolism and c-Myc-Induced Growth, Proliferation and Neoplasia

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Elucidating the Structure of Surface Species on Heterogeneous Catalysts

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Surface Selective Studies of Olivine Dissolution by ^{1}H-^{29}Si and ^{25}Mg MAS NMR

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Low Temperature (10K) 25Mg Solid-State NMR of DNA Repair Proteins and Their Complexes

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NMR Microscopy of Diffusive Transport in Natural Porous Mineral Grains

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A Metabolomic and Metabolic Flux Analysis Approach for Improving Hydrogen Production During Cellulose Fermentation

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Imaging Respiratory Structure and Function in Laboratory Animals

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MRI of Chronic Obstructive Pulmonary Disease

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Combined NMR/Optical Microscopy of Biofilm Physiology Studies

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Imaging Of Water and Gas Distribution in PEM Fuel Cell Stacks and Cells

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Structure of the PR Domain of RIZ1 Tumor Suppressor

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Structural Biology of the Human High Mobility Group A (HMGA) Proteins

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Investigation of the Role of Mg^{2+} in DNA Repair Proteins

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Investigation of Soot Morphology and Microstructure with Respect to the Oxidation

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Development of Organophosphorus Compounds for Solid-State Lighting Applications

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NMR for Catalyst Studies

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Membrane-Organized Chemical Photoredox Systems (DE-FG03-99ER14943)

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High-Performance Mass Spectrometry Facility

The High-Performance Mass Spectrometry Facility (HPMSF) provides state-of-the-art mass spectrometry (MS) and separations instrumentation that has been refined for leading-edge analysis of biological problems with a primary emphasis on proteomics. Challenging research in proteomics, cell signaling, cellular molecular machines, and high-molecular weight systems receive the highest priority for access to the facility. Current research activities in the HPMSF include proteomic analyses of whole cell lysates, analyses of macro-molecules, protein complexes and assemblies, quantification using various stable isotope labeling methods (e.g., metabolic or chemical labeling) or MS-peak intensities (i.e., label-free), targeted proteomics analyses of subcellular fractions, and detection of post-translational modifications (PTM) such as phosphorylation. More than two dozen microbial systems are currently being studied in HPMSF by researchers from throughout the country. In addition, there are several ongoing projects in higher order systems (including mammalian systems) that are investigating a broad range of biological questions from cancer screening to infectious diseases to fundamental questions on protein PTMs and protein-protein interactions.

Capabilities

The facility features state-of-the-art liquid chromatographic (LC) separations capabilities coupled to a complete suite of mass spectrometers for proteomics analysis. The available instruments range from a group of nine ion trap spectrometers for tandem mass spectrometry (MS/MS) work to high-performance Fourier transform ion cyclotron resonance (FTICR) spectrometers, which offer unparalleled mass measurement accuracy (>1 ppm) and mass resolving power (>100,000). Proteomics analysis on FTICR spectrometers is complemented by a quadrupole time-of-flight (QTOF) spectrometer that combines MS/MS analysis with high mass measurement accuracy. These spectrometers are coupled with very high-resolution separations (500-1000 peak capacity) that are highly beneficial to various areas of research.

The HPMSF is committed to maintaining state-of-the-art MS and separations capabilities. To this end, the facility's staff work to develop and implement new capabilities such as the ion funnel, Dynamic

Instrumentation & Capabilities

FT MS

- 7, 9.4, 11.5 and 12-T FTICR spectrometers
- 7T LTQ-FT
- Three Orbitraps™

Other MS

- Q-TOFFive ion trap spectrometers
- Four linear ion trap mass spectrometers
- Triple-quadrupole

Additional Capabilities

- Fifteen custom high-performance liquid chromatography (HPLC) systems
- Three Agilent capillary HPLC system
- Triversa NanoMate

Range Enhancement Applied to Mass Spectrometry (DREAMS), “smart” MS and MS^n capabilities and data analysis tools, all of which are incorporated into the capabilities of the facility as they become available. As part of this commitment, the facility added a 12-T FTICR spectrometer, which is being optimized for work on intact proteins for the identification of post-translational modifications and protein isoforms. In addition, Orbitrap™ mass spectrometers were recently added to the facility. This exciting new type of mass analyzer provides performance similar to the FTICR spectrometers but without the need for a superconducting magnet.

The members of the facility staff are highly skilled in all areas required for proteomics research, from sample preparation to analysis and data interpretation, and they are available to help develop methodologies to tackle these challenging problems. As needed, scientific staff not assigned to the facility can be accessed as matrixed members of the facility. Since its inception, more than 250 separate user projects have been undertaken in the facility, with some spanning over a year in duration.

An additional component integral to the HPMSF is the informatics support required to manage and analyze the large volumes of data generated. An in-house-developed relational database, Proteomics Research Information Storage and Management (PRISM) system, is used to manage downstream informatics data flow. This system integrates assorted algorithms and software tools (including in-house developed ICR-2LS, Decon2LS and VIPER, commercially available SEQUEST and MASCOT, and open source X!Tandem) to store, process, and reduce proteomic data to interpretable information. In addition, the HPMSF has developed state-of-the-art software for the acquisition of FTICR mass spectra. This Windows-based application enables many of the unique instrument control functions developed at EMSL.

Mass Spectrometry Research Capabilities

Ion Trap Mass Sectrometers. Nine ion trap MSs from ThermoFisher are available in the facility: two LCQ Classics, two LCQ Duos, one LCQ DECAXP, and four LTQs that provide greater than an order of magnitude improvement in dynamic range in comparison to LCQs. An example of one of these instruments is shown in Figure 1.

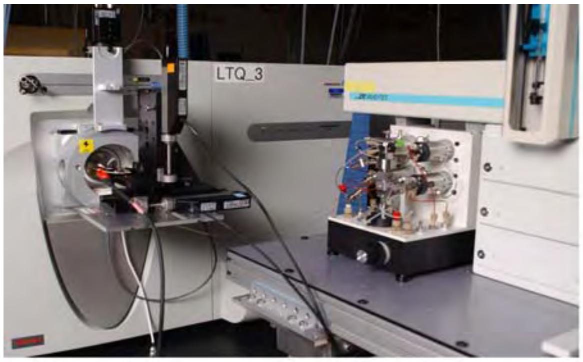

***Figure 1**. Ion trap MS in an HPMSF laboratory.*

The ion trap instruments have either a three-dimensional quadrupole ion-trap or a two-dimensional elongated trap designed for use with electrospray ionization sources. These instruments are well-suited to MS/MS spectrometer experiments because of their very high collection efficiency for product ions. The m/z range of this instrument is typically 150 - 2000, but it can be extended to m/z =4000 when necessary. The ion trap instruments have a maximum resolution of 10,000 in the zoom-scan mode, and 4000 in full-scan mode. In addition, the system is easily operated in either positive or negative ion mode with the addition of SF_6 as a sheath gas. These instruments are set up and run in production mode.

Fourier Transform Ion Cyclotron Resonance Mass Spectrometers. The 11.5-T ultrahigh-performance MS uses a wide-bore (205 mm), passively shielded (Figure 2) superconducting magnet. The spectrometer is equipped with an electrospray ionization source and an ion funnel. The 11.5-T FTICR has a resolution of >100,000 (at m/z ~1000) and a mass accuracy in the range of 1 ppm for peptide samples with molecular weights ranging from 500 to ~5000 Da. Ions are collected externally to the magnet in a series of quadrupoles that allow the researcher to eliminate irrelevant ions before analysis in the FTICR spectrometer. The 11.5-T FTICR instrument can be fitted with an HPLC system and with an infrared laser for multiphoton dissociation of ions in the ion cyclotron resonance (ICR) cell.

***Figure 2**. Wide-bore, passively shielded 11.5-T FTICR MS.*

The 9.4-T FTICR spectrometer (Figure 3) is a 150-mm-bore, actively shielded Bruker Daltonics APEX III. The original ion source has been replaced with a custom source that incorporates a dual-channel ion funnel for simultaneous introduction of calibrant ions, DREAMS technology, and automatic gain control. These modifications permit maximum use of the spectrometer's capabilities by maintaining the optimum number of ions in the ICR cell throughout an LC separation. The outstanding resolution of over 60,000 is maintained throughout the separation with a sensitivity comparable to the other FTICR instruments in the facility.

***Figure 3**. 150-mm-bore, actively shielded 9.4-T FTICR instrument.*

The HPMSF also houses a 7-T ThermoFinnigan LTQ-FT, a fusion of the linear ion trap-type mass spectrometer and the FTICR-MS. The two modes can be operated separately or together offering unique flexibility in the development of experiments in the laboratory.

FT Mass Spectrometers. HPMSF houses three ThermoFisher LTQ-Oribitrap spectrometers. These instruments are a fusion of the linear ion trap-type mass spectrometer with a new Orbitrap mass analyzer that combines the MS/MS based fragmentation of the linear ion trap with stable high sensitivity and mass accuracy of the Orbitrap component. The LTQ-Orbitrap provides the best sensitivity, mass accuracy, and mass resolution available, all of which are critical analytical measures for achieving success in the field of proteomic research.

LTQ-Orbitraps, LTQ-FT, 11.5-T and 9.4-T FTICR spectrometers are seamlessly integrated with the facility's automated HPLC (5000 psi) system for unattended operation 24 hours a day, 7 days a week.

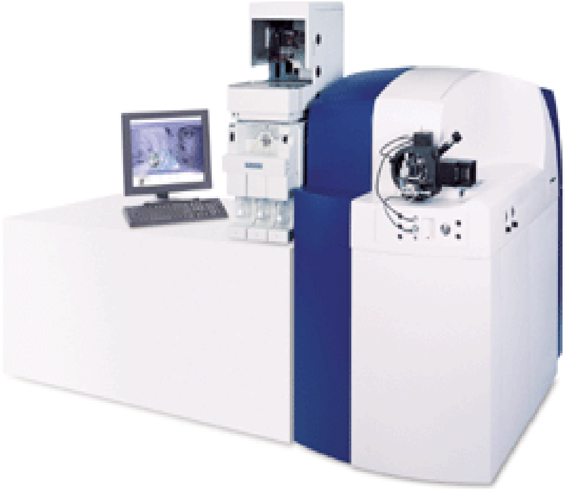

Figure 4. QTOF instrument in the HPMSF.

The Waters' Micromass Ultima application program interface (API) QTOF instrument is an orthogonal extraction-TOF MS that has enabled automated exact mass measurement with the ultimate performance (Figure 4) in MS and MS/MS. The instrument features optimized resolution, enhanced ion optics for enhanced sensitivity, a quadrupole mass filter, and a collision cell for MS/MS analyses. These features are also accessible over an enhanced linear dynamic range, enabling rapid and reliable quantification. This powerful combination of capabilities delivers simple exact mass measurement of precursor and fragment ions with maximum sensitivity to yield the highest confidence in structural elucidation and databank search results.

Figure 5. Capillary ultrahigh pressure separations capability.

A signature capability of the facility is the efficient coupling of capillary separations (Figure 5) to various mass spectrometers. Instruments for both LC and capillary electrophoretic separations are available. In-house-developed capillary HPLC systems are available for nano-scale protein and peptide separations. Advanced biological separation capabilities are available for producing unique and sophisticated separations of biomiolecules for the following pressure régimes: high-pressure liquid chromatography (HPLC; ≤5000 psi); very high-pressure LC (VHPLC; ~10,000 psi); and ultra high-pressure LC (HPLC; ~20,000 psi). Additional capabilities are available for packing custom LC columns in a wide range of lengths (10 – 2000 mm), internal diameters (10 μm to 1 mm), and for a wide range of chemistries and separations modes (reversed-phase, ion-exchange, size-exclusion, etc.). LC systems for 1-D and 2-D proteomics separations, on-line sample clean-up, on-line concentration, and ultra-low-level LC/MS analyses of proteolytic digests have been developed along with unique systems automation and integration capabilities. Continuing developments of high-pressure LC systems feature a PAL autosampler with cooled sample holder, VALCO high-pressure valves, and ISCO syringe pumps. Computer software has been developed that allows the system to be configured with any of our spectrometers through DCOM communication protocols.

The 7-T FTICR spectrometer is based on a 160-mm-bore, superconducting magnet. This instrument incorporates an ESI ion source with an ion funnel, an RF quadrupole for collisional focusing followed by RF quadrupoles for ion selection, external accumulation, and ion guidance to the ICR cell. The vacuum chamber of this instrument employs a custom cryopanel-pump assembly, which provides extremely high pumping speeds enabling online applications. The instrument is currently used for "smart" data-directed LC-MS/MS research. (Figure 6).

***Figure 6**. 7-T FTICR spectrometer.*

The 12-T FTICR (Figure 7) has a 100-mm-bore magnet that is actively shielded. The original ion optics have been upgraded to include an ion funnel and additional quadrupole stages for enhanced ion transmission and future implementation of data-directed ion selection for MS/MS studies. The system is being optimized for comprehensive high-throughput profiling (i.e., accurate mass measurements and quantitation) of intact proteins. Additionally, a "top-down" protein characterization using a variety of dissociation schemes, such as collisionally induced and electron capture dissociation, can be performed on this spectrometer. Protein separation schemes based on reversed-phase capillary LC, CIEF, and high-field asymmetric ion mobility spectrometry are in use and/or under development with this system.

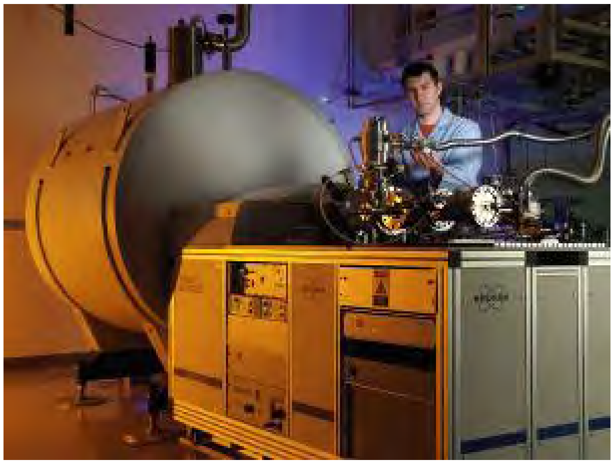

***Figure 7**. 12-T FTICR spectrometer.*

Instrument Upgrades

In Fiscal Year 2007, the following capability development and procurement activities occurred in the HPMSF:

- A **ThermoFisher LTQ-Oribitrap** spectrometer was installed in EMSL in July 2007. This instrument is now fully functional and is providing much needed additional throughput for analysis of proteomic samples. Funding for this instrument was provided by a National Institutes of General Medical Sciences Glue Grant titled, "Inflammation and the Host Response to Injury."

- A new **ThermoFisher TSQ Quantum Ultra triple-quadrupole mass spectrometer** was installed in September 2006. This instrument is now fully functional and is providing much needed multiple reaction monitoring (MRM) for targeted proteomic analysis. Among instruments available for this kind of analysis, the TSQ-Quantum Ultra provides the best mass accuracy and mass resolution available. The TSQ Quantum was also the only commercially available platform with FAIMS incorporated. (Recently, FAIMS has also been introduced as an option for ThemoFisher LTQ instruments.) The application of FAIMS to MRM measurements should reduce the chemical noise background resulting in increased S/N and lower limits of detection. Funding for this instrument was provided from the Entertainment Industry Foundation (EIF) Women's Cancer Research Fund and is one of three major initiatives within EIF's Women Cancer Programs. The EIF is a non-government foundation and the work funded by the foundation focuses on the early diagnosis of breast cancer through the use of biomarkers. The TSQ Quantum is used to validate potential biomarkers identified by the EMSL high-throughput proteomics platform.

- **Triversa NanoMate:** This system has been incorporated into EMSL's novel integrated top-down and bottom-up approaches to enable concurrent liquid chromatography-mass spectrometry analysis and fraction collection for comprehensive high-throughput intact protein profiling. The approach employs high-resolution, reversed-phase liquid chromatography separations coupled online with a 12-Tesla Fourier transform ion cyclotron resonance spectrometer to profile and identify modified proteins.

Mass Spectrometry Identification of Endogenously Nitrated Proteins in Mouse Brain: Links to Neurodegenerative Disease

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(b) UCLA School of Medicine, Los Angeles, California

Parkinson's, Alzheimer's, and Lou Gehrig's diseases and other brain disorders are among a growing list of maladies attributed to oxidative stress, which is the cell damage caused during metabolism when oxygen in the body assumes ever more chemically reactive forms. EMSL mass spectrometry capabilities were used to identify proteins sensitive to nitrating conditions in vivo, resulting in a dataset in which more than half the proteins were indicated in neurodegenerative disorders.

Increased nitrotyrosine modifications of proteins have been documented in multiple pathologies in a variety of tissue types linked to oxidative stress, as well as playing a role in the redox regulation of normal metabolism. To identify proteins sensitive to nitrating conditions *in vivo*, a comprehensive proteomic survey of the whole mouse brain using liquid chomatography/liquid chomatography-mass spectroscopy/mass spectroscopy (LC/LC-MS/MS) analyses was performed. This effort generated a mammalian brain dataset in which 7792 proteins were identified (Figure 1) (Sacksteder et al. 2006).

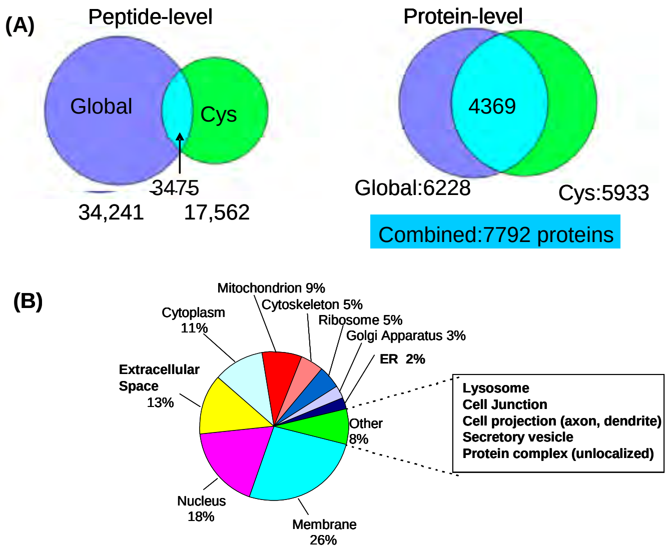
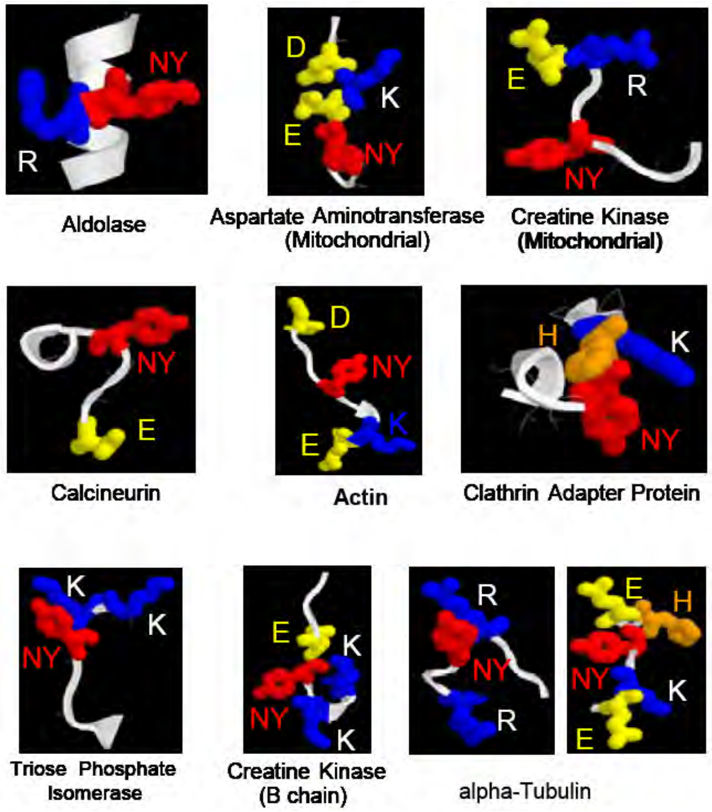


Figure 1. *Extensive mouse brain proteome coverage from two-dimensional LC/LC-MS/MS analyses.*

This large-scale analysis resulted in the identification of 31 unique nitrotyrosine sites within 29 different proteins. Over half of the nitrated proteins identified are involved in Parkinson’s disease, Alzheimer’s disease, or other neurodegenerative disorders. Similarly, nitrotyrosine immunoblots of whole-brain homogenates show that treatment of mice with 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine, an experi-mental model of Parkinson’s disease, induces increased nitration of the same protein bands observed to be nitrated in brains of untreated animals. Comparing sequences and available high-resolution structures around nitrated tyrosines with those of unmodified sites indicates a preference of nitration *in vivo* for surface-accessible tyrosines in loops, a characteristic consistent with peroxynitrite-induced tyrosine modification (Figure 2). In addition, most sequences contain cysteines or methionines proximal to nitrotyrosines, contrary to suggestions that these amino acid side chains prevent tyrosine nitration. More striking is the presence of a positively charged moiety near the sites of nitration, which is not observed for non-nitrated tyrosines. Together, these observations suggest a predictive tool of functionally important sites of nitration and that cellular nitrating conditions play a role in neurodegenerative changes in the brain. Future studies should extend these proteomic measurements to consider the relationship between protein nitration and specific neurodegenerative diseases as well as tyrosine-kinase-signaling pathways.



Aldolase

Aspartate Aminotransferase (Mitochondrial)

Creatine Kinase (Mitochondrial)

Calcineurin

Actin

Clathrin Adapter Protein

Triose Phosphate Isomerase

Creatine Kinase (B chain)

alpha-Tubulin

Figure 2. *Three-dimensional structures around nitrotyrosines in identified proteins.*

Citation

Sacksteder CA, WJ Qian, TV Knyushko, H Wang, MH Chin, G Lacan, WP Melega, DG Camp, RD Smith, DJ Smith, TC Squier, and DJ Bigelow. 2006. “Endogenously Nitrated Proteins in Mouse Brain: Links to Neurodegenerative Disease.” *Biochemistry* 45(26):8009-8022.

Comparing Proteomics Analysis of Nipple Aspirate Fluids: Discovering Biomarkers for Early Detection of Breast Cancer

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(b) University of Texas M.D. Anderson Cancer Center, Houston, Texas
(c) Fred Hutchinson Cancer Research Center, Seattle, Washington

This study represents the largest scale characterization of the nipple aspirate fluid proteome to date. The in-depth comparison of nipple aspirate fluid from cancerous and contralateral non-cancerous breasts of women with early-stage breast cancer provides a basis for early detection of breast cancer.

Breast cancer is the most common type of cancer and the second leading cause of cancer deaths in women in the United States. Presymptomatic screening to detect early-stage breast cancer could potentially reduce breast cancer-related mortality. Unfortunately, currently available breast cancer screening tools such as mammography and breast examination miss up to 40 percent of early-stage breast cancers. In addition, an invasive biopsy (e.g., needle or surgical biopsy) must typically be performed to confirm the presence of malignant disease by cytologic or histologic evaluation, if an area of suspicion is identified by the screening. Therefore, it is of crucial importance to develop noninvasive techniques that would complement current methodologies for the detection and prognosis of small breast lesions at the molecular level, providing a significant opportunity to distinguish between malignant and benign lesions and to treat a neoplasm before it invades the tissue.

The breast epithelium exfoliates cells as a renewal of tissue and secrets fluids into its ductal and lobular system, where most breast carcinomas (approximately 70 to 80 percent) originate. Using a handheld suction cup, this breast fluid can be extracted noninvasively through the nipple and is thus referred to as nipple aspirate fluid (NAF). Compared with serum/plasma, proximal fluids from the breast potentially offer a superior source of biomarkers for breast cancer because the proteins present are specifically released from breast tumor tissue. Several studies have indicated that NAF contains potentially diagnostic or prognostic markers of breast cancer and, in particular, the application of proteomics for developing more specific biomarkers appears to be promising (Varnum et al. 2003; Alexander et al. 2004; Pawlik et al. 2006). However, these studies provided only very limited NAF protein identifications (<100), presumably because of the low protein yields and the high dynamic range of protein abundances in the breast fluid.

In this study, NAF samples from 15 early-stage breast cancer patients were used to generate a pooled sample using NAF from the diseased breast and a non-cancerous pool using NAF from the contralateral disease-free breast. The overall comparative proteomics strategy is depicted in Figure 1. To improve the detection in downstream proteomics analysis, 12 proteins of high abundance were initially removed from both the cancerous and non-cancerous NAF pools separately by applying an IgY-12 immunoaffinity depletion chromatography step. Both the flow-through (i.e., lower abundance proteins) and the bound (i.e., the 12 high-abundance proteins and potentially other proteins that bind through mechanisms such as protein-protein interaction) portions were subjected to trypsin digestion. Next, the resulting tryptic peptides were separated into cysteinyl peptides and non-cysteinyl peptides through the cysteinyl peptide enrichment (CPE) procedure, followed by strong cation exchange chromatography (SCX) fractionation and LC-MS/MS analyses.

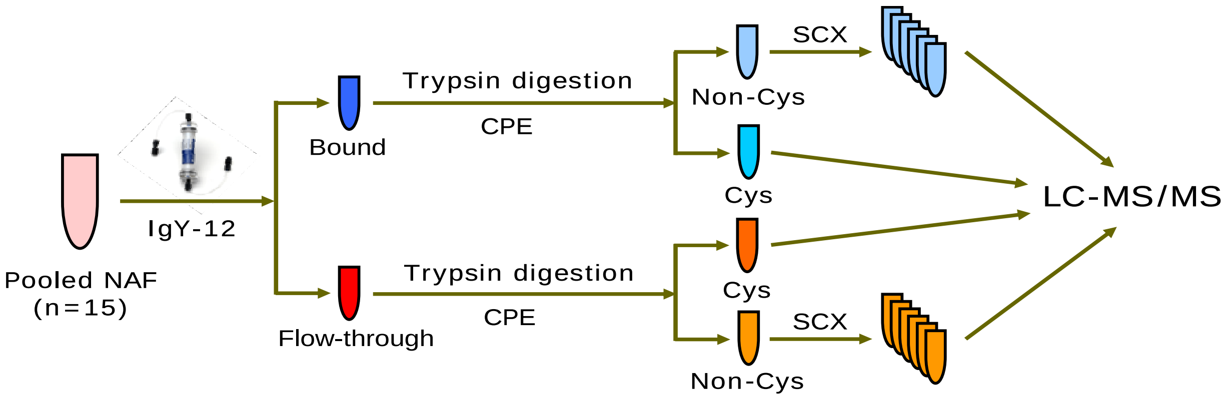

Figure 1. *Schematic illustration of large-scale analysis of NAF by liquid chromatography-tandem mass spectroscopy (LC-MS/MS).*

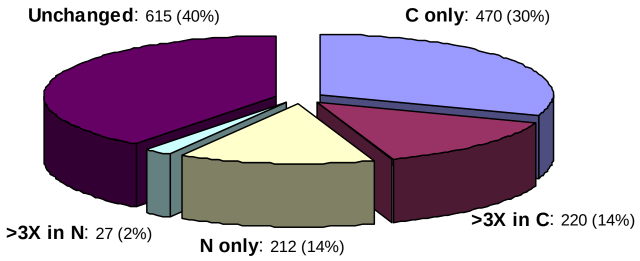

Figure 2. *Differential expression of NAF proteins.* ***N*** *= normal contra-lateral NAF;* ***C*** *= cancerous NAF.*

The highly effective combination of immunoaffinity depletion, in-depth fractionation, and ultrahigh resolution LC separation employed in this study led to the confident identification of a total of 11,364 unique peptides and 1997 non-redundant proteins, representing the most comprehensive proteome coverage to date for human NAF. Significantly, comparative analysis of the IgY-12 flow-through proteins using spectrum counting revealed 470 proteins expressed solely in the cancerous NAF, exemplified by ErbB-3, which has been previously found over-expressed in breast carcinomas using real-time quantitative RT-PCR assays. A group of 220 proteins displayed greater than a threefold increase in abundance in the cancerous NAF (Figure 2). Many over-expressed proteins detected in this investigation are known to be correlated to breast carcinomas from previous studies that measured either their mRNA levels using microarray or protein levels using ELISA. It is anticipated that NAF proximal fluid analysis in conjunction with the proteomic analysis of other breast tissue-derived samples (e.g., tumor interstitial fluid, ductal lavage fluid) that additional specific and sensitive breast cancer biomarkers can be discovered. The subsequent pre-clinical validation of these candidate biomarkers through the application of affinity reagents in combination with either multi-protein biomarker panels or multiple reaction monitoring (MRM) experiments would thereby advance the goal of early detection of breast cancer through a blood test.

Citations

Alexander H, AL Stegner, C Wagner-Mann, GC Du Bois, S Alexander, and ER Sauter. 2004. "Proteomic Analysis to Identify Breast Cancer Biomarkers in Nipple Aspirate Fluid." *Clinical Cancer Research* 10(22):7500-7510.

Pawlik TM, DH Hawke, Y Liu, S Krishnamurthy, H Fritsche, KK Hunt, and HM Kuerer. 2006. "Proteomic Analysis Of Nipple Aspirate Fluid from Women with Early-Stage Breast Cancer Using Isotope-Coded Affinity Tags and Tandem Mass Spectrometry Reveals Differential Expression of Vitamin D Binding Protein." *BMC Cancer* 66(68)8-77.

Varnum SM, CC Covington, RL Woodbury, K Petritis, LJ Kangas, MS Abdullah, JG Pounds, RD Smith, and RC Zangar. 2003. "Proteomic Characterization of Nipple Aspirate Fluid: Identification of Potential Biomarkers of Breast Cancer." *Breast Cancer Research and Treatment* 80(1):87-97.

Proteomic Comparison between Virulent and Avirulent *Burkholderia mallei* Strains

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The bacterium Burkholderia mallei can cause severe human illness and has been classified by the Centers for Disease Control and Prevention as a category B agent in the list of potential bioterrorism agents. Differentiating between virulent and avirulent B. mallei strains is difficult, which complicates subsequent treatment and threat assessment. This work is using EMSL's high-throughput proteomics capabilities to compare the virulent and avirulent strains to reveal information as to the source of virulence.

Although most of the 30 species of *Burkholderia* bacteria are saprophytes or plant pathogens, two species pose a significant threat to animal and human health. One species, *B. pseudomallei*, the causative agent for the infectious disease melliodosis, affects populations throughout Southeast Asia and Australia. The other species, *B. mallei*, is primarily an animal pathogen and is the causative agent of the disease known as glanders. This worldwide disease poses a significant health threat to cystic fibrosis patients and immunocompromised individuals, and is considered a potential biowarfare agent (Huelseweh et al. 2006). While several avirulent strains of *B. mallei* are known to exist, the source of attenuation is not. Currently, there is no rapid discriminating diagnostic assay, vaccine, or reliable therapy for *B. mallei*; high DNA homology severely limits the ability to distinguish avirulent and virulent strains by standard molecular biology techniques.

We hypothesize that several virulence factors account for the differential pathogenicity of *B. mallei* strains. To test this hypothesis, we are using a high-throughput liquid chromatography-mass spectrometry-based approach (Hixson et al. 2006; Zimmer et al. 2006) to compare proteins expressed in the virulent ATCC 23344 strain with those expressed by the nonvirulent NCTC 10247 strain and to identify differences in protein expression and abundance under identical *in vitro* growth conditions. The genome of *B. mallei* ATCC 23344 has been fully sequenced and known to contain several common virulence factors, including a type-III secretion system, lipopolysaccharide (LPS)-biosynthesis genes, iron-response genes, quorum-sensing elements, integration host factor (*ihf*A and *ihf*B), and genes that respond to reactive oxygen or nitrogen intermediates.

Using this approach, we detected and quantified 751 proteins, from which 126 exhibited a twofold abundance difference ($p \leq 0.05$) between the avirulent and virulent strains (Figure 1). Thirty-one unique proteins were observed in the virulent ATCC 23344 strain, and of these, three proteins— 1) integration host factor B, 2) ferreodoxin (Rivera-Marrero et al. 1998), and 3) the chemotaxis protein CheZ (Lee et al. 2001)—have properties identified as virulence factors in other systems. Additionally, the LPS biosynthesis proteins were fivefold more abundant in the virulent strain. Analysis of the avirulent NCTC 10247 strain revealed 135 uniquely expressed proteins, of which more than 10 percent have annotations as conserved hypothetical genes (i.e., no known functions) and are ideal targets for further genetic and molecular biological assays.

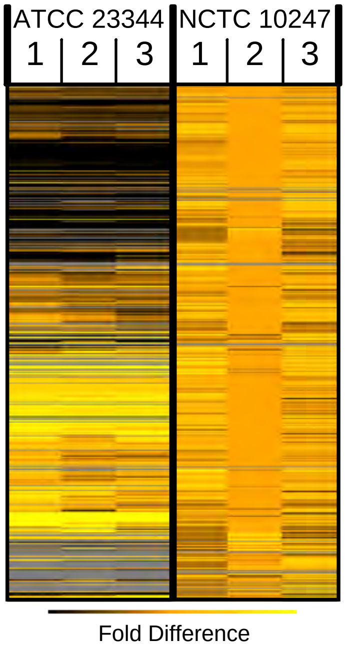

Figure 1. *Relative abundance data plot for 751 proteins from B. mallei global proteome digestion, triplicate analysis. Mass spectrometry intensity values were normalized to ribosomal protein abundances, avirulent strain NCTC 10247 was used as the baseline comparator. Results show significant differences between the virulent and avirulent strains, which may lead to further discovery or development of clinical biomarkers.*

Although this work has just recently begun, peptides examined from a global preparation of *Burkholderia* grown *in vitro* have already revealed key differences in protein expression between strains of *B. mallei*. Remaining work will examine peptides from the cytoplasm and membrane components of these two strains.

Citations

Hixson KK, JN Adkins, SE Baker, RJ Moore, BA Chromy, RD Smith, SL Mc-Cutchen-Maloney
and MS Lipton. 2006. "Biomarker Candidate Identification in*Yersinia pestis* using Organism-Wide Semiquantitative Proteomics." *Journal of Proteome Research* 5(11):3008-3017.

Huelseweh B, R Ehricht, H-J Marschall. 2006. "A Simple and Rapid Protein Array Based Method for the Simultaneous Detection of Biowarfare Agents." *Proteomics* 6(10):2972-2981.

Lee SH, SM Butler, A Camilli. 2001. "Selection for *In Vivo* Regulators of Bacterial Virulence." *Proceedings of the Nationall Academy of Sciences USA* 98(12):6889-6894.

Rivera-Marrero CA, MA Burroughs, RA Masse, FO Vannberg, DL Leimbach, J Roman and JJ Murtagh. 1998. "Identification of Genes Differentially Expressed in *Mycobacterium tuberculosis* by Differential Display PCR." *Microbial Pathology* 25(6):307-316.

Zimmer JS, 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 Review* 25(3):450-482.

Probing Oxidative Stress Using Intact-Protein, High-Field LC-FTICR Mass Spectrometry

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Mechanisms that regulate the removal of nitrated and oxidized proteins in cells are critical for preventing a number of diseases (such as diabetes, cardiovascular disease, cancer, and neurological disorders), as well as for reducing the effects of aging. In this work, we used high-resolution liquid chromatography (LC) separations in conjunction with high-mass-measurement accuracy and high-resolution measurements afforded by 12 tesla Fourier transform ion cyclotron resonance (FTICR) mass spectrometer in the EMSL High-Performance Mass Spectrometry Facility to probe oxidative stress in calmodulin, which is a signaling protein in macrophages. Importantly, we identified a novel oxidation-dependent lysine cleavage that potentially acts as a biomarker of oxidative stress

Oxidative species not only mediate static and cidal effects on a variety of pathogens, but also nitrate and oxidize host proteins during the immune response. These post-translational modifications (PTMs) to intracellular proteins in various inflammatory states also are implicated in many age-related diseases. In this context, the accumulation of nitrotyrosines in proteins may result from an aberrant repair pathway. Previous works have postulated denitrase activity in various tissues based on the loss of immunoreactivity involving antibodies against nitrotyrosine. However, attributing the loss in immunoreactivity to denitration is equivocal, as this effect may be caused by degradation of the nitrated protein, alterations in protein structure that cover the epitope, chemical alteration of the nitrotyrosine, and/or enzymatic denitration.

Characterization of the product following denitration and corresponding loss of immunoreactivity requires the use of an analytical tool that can confirm the involvement of specific proteins, thereby ruling out the ambiguous interpretations based on antibody recognition.

We used intact protein reversed phase LC-FTICR mass spectrometry to monitor the time dependent changes in the nitration of calmodulin (nYCaM) in macrophages following macrophage activation with lipopoly-saccharide endotoxin (Figure 1). Tentative identifications of PTMs were assigned by combining tryptic peptide information generated from bottom-up analyses with online collision-induced dissociation tandem mass spectrometry at the intact protein level, which confirmed localization of the nitrated sites. Our results indicate that macrophage activation associated with an oxidative burst stimulates a dramatic reduction in the abundance and diversity of oxidatively modified proteins. More specifically, we established that macrophage repair pathways can repair nitrated tyrosines and oxidized methionines within a signaling protein (i.e., calmodulin) to their original unmodified states to retain optimal protein function.

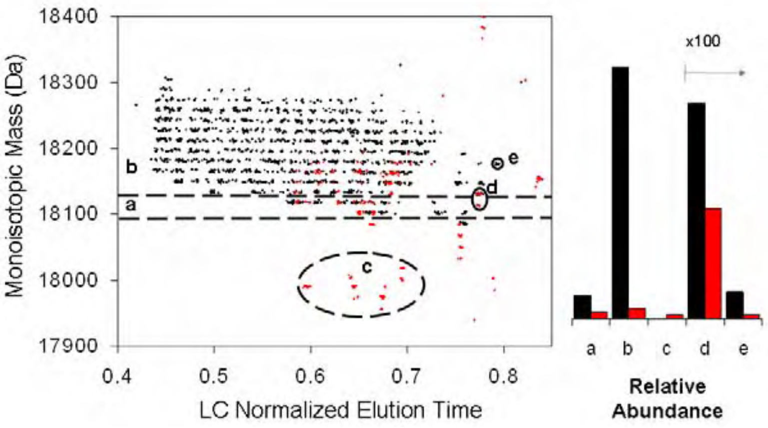

***Figure 1**. The time vs. mass two-dimensional display (left) highlights our ability to resolve intact protein masses of individual oxidized CaM species that are indicators of denitrase activity. CaM species detected prior to (red symbols) and following (black symbols) incubation with cell lysate from activated macrophages: a) CaM & CaMox; b) nYCaMox & 2nYCaMox; c) CaM-Lysine and CaMox-Lysine; d) nYCaM, and e) 2nYCaM. The panel at the right displays the relative abundance of CaM within each of these five areas. Definitions of the abbreviations follow: CaM, calmodulin; CaMox (nYCaMox), oxidized CaM containing methionine sulfoxides or (and) nTyrs.*

We also identified a modification dependent C-terminal lysine cleavage that is likely to alter calmodulin function. We propose that the cleaved calmodulin is a useful biomarker of intracellular oxidative stress conditions because of both the oxidation dependence of this lysine cleavage and the stability of the cleavage product. This stability is in contrast to the reversible modifications we observed for nitrotyrosine and methionine sulfoxide. The transient nature of nitrotyrosine and methionine sulfoxide renders these currently used biomarkers as inaccurate. Portions of this work have been detailed in a manuscript accepted for publication in the journal *Biochemistry*.

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

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(b) W.R. Wiley Environmental Molecular Sciences Laboratory, Richland, Washington

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.

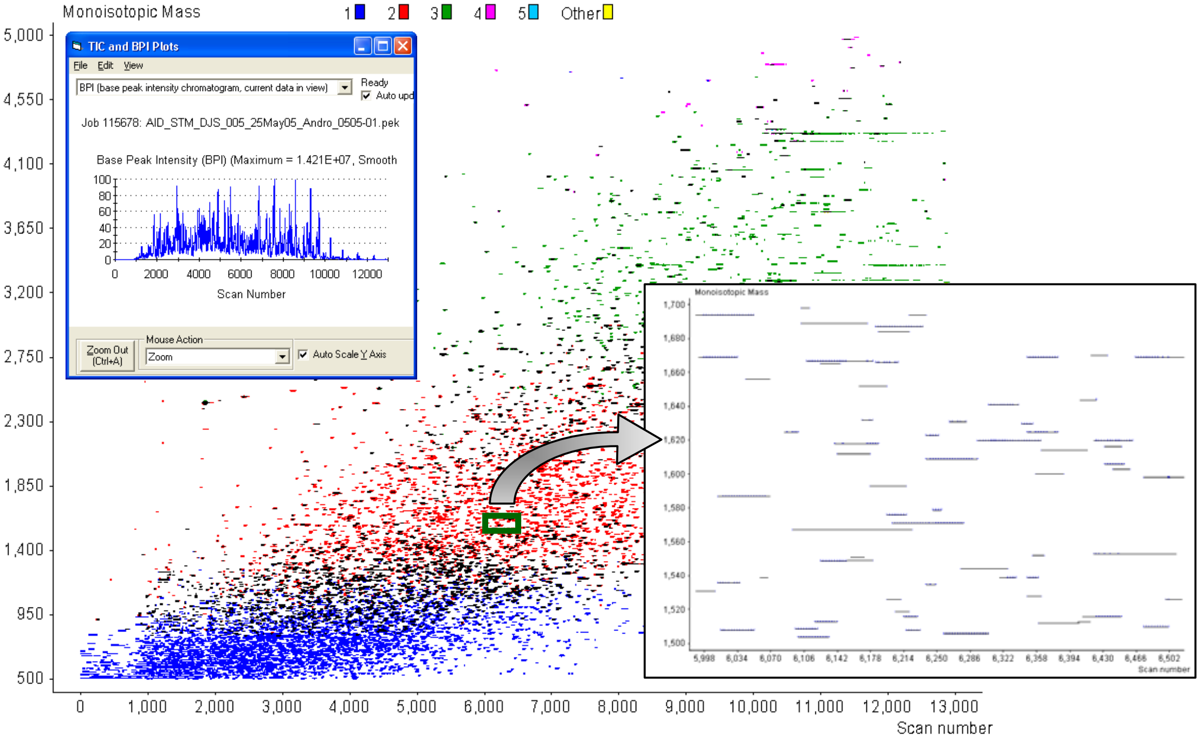

Figure 1. *The large graphic shows a plot of monoisotopic masses vs. scan number (time), color-coded by charge state. The upper left inset is a total ion chromatogram of the entire dataset, while the lower right inset shows 68 LC-MS features resolved in both the mass and time dimensions.*

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.

Proteomic Analysis of the *Salmonella enterica* Subspecies *serovar Typhimurium* Isolated from RAW 264.7 Macrophages: Identification of a Novel Protein that Contributes to the Replication of *s. Typhimurium* Inside Macrophages

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(e) Oregon Health Sciences University, Portland, Oregon

The pathogen Salmonella enterica is known to cause both food poisoning and typhoid fever. Because of the emergence of antibiotic-resistant isolates and the threat of bioterrorism (e.g., through contamination of food supplies), there is a growing need to study this bacterium.

In this study, a comparative peptidomics approach was used to study the *Salmonella enterica* subspecies *serovar Typhimurium* cultured under four conditions: 1) rapid growth in rich medium, 2) a stationary phase sustained in nutrient-depleted medium, and 3) short-term and 4) long-term exposure to an acidic, low-magnesium, minimal-nutrient medium designed to mimic the macrophage phagosomal environment within which Salmonella are known to survive. Native peptides from cleared cell lysates were enriched by isopropanol extraction and analyzed by liquid chromatography-mass spectrometry (LC-MS) and the accurate mass and time (AMT) tag approach. We identified and quantified 5163 peptides originating from 682 proteins, and the data clearly indicated that Salmonella exposed to the phagosome-mimicking medium had relatively high abundances of a wide variety of protein degradation products, especially from ribosomal proteins. The same Salmonella samples also were analyzed using traditional bottom-up proteomic methods, and when the peptidomic and proteomic data were analyzed together using a hierarchical cluster analysis, two clusters, putative growth proteins (Gr.P.) and putative stress response factors (S.R.F.), of proteins targeted for proteolysis were identified (see Figure 1).

Each column in Figure 1 corresponds to the sample analyzed by LC-MS, and each row represents an individual protein (278 total). All of the data were simultaneously clustered, and the abundance values are indicated by the color bar at the bottom of the figure. The two protein clusters are indicated, and the four culture conditions are designated as follows:

1. L – Rapid growth in rich medium
2. S – Stationary phase in nutrient depleted medium
3. M – Short-term exposure to phagosome-mimicking medium
4. N – Long-term exposure to phagosome-mimicking medium.

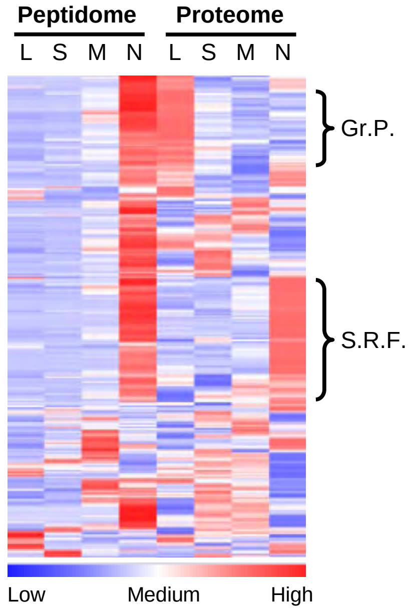

Figure 1. *Peptidomic and proteomic co-cluster analysis.*

The Gr.P. cluster consisted of 48 proteins that were highly abundant in rapidly growing Salmonella and highly fragmented in cells exposed to the phagosome-mimicking medium. Almost all of these proteins (i.e., 37 of 48) were ribosomal proteins, which correlates well with a catabolic pathway known to be activated in Salmonella during stressful conditions and to target ribosomes.

The S.R.F. cluster consisted of 71 proteins that were both highly abundant and highly fragmented in cells exposed to the phagosome-mimicking medium. That Salmonella would up-regulate the expression of stress response factors only to target them for degradation is seemingly paradoxical. However, translational fidelity is known to dramatically decrease during stress, which results in mistranslated proteins that are significantly less likely to properly fold; consequently, their exposure to proteolysis is increased. Therefore, two modes of protein degradation are likely up-regulated by phagocytosed Salmonella: 1) catabolism of ribosomal proteins and 2) proteolysis of defective stress response factors.

These results led to the hypothesis that the Lon protease targets ribosomal proteins for degradation in phagocytosed Salmonella. To investigate this hypothesis, both wild-type and Lon *s. Typhimurium* were cultured in both rich and phagosome-mimicking media, and their peptidomes were analyzed using the AMT tag approach. A preliminary analysis of the resulting data indicated, surprisingly, that knocking out Lon actually resulted in an increase in ribosomal protein degradation, as well as a number of other effects.

User Projects

Zangar NAF R33

RC Zangar, SM Varnum, Pacific Northwest National Laboratory, Richland, Washington

Identification of Post-translational Modifications and Protein Complexes under Conditions of Oxidative Stress

CA Sacksteder, TC Squier, Pacific Northwest National Laboratory, Richland, Washington

Proteomic Analysis of the HMEC Mitogenic Response

BD Thrall, T Liu, DG Camp, K Waters, Pacific Northwest National Laboratory, Richland, Washington

Identification of Protein Components of Vaccinia Virus Particles

B Moss, W Resch, National Institute of Health, Bethesda,, Maryland

Identifying Targets for Therapeutic Interventions using Proteomic Technology

JN Adkins, KD Rodland, N Manes, Pacific Northwest National Laboratory, Richland, Washington

HM Mottaz, Environmental Molecular Sciences Laboratory, Richland, Washington

F Heffron, S Wong, J Gustin, J Rue, R Estep, Oregon Health Sciences University/Oregon Graduate Institute, Portland, Oregon

Proteomic Characterization of Cerebrospinal Fluid (CSF) by High Resolution LC-MS/MS

S Warren, Massachusetts General Hospital East and Harvard University School of Medicine, Charlestown, Massachusetts

JM Jacobs, DG Camp, Pacific Northwest National Laboratory, Richland, Washington

Characterization of the Tumor Cell Lamellipodia Phosphoproteome

JM Jacobs, DG Camp, Pacific Northwest National Laboratory, Richland, Washington

RL Klemke, Y Wang, University of California, San Diego, La Jolla, California

Unraveling the Molecular Biology of Host-Pathogen Interactions

L Shi, Pacific Northwest National Laboratory, Richland, Washington

Protein Complex Identification using Novel Affinity Resins
MU Mayer-Cumblidge, L Shi, TC Squier, P Yan, Pacific Northwest National Laboratory, Richland, Washington

S Verma, T Wang, unknown, Washington

FedEx1

MS Lipton, AS Beliaev, MF Romine, MJ Marshall, IA Agron, GE Pinchuk, Pacific Northwest National Laboratory, Richland, Washington

Shew Strains

MS Lipton, S Deng, Pacific Northwest National Laboratory, Richland, Washington

Reactive Oxygen and Nitrogen Species, Produce Dynamic Protein Modifications and Protein Complexes in RAW 264.7 Macrophage Cells

HS Smallwood, Pacific Northwest National Laboratory, Richland, Washington

Age Related Post Translational Modifications to Proteins that Alter Protein Complexes Determined by FTICR-MS

HS Smallwood, Pacific Northwest National Laboratory, Richland, Washington

Identification and Post-Translational Modification of Mitotic Regulatory Proteins

DL Stenoien, Pacific Northwest National Laboratory, Richland, Washington

Proteomics of HCMV

SM Varnum, JM Jacobs, Pacific Northwest National Laboratory, Richland, Washington

J Dumortier, Oregon Health Sciences University/Oregon Graduate Institute, Beaverton, Oregon

Thrust Area 1: Characterization of Purified Proteins for Distribution to Grand Challenge Participants (EMSL User Support)

L Shi, Pacific Northwest National Laboratory, Richland, Washington

Advanced Proteomics and Metabolomics Studies of Type 1 Diabetes

TO Metz, JM Jacobs, DG Camp, Pacific Northwest National Laboratory, Richland, Washington

Proteomic Studies of Inflammation and the Host Response to Injury

LL Moldawer, University of Florida, Gainesville, Florida

W Qian, T Liu, Pacific Northwest National Laboratory, Richland, Washington

A Proteome for Specific Cell Types in *Caenorhabditis elegans*

DG Moerman, University of British Columbia, Vancouver, British Columbia, Canada

Proteomic Characterization of *in vivo* and *in vitro* Model Systems of Hepatitis C Virus Infection: Global Quantitative Proteome AMT Tag Measurements of Cellular Protein Expression

JM Jacobs, Pacific Northwest National Laboratory, Richland, Washington

MG Katze, DL Diamond, University of Washington, Seattle, Washington

Biomarker Development for Chronic Obstructive Pulmonary Disease

DL Springer, JG Pounds, Pacific Northwest National Laboratory, Richland, Washington

RE Johnson, Battelle Columbus, Columbus, Ohio

The Use of Novel Proteomics in the Plasma and Tumor Microenvironment for Class Prediction in Human Breast Cancer

LL Moldawer, SR Grobmyer, University of Florida, Gainesville, Florida

Molecular Mechanisms Underlying Cellular Adaptive Response to Low Dose Radiation

CA Sacksteder, TC Squier, MA Gritsenko, Pacific Northwest National Laboratory, Richland, Washington

Identify Biomarkers for COPD (Chronic Obstructive Pulmonary Disease) in Humans using Proteomic and Metabonomic Analysis of Serum and Urine

SM Varnum, JG Pounds, Pacific Northwest National Laboratory, Richland, Washington

Characterization of the Neurite Phosphoproteome

F Yang, Pacific Northwest National Laboratory, Richland, Washington

Y Wang, RL Klemke, University of California, San Diego, La Jolla, California

Determining Proteins Expression is Ralstonia bacteria that Survive in Ultra Pure Water

KL Ogden, University of Arizona, Tucson, Arizona

Use of FTICR Mass Spectrometric Proteomics Analysis for the Identification of Novel Targets in Pain Research

M Yeo, WB Liedtke, Duke University, Durham, North Carolina

Proteome Analysis of Members of the Family Anaplasmataceae

Y Rikihisa, T Kikuchi, Ohio State University, Columbus, Ohio

Fragmentation and Characteristic Study of Peptides Missed by SEQUEST

G Tan, VH Wysocki, University of Arizona, Tucson, Arizona

Proteomics of *Burkholderia mallei*

MS Lipton, Pacific Northwest National Laboratory, Richland, Washington

SE Schutzer, University of Medicine and Dentistry, New Jersey Medical School, Newark, New Jersey

The Schizophyllum Commune Proteome

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JS Horton, Union College, Schenectady, New York

AC Gathman, W Lilly, Southeast Missouri State University, Cape Girardeau, Missouri

E Kothe, Friedrich-Schiller University, Jena, Germany

H Wosten, Universiteit Utrecht, Utrecht, Netherlands

IV Grigoriev, Joint Genome Institute, Walnut Creek, California

TJ Fowler, Southern Illinois University Edwardsville, Edwardsville, Illinois

Advanced Proteomics and Metabolomics Studies of Type 2 Diabetes and Pre-Diabetes

TO Metz, RD Smith, DG Camp, W Qian, Pacific Northwest National Laboratory, Richland, Washington

J Baynes, University of South Carolina, Columbia, South Carolina

R Hoffman, University of Leipzig, Leipzig, Germany

Proteomics of *in situ* Biostimulated Sediments

PE Long, MS Lipton, Pacific Northwest National Laboratory, Richland, Washington

Analysis of the Proteome and Transcriptome of *in vivo Salmonella typhimurium* Infected Ileum

LG Adams, Texas A&M University, College Station, Texas

Analysis of the Proteome and Transcriptome of *in vivo Brucella* spp., *Yersinia pestis*, *Francisella tularensis*, *Mycobacterium* spp., *Salmonella typhimurium* Infected Ileum

J Turse, LG Adams. Texas A&M University, College Station, Texas

Cellular Response to Virus Infection: Global Proteome Analysis of Macaque Models of HIV and Influenza Infection

MG Katze, DL Diamond, University of Washington, Seattle, Washington

Trauma-Induced Reprogramming: Changes in Lipid Raft Protein Content

J Cuschieri, University of Washington, Seattle, Washington

Characterization of the SATB1 Phosphorylations upon Ionization Radiation

R Zhao, Environmental Molecular Sciences Laboratory, Richland, Washington

T Kohwi-Shigematsu, J Li, Lawrence Berkeley National Laboratory, Berkeley, California

Translation Repressor, 4E-BP2, is covalently Modified in the Mammalian Brain

S Wu, Pacific Northwest National Laboratory, Richland, Washington

MA Bidinosti, N Sonenberg, McGill University, Montreal, Quebec, Canada

Informatics Tool for Proteomic Biomarker Detection using Large-Scale nanoLC-FT Mass Spectrometry Data

CR Jimenez, E Marchiori, Vrije Universiteit Amsterdam, Amsterdam, Netherlands

Cyanobacteria Membrane Biology Grand Challenge: Systems Analysis of the Dynamics of Membrane Architecture, Composition, and Function- Proteomic, Metabolomic, and Metallomic Characterization

JM Jacobs, DW Koppenaal, TO Metz, Pacific Northwest National Laboratory, Richland, Washington

HB Pakrasi, J Stockel, Washington University in St. Louis, St. Louis, Missouri

Quantitative Characterization of Protein Post-Translational Modifications using Mass Spectrometry

W Qian, S Ding, Q Zhang, T Heibeck,. Pacific Northwest National Laboratory, Richland, Washington

Proteome Enabled Discovery of Growth and Survival Strategies of the High Level Nuclear Waste Actinomycete, *Kineococcus radiotolerans*

CE Bagwell, Savannah River Technology Center, Aiken, South Carolina

Alpha Project Phosphoproteomics

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Pilot Study on Examination of LIRKO Islets and Serum Using Quantitative Proteomic Approaches

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Development of High Throughput Proteomic Production Operations (PNNL Scope # 40601, Dick Smith's OBER Proteomics)

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Biomarkers for Early Detection and Other Stages (PNNL Scope # 46308, RD Smith's Hutch 1 project)

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High Throughput Proteomic & Metabolomic Early Biomarkers (PNNL Scope #47174, RD Smith's EIF project)

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Ion Funnel Development (PNNL Scope #48165, K.Tang JPL-Ion Funnel Project)

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NBACC: Host/Pathogen Interactions (PNNL Scope # 49488, Lipton's NBACC Host project)

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Global and Targeted Proteomic Identification of Oxidative Modifications

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Control of Hydrogen Release and Uptake in Condensed Phases (Scope #48587)

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Cerebrospinal Fluid Proteome

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High-Throughput Evaluation of Breast Cancer Markers

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Platelet Secretome

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LC-MS-Based Metabolomics for Computational Toxicology

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Identification of Metal Reductases (NABIR)

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Biomarker Discovery in Pathogens by Proteomics

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Secretome Analysis of Environmental Nanoparticle Induced Biomarkers

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LC-FTMS Analysis of Organophosphates

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Environmental Proteomic Analysis of Anaerobic Methane Oxidizing Systems

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Proteome Analysis of *Anaeromyxobacter dehalogenans* strain 2CP-C

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A Proteomic Dissection of the Hg(II) Toxicity Paradox

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Technology Development in Support of NCRR

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OCD_Identification of Potential Plasma Biomarkers for Insulin Resistance Using Proteomics

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Characterization of Signaling Events Induced by Low Dose Ionizing Radiation

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Mitotic Regulation of the Nuclear Pore Complex Protein Interaction Network

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A proteomic Investigation of Changes in Lipid Droplet-Bound Proteins

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Platelet Proteome for Normal and Type-2 Diabetics

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Pathogen Strain Detection Based on Changes in Expressed Proteins

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Subunit Structures of Arabidopsis RNA Polymerase IV Complexes

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Characterization of Application-Relevant Biosilica-Precipitating Peptides of a Diatom

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Global Proteomic Analysis of Human Ehrlichiosis Agents

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Proteomic Analysis of Differential Growth in *Desulfovibrio* spp. for a Systems Biology Level Investigation

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Coupling Temporal Variations in Geochemistry to Activities of Microbial Populations in the Deep Subseafloor Biosphere

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Proteomics of Populus: Understanding Protein Expression Involved in Carbon Allocation

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Exploring the Proteome of *E. coli* Following Adaptation to Environmental and Genetic Perturbation

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Determination of the CCR5 and CXCR4 Antagonist and Agonist Binding Site

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Proteomic-Based Mechanistic Analysis of Components Involved in the Immunoprotective Pathways Regulated by Low-Dose Radiation and the Medicinal Mushroom *Trametes versicolor*

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Ground Squirrel Proteome: Protein Modifications through Torpor And Arousal

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Community Proteomic Analysis of a Near-Shore Anoxic Basin: Saanich Inlet

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Neuropeptides and Vasoactive Protein Detection from Human Skin

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Identification of Organophosphate Modification on Proteins Associated with the Central Nervous System

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Protein Modifications Associated with Hibernation

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Protein Complexes Altered by Oxidative Stress and Determined by FTICR-MS

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WaNPRC Macaque Proteomics for Models of Influenza Infection and AIDS

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Identification and Characterization of Soluble Factors in Delayed Effects of Low Dose Radiation

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Spatially Resolved Proteomic studies of Brains Obtained from Control Mice and Treated Mice Simulating Parkinson's Disease

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Genomes-to-Life Protein Complex Isolation Capability

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Proteomics of Filamentous Fungi

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Sustrate Identification for Ser/Th Protein Phosphatase

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Identification of Functional Pathways Associated with Clinical Tamoxifen-Resistance in Breast Cancer by Advanced Mass Spectrometry

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Membrane Proteins of Placental Parasites

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Interfacial and Nanoscale Science Facility

The Interfacial & Nanoscale Science Facility (INSF) is a world-class resource for scientific expertise and instrumentation focused on the study of interfacial phenomena and nanoscience and technology. This section summarizes the capabilities available in the INSF, along with research programs associated with facility users. Activities in the facility address national needs in environmental restoration, waste management, pollution prevention, energy production and storage, and national and homeland security through research that specializes in preparation, characterization, and reactivity of surfaces and interfaces. The range of scientific expertise and instrumentation within the facility provides a unique environment for research in areas such as nanoscience and nanotechnology; interfacial catalytic chemistry; designed oxide interfaces, including environmental aerosol and mineral interfaces; materials and chemoselective interfaces; and areas within microanalytical science, such as chemical sensing.

The INSF and its scientific staff provide a broad range of instrumentation, laboratory capabilities, and expertise. Instrumentation is available for chemical synthesis, analytical chemistry, separations, electrochemistry, thin-film deposition, catalytic reactors, ion-beam processing, and microfabrication. Capabilities include an accelerator facility for material modification and analysis using ion beams along with interface characterization; scanning probe microscopies; electron microscopy and x-ray analysis; spectroelectrochemistry; high-spatial/energy resolution surface analysis; catalyst preparation, characterization, and reaction engineering; a fully equipped clean room for microfabrication, microanalytical systems development, and testing laboratories; inorganic, organic, polymer, and biochemical synthesis and characterization facilities; a full complement of thin-film deposition and characterization facilities; and fully equipped analytical support laboratories. The combination of surface and interface characterization techniques that provide high spatial, depth, and energy resolution for a broad array of methods is unmatched anywhere in the world. Many systems are coupled directly to film growth chambers, and samples can be moved among 16 different systems under controlled environments without exposure to air.

Instrumentation & Capabilities

- Thin-film deposition
- Surface analysis suite
- Electron microscopy suite
- Scanning probe microscopy
- Ion-beam processing and analysis
- Surface Science and Catalysis Laboratory
- Catalytic reactors
- X-ray diffraction laboratory
- Microfabrication
- Chemical and biological sensing
- Other analytical and characterization laboratories

Staff assigned to the INSF perform innovative research in the areas of surface and interfacial chemistry, advanced materials synthesis and characterization, and microanalytical science. Our activities emphasize research relevant to the four U.S. Department of Energy (DOE) mission areas—science, energy resources, environmental quality, and national security—and to operation of a world-class user facility that supports the DOE science mission. Our staff also plays a major role in the continued success of the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) by providing support, training, and collaboration to onsite users. Over the past seven years, research activities in the INSF have focused on four major thrust areas: 1) films and interphases, 2) surface chemistry and catalysis, 3) material interfaces, and 4) microsensors, microfluidics, and new biotechnologies. Staff assigned to the INSF continue to focus their efforts in these four areas with research on the following topics:

- *Oxide and Mineral Films and Surfaces*. Structural and chemical properties of model single-crystal oxide and complex mineral surfaces.
- *Electronic and Catalytic Materials*. High dielectric materials, magnetic oxide semiconductors, and oxide catalysts.
- *Nanoscale Materials*. Oxide quantum dots and nanofilms of magnetic and oxygen ion-conducting oxides, buried nanoclusters in oxides.
- *Interfacial Properties and Reactivity*. Reactions at oxide and mineral interfaces and the structural and chemical properties.
- *Microanalytical Separations and Sensing*. Development of new microanalytical and sensing principles, tools, and testing.
- *Environmental Studies*. Waste separations, structural and chemical stability of waste forms under different radiation and chemical environment, atmospheric aerosols.
- *Analysis and Characterization*. Fully equipped analytical laboratories and characterization facilities.

Films and Interphases. The physical and chemical properties of the region between single phases of a material (i.e., the interphase) have a major influence on many characteristics of the material, including stability, electronic properties, atomic and ionic transport, and chemical reactivity. Research programs include the synthesis of thin films and nanostructured materials, both of which contain a high concentration of interphase regions. Research activities also involve studies of solid/solid, solid/liquid, and solid/gas (or vacuum) interphase regions. Although most studies are focused on inorganic materials and interphases, organic and biological systems are becoming an increasingly large part of our work.

Surface Chemistry and Catalysis. Basic research is carried out with the most simple, well-defined, environmentally relevant crystallographic structures (e.g., mineral carbonates, metal oxides) for which molecular theory and spectroscopy are immediately applicable. The work then progresses to materials with more complex structures, such as iron and titanium oxides with substitutional impurities. For example, fundamental studies of the oxygen storage and release properties of pure and zirconium-doped ceria single-crystal thin films are aimed at understanding how these “oxygen storage materials” perform in an automobile exhaust system catalytic converter. In addition to fundamental surface chemistry research, we are developing materials and reactor designs for a number of heterogeneous catalytic processes. One study involves synthesizing, characterizing, and testing a group of novel, mesoporous, silica-supported, solid-acid catalysts for use in petroleum-refining processes.

Material Interfaces. Studies are being conducted in several areas: solid/solid interfaces in a wide variety of materials, radiation effects in materials, fundamental defect properties and interactions, atomic and ionic transport, and aerosol characterization. Many of the studies on solid/solid interfaces involve 1) characterization of interfaces between thin films and substrates, between ion-beam-modified surfaces and the original substrate, or between nanoclusters and host matrices; 2) segregation or diffusion of point defects, impurities, dopants, or gas atoms to or from such interfaces; 3) transport of hydrogen, oxygen, or other gases across such interfaces; 4) formation or destruction of such interfaces from radiation damage processes; and 5) stability of interfaces under a wide range of environmental conditions. Studies on radiation effects include experimental research on materials for immobilization of nuclear waste and plutonium, as well as materials for next-generation nuclear power production, wide-band-gap semiconductors, and multiscale computer simulations of damage production processes, defect diffusion, and microstructure evolution. Studies on atomic and ionic transport include ion exchange processes in nuclear waste glasses, hydrogen storage and transport in materials, and oxygen transport in fast ion conductors.

Microsensors, Microfluids, and Nanobiotechnology. This research includes four primary thrust areas: 1) array-based vapor sensors, 2) nanoscience, 3) bioanalytical microfluidics, and 4) radioanalytical microfluidics. Key areas of science in array-based vapor-sensing include rational design, development, and synthesis of polymeric-sensing materials, linear free-energy models for vapor/polymer interactions, organic thin films, photo-patterning methods for sensor materials, integrated sensor systems, and multivariate data analyses. The nanoscience area includes development of monolayer-protected gold nanoparticles for use on sorptive sensing films, single-enzyme nanoparticles as a new nanostructure for enzyme stabilization, and multi-functional nanoparticle assemblies for biodetection. The latter two areas represent a new thrust in nanobiotechnology, and a laboratory within EMSL has been established for synthesizing enzyme nanostructures and studying enzyme kinetics and enzymes in nanostructured matrices. Experimental research in bioanalytical microfluidics and radioanalytical microfluidics is now located primarily in other facilities, but close scientific ties with EMSL are maintained.

Capabilities

Thin-Film Deposition. Thin-film deposition capabilities include oxygen plasma-assisted molecular beam epitaxy (MBE) systems (Figure 1), a metal organic chemical vapor deposition system (MOCVD), and a sputter deposition system. The MBE systems consist of growth chambers connected to surface characterization chambers through sample transfer lines. The growth chambers have various electron beam and effusion cell sources along with reflection high-energy electron diffraction and quartz crystal oscillators to monitor the growth. The surface characterization chambers are equipped with several surface-science capabilities including x-ray photoelectron spectroscopy (XPS)/diffraction, Auger electron spectroscopy (AES) low-energy electron diffraction (LEED), and atomic force microscopy/ scanning tunneling microscopy (AFM/STM). The MOCVD system is specially designed for epitaxial growth of oxide thin films. The system comprises a rotating disk reactor, two metal organic source delivery systems (bubbler vapor-phase and direct liquid source-injection), an oxygen microwave plasma unit, a spectroscopic ellipsometer, and

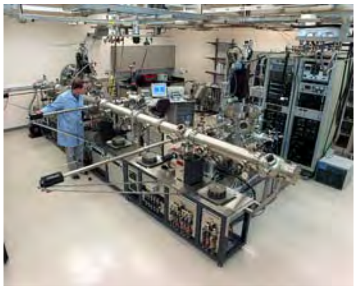

***Figure 1**. Oxygen plasma-assisted MBE system.*

a Fourier transform infrared (FTIR) spectrometer. The system is capable of growing uniform (in both thickness and composition) oxide thin films with abrupt interfaces. The sputter deposition system consists of radio frequency and direct current sputtering sources.

Figure 2. *X-ray photoelectron spectrometer.*

Surface Analysis Suite. The surface analysis suite consists of a Physical Electronics Instruments (PHI) Quantum 2000 high-resolution, x-ray photoelectron spectrometer (Figure 2), a Kratos Axis multi-technique surface analysis system (SAS), a PHI Model T2100 time-of-flight secondary ion mass spectrometer (TOF-SIMS), and a PHI Model 680 AES/scanning Auger microprobe. The Quantum 2000 XPS system is unique in that it uses a focused monochromatic Al K α x-ray beam that can be varied in size from as small as 10 μm in diameter to approximately 200 μm. The TOF-SIMS system uses a pulsed and focused ion source and TOF analyzer to obtain high spatial- and mass-resolution data from a specimen surface. The multi-technique SAS enables surfaces to be probed with a variety of complementary analysis methods, and contains electron imaging, electron spectroscopy, and both primary and secondary ion-scattering capabilities. The Model 680 auger electron spectrometer (AES)/scanning Auger microprobe is based on a field-emission electron source and a cylindrical mirror analyzer. The electron beam size can be focused as low as 10 nm at 20 kV, although somewhat larger beams are typically used to collect AES data. Instrument features and capabilities include beam rastering, scanning electron microscope (SEM) imaging, mapping, specimen cleaning and depth profiling using a sputter gun, and sample rotation to allow "Zalar" rotation during sputtering. The system also is configured with an x-ray detector for near-surface analysis in combination with AES surface analysis.

Figure 3. *High-resolution TEM.*

Electron Microscopy Suite. The electron microscopy suite consists of a LEO 982 field-emission scanning electron microscope (FESEM), a high-resolution transmission electron microscope (TEM) (Figure 3), and another cryo-TEM dedicated for biological work (Cryo TEM). The FESEM is an ultrahigh-performance SEM with a resolution of 1 nm at 30 kV and 4 nm at 1.0 kV. It has a large specimen chamber equipped with multiple detectors, a below-lens secondary electron detector, an in-lens secondary electron detector, a backscatter electron detector, an energy-dispersive x-ray detector, and an electron backscatter diffraction detector. The JEOL 2010 is a high-resolution TEM with a spatial resolution of 0.194 nm. This instrument has a medium acceleration voltage of 200 kV, a high-brightness electron source, digital image recording, a computer-controlled sample goniometer, and a geometrically optimized x-ray detector. It has a wide range of illumination lens conditions: TEM mode, energy-dispersive spectroscopy mode, nanometer beam electron diffraction, and convergent beam electron diffraction. The TEM is post-column attached with a Gatan image filter, giving an optimized energy resolution of approximately 1.2 eV, which allows analysis of light elements by electron energy-loss spectroscopy and elemental mapping in the electron spectroscopic imaging. The Cryo TEM is primarily used for biological imaging and tomography. The spatial resolution of the instrument is about 0.45 nm, and it has an accelerator voltage in the range of 80 to 120 kV.

Scanning Probe Microscopy. The scanning probe microscopy laboratory has a Digital Instrument Nanoscope IIIa AFM, a Topometrix TMX 1000 Explorer SPM, and an Omicron variable non-contact ultrahigh vacuum (UHV) AFM/STM system with surface-science capabilities including XPS, Auger electron microscopy, plasma cleaning, and deposition. The instrument is capable of operating in both air and liquid environments and in several modes that include contact, tapping, frictional force, phase/frequency, capacitance, and magnetic/electrostatic force. As a real space probe, the instrument can be used to probe surface morphology, defects, and electrostatic, magnetic, dopant concentration, and mechanical properties of conducting and non-conducting materials. The Topometrix TMX 1000 Explorer SPM can be used for both AFM and STM in air and in liquid and is particularly useful for larger samples. This instrument includes both contact and non-contact AFM modes. STM requires an electrically conductive sample and produces images based on the topography and electronic structure of the sample. AFM samples may be insulating or conducting; the image is based on the force between the AFM probe and the sample and is primarily a map of the surface topography. The Omicron variable scanning probe microscope can be used for both STM and AFM under UHV conditions. As a real space probe, this instrument is designed to probe surface structure, defects, and morphology of conducting and non-conducting materials. In addition to STM/AFM, the vacuum system also is equipped with other surface-science capabilities that include LEED, XPS, AES, and oxygen plasma cleaning.

***Figure 4**. Accelerator facility.*

Ion-Beam Processing and Analysis. The accelerator facility (Figure 4) is equipped with capabilities to perform material modification and analysis using high-energy ion beams. The facility has two ion sources, a 3-MeV tandem ion accelerator, injector and analyzing magnets, beam lines, and four end stations. The end station on the +30° beam line is equipped with LEED, AES, XPS, oxygen plasma, and sputter cleaning sources and effusion cells in addition to the conventional ion-beam capabilities. Ion-beam capabilities include fixed and movable detectors for Rutherford backscattering spectrometry/channeling, nuclear reaction analysis (NRA), and elastic recoil detection analysis (ERDA). This beam line extends through the end station to another end station where experiments can be performed with the beam size of 20 microns or greater. The micro-beam end station is also equipped with capabilities for conventional ion-beam techniques including RBS, NRA, and proton-induced x-ray emission (PIXE). The +15° beam line is equipped with a raster scanner for ion implantation and ion-beam modification of materials, and the end station is equipped with all the conventional ion-beam capabilities. In addition, this beam line is equipped with heavy ion elastic recoil detection analysis capability for material characterization. The −15° end station is designed to carry out routine analytical work. The NEC RC 43 end station attached to this beam line is equipped with most of the standard ion-beam analytical capabilities including RBS, NRA, PIXE, particle-induced gamma emission, proton elastic scattering analysis, scanning transmission ion microscopy, and ERDA.

Surface Science and Catalysis Laboratory. Three UHV surface chemistry systems designed for studies of the molecular-level chemistry of adsorbates on metal oxide surfaces are available in the Surface Science and Catalysis Laboratory. These systems are equipped with a number of spectroscopic tools to follow changes in adsorbate chemistry, including high-resolution electron energy-loss spectroscopy, SIMS, ultraviolet photoemission, XPS, AES, and LEED. In addition, both electron-stimulated desorption and temperature-programmed desorption (TPD) studies are routinely performed in some systems. Typical information obtainable in TPD experiments includes the quantity and nature (intact or dissociated molecule) of an adsorbed gas. In addition, estimates of the sticking coefficient and the activation energy for desorption and/or reaction of the adsorbed molecule can be made. One of these systems has a combination of surface-science and high-pressure catalysis capabilities and is capable of measuring gas/solid reaction rates under realistic, high-pressure (approximately 1 atm) conditions using model, low-surface-area solid samples. Reaction rates as a function of temperature and varying reagent partial pressures also can be measured in this system.

Catalytic Reactors. The Reaction Engineering Laboratories are equipped with a variety of analytical capabilities and catalytic reactors including an Advanced Scientific Designs, Inc. RXM-100 catalyst testing and characterization instrument and a Zeton Altamira reactor test stand. The RXM-100, a multi-functional instrument used for catalyst studies, combines UHV and high-pressure capabilities in a single instrument without compromising specifications or ease of use. A number of measurements can be made using this instrument including chemical adsorption, physical adsorption, surface area, pore size, pore distribution, and temperature programmed characterization (desorption, reduction, and oxidation). An online mass spectrometer, gas chromatograph, FTIR, and thermal conductivity detector can be used to analyze effluent gases. The instrument has the capability of running up to 10 different gases simultaneously. In addition, high-pressure reactions (up to 1000 psi) can be run within a few minutes of each other on the same system, with little change in system configuration. This system offers extensive flexibility in catalyst testing and decreases inefficiency and contamination problems that arise from transferring materials between systems and waiting for data from other sources. The Zeton Altamira reactor test stand comprises three types of reactors generally used in bench-scale testing of catalysts: a fixed bed reactor, a Rotoberty reactor, and a continuous stirred tank reactor. This design allows users to evaluate catalyst performance and study chemical reactions in various reactor configurations.

X-Ray Diffraction. The suite of x-ray diffraction (XRD) equipment in EMSL consists of four instruments: a general-purpose XRD system for studying polycrystalline samples under ambient conditions, a special applications XRD system with low- and high-temperature sample stages covering the range of −193°C to +1000°C, and a four-circle XRD system. The general-purpose system is most often used to examine powder samples (x-ray powder diffraction), but it also can be used to study certain types of thin films. In addition to its non-ambient capabilities, the special applications system is equipped to examine thin-film samples in more detail, including grazing-incidence XRD (GIXRD) and x-ray reflectivity

(XRR) measurements. The four-circle system is typically configured for high-resolution x-ray diffraction studies of epitaxial thin films. Additional applications of the four-circle system include stress measurements, texture analysis, GIXRD, and XRR.

Chemically Selective Materials and Sensors. Development and evaluation of sensor materials and chemical microsensors are supported by a wet chemistry laboratory for organic, polymer, and nanomaterial synthesis; a laboratory for evaluation of chemical sensor and sensor materials using automated vapor generation and blending systems; and a clean room with selected microfabrication capabilities. A variety of techniques for applying sensing materials to sensor devices are available, and numerous electronic test instruments are available in the sensing laboratories and the EMSL Instrument Development Laboratory. These capabilities are complemented by a range of surface analysis and characterization instruments as well as conventional analytical instrumentation in EMSL. Users may wish to bring new sensing materials to EMSL for application to sensing devices and evaluation, while others may bring complete sensor systems with data collection capabilities to couple to EMSL automated vapor generation systems. Research areas include sensor arrays, sensor materials design and synthesis, sensing material/analyte interactions, and chemometric methods.

Microfabrication. Microfabrication equipment provides a significant research and development capability in the areas of microstructures, microsensors, and microanalytical systems. Unlike highly automated industrial production equipment, the microfabrication equipment in EMSL has multipurpose functionality. The equipment supports a variety of microprocessing activities that include thin-film deposition, various thermal treatments, microphotolithography, chemical etching, inspection and characterization, bonding and packaging, and testing and measurement.

Instrument Upgrades

In Fiscal Year 2007, the following capability developments and procurements occurred in the INSF.

- **VersaProbe: Scanning Multi-probe Surface Analysis System (SMSAS) -** A flexible, multi-technique surface analysis system was added to EMSL's suite of instrumentation to meet high user demand for surface characterization. This instrument is a multi-technique surface analysis instrument based on elemental mapping using either scanning small spot x-rays or the electronics in the analyzer. This scanning technology provides high-performance micro-area spectroscopy, chemical imaging, and secondary electron imaging with high spatial resolution. This system includes a monochromatic high resolution aluminum x-ray source, a non-monochromatic dual anode x-ray source, a high-resolution hemispherical analyzer for x-ray photoelectron spectroscopy; an intense helium lamp for ultraviolet photoelectron spectroscopy; an argon ion gun for sputter depth profiling; and a C^{60} ion gun for high-resolution sputter depth profiling in organic and bio systems. This system has an excellent dual beam charge neutralization method that provides effortless analysis of insulating samples using a combination of low-energy ions and electrons. The system is equipped with a side chamber with limited processing and analytical for sample transfer and processing under controlled environment.

- **Time-of-flight, secondary ion mass spectrometer:** The latest version of a rapidly evolving method for determining chemical functionality of organic and inorganic surfaces was installed. This ultra-high vacuum surface analytical system is designed to examine surface structure, composition and chemical state by means of secondary ion detection during ion sputtering. The instrument is furnished with a C^{60} ion gun, a liquid metal ion gun with gold or bismuth sources, and a Cs^+/O_2^+ sputter ion gun with emission current stabilizers. The capabilities include surface spectroscopy with high sensitivity and mass resolution, surface imaging with high lateral resolution, depth profiling with high depth resolution and 3-D analysis. The ability to provide cluster ions such as Bi_n^+ and C_{60}^+, will enable EMSL users to obtain substantial improvements in detection yields, especially in biological materials. The C_{60} ion gun can provide ultimate high mass sensitivity, superior imaging and a powerful organic sputter depth profiling capability with C_{60}^+ or C_{60}^{2+} ions. This new instrumentation provides the user the flexibility to image with minimal shadowing on samples with high surface topography as well as the highest commercially available mass resolution performance.The system is equipped with a side chamber with limited processing and analytical capabilities..

Epitaxial Growth and Microstructure of Cu_2O Nanoparticle/Thin Films on $SrTiO_3(100)$

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Discovering ways of using energy more efficiently and searching for new sources of energy are two major challenges for the scientific research community. Even though solar energy is recognized as a potential source of energy for human endeavors, finding a way to effectively harness this resource is still a challenge. One possible way of harnessing solar energy is to use it to separate water into its elemental components—hydrogen and oxygen—and then use the hydrogen as fuel. It has been found that cuprous oxide (CuO_2) nanoparticles may be used in this process. The goal of this research is to study the growth and morphological features of cuprous oxide nanoparticles and the optimal conditions for producing useful cuprous oxide nanoparticle.

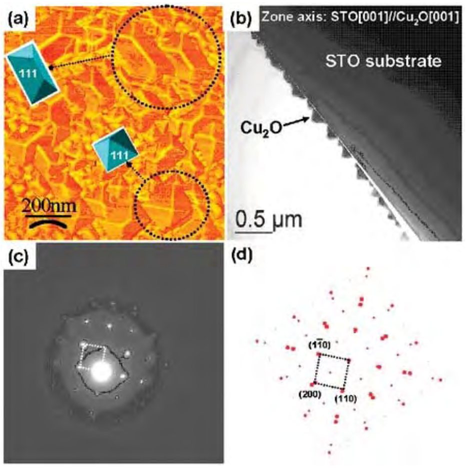

Figure 1. *Microstructure of sample A. (a) atomic force microscopy (AFM) image showing the surface topographic structure of the as-deposited film. The insets are the Wulff shape construction of the Cu_2O pyramid, which is defined by the {111} planes. (b) Cross-sectional transmission electron microcopy (TEM) image showing the height of the pyramid. (c) Selected area electron diffraction pattern of both the film and the substrate, which reveals an epitaxial orientation relationship between the film and the substrate: Cu2O[001]//STO[001] and Cu2O(100)//STO(100). (d) Computer calculated diffraction pattern.*

Cu_2O is a p-type semiconductor that shows a unique electronic structure for applications related to chemical and photochemical process such as water splitting under visible light irradiation (Kosugi and Kaneko 1998; Zuo et al. 1999; Ling and Wolfe 1993; Ikeda et al. 1998; Hara et al. 1998; Lyubinetsky et al. 2003). However, Cu_2O has not been practically used for this purpose because of its low energy conversion efficiency (≤1%). Electron-hole pairs generated by light in a micron-sized Cu_2O grain are normally hard to separate. Two methods have been proposed to overcome the charge recombination problem. In the first method, the morphology and size of the grown Cu_2O grains is controlled, such as in the development of nanoparticles. In the second method, by choosing an appropriate substrate to grow thin film/nanoparticles of Cu_2O, a hetero-junction may be formed, which will help to effectively separate the electron-hole pairs and, therefore, to enhance the energy conversion efficiency. It has been demonstrated by Lyubinetsky et al. (2005) that molecular beam epitaxy (MBE) allows controlled growth of Cu_2O nanoparticles on a $SrTiO_3$ (STO) substrate. One of the fundamental questions that remained to be addressed is the possibility of growing stable Cu_2O thin films on an STO(100) substrate using the MBE method.

In this paper, we report the epitaxial growth of Cu_2O thin films on an STO(100) substrate. To obtain the phase of Cu_2O, the pressure-temperature phase diagram was used. The morphology of the grown Cu_2O with respect to the growth parameters, including the growth rate, was examined in detail. The films were grown in a dual-chamber ultrahigh vacuum system equipped with an electron cyclotron resonance oxygen plasma source. The details of the oxygen-plasma-assisted MBE (OPA-MBE) system along with its growth capabilities are discussed elsewhere. The *in situ* film growth was monitored using reflection high-energy electron diffraction. The chemical state of the copper at the very top of the film and inside the film was analyzed using x-ray photon-electron spectroscopy (XPS). The valence state of the copper inside the film was analyzed following Ar^+ ion sputtering of the film to remove approximately 5 nm of top layer. The surface morphology of the as-grown layer was analyzed using atomic force microscopy (AFM). The phase of the grown layer was identified by a combination of x-ray diffraction (XRD), XPS, and cross-sectional high-resolution TEM imaging as well as selected area electron diffraction. The phase and the relative orientation of the grown film were revealed by the XRD patterns. Films grown under the two different growth rates were similarly dominated by the Cu_2O phase, which shows a preferred orientation with respect to the substrate [Cu_2O (200)//STO(100)]. A complete orientation relationship between the film and the substrate will be evaluated based on the cross-sectional TEM imaging and selected area electron diffraction as described in the subsequent sections. In addition, XRD data show the existence of trace amounts of CuO in sample A. Combined with the XPS analysis, it has been found that this minor amount of CuO phase corresponds to a surface layer of CuO on the Cu_2O (Figure 1).

Cu_2O was grown on STO(100) by OPA-MBE. The microstructure of the grown layer and the copper valence state were analyzed using XRD, XPS, AFM, and TEM as well as electron diffractions. The grown layer was dominated by the Cu_2O phase, possessing an epitaxial orientation with the substrate—Cu_2O[001]//STO[001] and Cu_2O(100)//STO(100). Cu_2O film morphologically shows dependence on the growth rate. Typically, a fast growth will lead to the formation of a thin film with a relatively smooth surface. A slow growth will lead to the development of nanoparticles, featuring the formation of Cu_2O pyramids, with the pyramids invariantly defined by the Cu_2O {111} planes. Given the fact that the {111} planes correspond to the lowest surface energy of Cu_2O, a slow growth will lend the system enough time to allow it to adopt the pyramid configuration by which the overall energy of the system was minimized.

Citations

Hara M, T Kondo, M Komoda, S Ikeda, K Shinohara, A Tanaka, JN Kondo, and K Domen. 1998. "Cu_2O as a Photocatalyst for Overall Water Splitting under Visible Light Irradiation." *Chemical Communications*
3:357-358.

Ikeda S, T Takata, T Kondo, G Hitoki, M Hara, JN Kondo, K Domen, H Hosono, H Kawazoe, and

A Tanaka. 1998. “Mechano-Catalytic Overall Water Splitting.” *Chemical Communications* 20:2185-2186.

Kosugi T and S Kaneko. 1998. “Novel Spray-Pyrolysis Deposition of Cuprous Oxide Thin Films.” *Journal of the American Ceramic Society* 81(12):3117-3124.

Ling J and JP Wolfe. 1993. “Bose-Einstein Condensation of Paraexcitons in Stressed Cu_2O.” *Physical Review Letters* 71(8):1222-1225.

Lyubinetsky I, S Thevuthasan, DE McCready, and DR Baer. 2003. “Formation of Single-Phase Oxide Nanoclusters: Cu_2O on $SrTiO_3$(100).” *Journal of Applied Physics* 94(12):7926-7928.

Lyubinetsky I, AS Lea, S Thevuthasan, and DR Baer. 2005. “Formation of Epitaxial Oxide Nanodots on Oxide Substrate: Cu_2O on $SrTiO_3$(100).” *Surface Science* 589(1-3):120-128.

Zuo JM, M Kim, M O’Keeffe, and JCH Spence. 1999. “Direct Observation of d-Orbital Holes and Cu-Cu Bonding in Cu_2O.” *Nature* 401(6748):49-52.

Electron-Beam Induced Recrystallization in Amorphous Apatite

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Damage accumulation or recovery in certain materials under irradiation is a long lasting research topic. Crystalline apatite amorphized by energetic ion irradiation and the amorphous apatite recrystallized under further electron-beam (e-beam) irradiation are decided by local ion- and electron-solid interactions.

Apatite silicates, which are well known as extremely durable minerals, are proposed as host phases for immobilization of actinides and fission products (Weber et al. 1997). While it is known that alpha decay and heavy ion irradiation leads to amorphization of apatite materials, the effects of light ions and/or electron irradiation are not clearly understood. E-beam irradiation has proven to be capable of inducing amorphization in materials such as silicon carbide (Inui et al. 1990a; Isimaru et al. 2003), quartz (Inui et al. 1990b; Hobbs and Pascucci 1980), and coesite (Gong et al. 1996); while, in contrast, it can also cause an annealing effect in amorphous strontium titanate (Zhang et al. 2005) and other apatites (Weber and Matzke 1986; Wang and Weber 1999). Thus, the study of e-beam irradiation characteristics for apatite materials is of technological and scientific importance.

In this study, the micro-structural changes in ion-beam-amorphized $Sr_2Nd_8(SiO_4)_6O_2$ were investigated under 200 keV e-beam irradiation to further our understanding of the effects of e-beam irradiation on growth or recovery of the amorphous state. Ion irradiation, subsequent ion beam analysis based on channeling Rutherford backscattering spectroscopy (RBS), transmission electron microscope (TEM) observations, and *in situ* e-beam irradiations were performed in the EMSL.

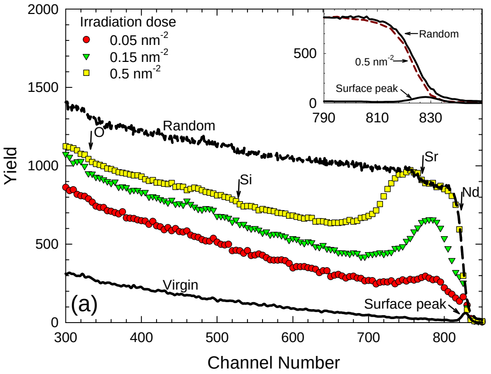

Figure 1. *Series of <100>-aligned RBS spectra for $Sr_2Nd_8(SiO_4)_6O_2$ irradiated with 1.0-MeV Au^+ to different ion fluences. An enlargement of the high-energy end of the spectrum is shown as the insert.*

High-dose irradiation of $Sr_2Nd_8(SiO_4)_6O_2$ by 1.0 MeV Au at 300 K leads to accumulated damage in crystal. The spectra for low-, medium-, and high-fluence irradiations illustrate the damage evolution process, where the incremental increase of the scattering yield above the virgin channeling spectrum can be easily resolved. With increasing ion fluence, the peak height increases and eventually reaches the random level. Further irradiation leads to the growth of a continuous amorphous layer that extends from the damage peak region toward the surface and into the bulk. An amorphous layer with thickness of approximately 250 nm is formed after 5.0×10^{13} cm^{-2} irradiation with some residual crystallinity at the sample surface, as shown by the lower scattering yield compared to the random yield in the inset in Figure 1.

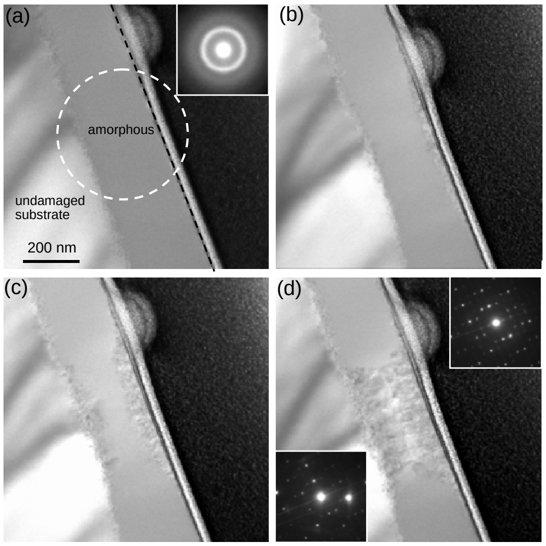

Figure 2. *Structural changes of $Sr_2Nd_8(SiO_4)_6O_2$ under electron irradiation: (a) 0 seconds, (b) 840 seconds, (c) 1980 seconds, (d) 3600 seconds. Electron flux was fixed at 0.29 A cm-2 (1.82 x 1018 cm-2s-1).*

Figure 2 shows the time evolution of e-beam-induced effects in amorphized $Sr_2Nd_8(SiO_4)_6O_2$ with an electron flux of 0.29 Å cm^{-2} (1.82 x 1018 cm^{-2s-1}) at room temperature. The initial amorphous layer before electron irradiation is shown in Figure 2(a). After 840 seconds of irradiation, recrystallization is observed from both of the amorphous/crystalline (a/c) interface and the surface. Recrystallization proceeds from both sides with almost the same rates as the electron irradiation continues to 1980 seconds. After irradiating for 3600 seconds, the recrystallization from both sides meet. It is proposed that the epitaxial recrystallization starts

from the a/c interface and the remnant crystallinity at the surface because the undamaged single crystalline substrate can act as a template material during the recrystallization process.

The recrystallization thickness is shown in Figure 3 as a function of irradiation time under two different electron fluxes. For both electron fluxes, the recrystallization process shows two linear stages: rapid regrowth up to approximately 250 seconds followed by a slower regrowth that is strongly flux-dependent up to measurement times of approximately 3000 seconds. The rapid motion of the a/c interface during the initial stage is considered to be associated with electron-enhanced defect annihilation at a/c interface, similar to that observed in $SrTiO_3$. Besides, nanocrystallities, which are considered to exist at the a/c interface, are also considered to play a role for the rapid motion of the a/c interface. After the initial stages, at which most of the defects near the a/c interface have been annihilated, the recrystallization processes are stabilized at decreasing rates as indicated by the decreased slopes with further irradiation time.

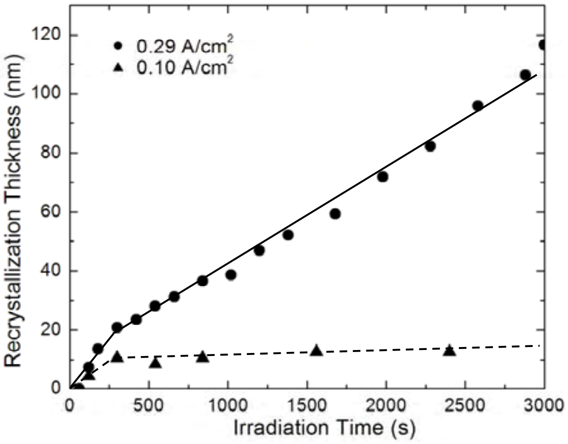

Figure 3. *Amorphous-to-crystalline phase transition as a function of 200-keV e-beam irradiation time under two different electron fluxes at RT.*

Ionization-induced processes, in which incident electrons primarily transfer their energy by inelastic interaction with target atoms to induce localized electronic excitations, may play an important role for the observed recrystallization in this work. Since the localized electronic excitations can disturb local atomic bonds and structure, they may effectively lower the energy barrier for defect recovery and recrystallization processes, which may involve local atomic hopping or rotation of atomic polyhedra (Zhang et al. 2005).

In conclusion, epitaxial recrystallization is observed from both the amorphous/crystalline interface and the surface, and the recrystallization is more pronounced with increasing e-beam flux. Because the temperature increase induced by e-beam irradiation is estimated to be less than 7 K and maximum energies transferred to target atoms are below the displacement energies, ionization-induced processes are considered to be the primary mechanisms for the solid-phase epitaxial recrystallization observed in this study.

Citations

Gong WL, LM Wang, RC Ewing, and J Zhang. 1996. "Electron-Irradiation- and Ion-Beam-Induced Amorphization of Cosite." *Physical Review B* 54(6):38003808.

Hobbs LW and MR Pascucci. 1980. "Radiolysis and Defect Structure in Electron-Irradiated α-Quartz." *Journal de Physique Colloque* 41(C6):237-242.

Inui H, H Mori, and H Fujita. 1990a. "Electron-Irradiation-Induced Crystalline to Amorphous Transition in Alpha-SiC Single Crystals." *Philosophical Magazine B* 61(1):107-124.

Inui H, H Mori, T Sakata, and H Fujita. 1990b. "Electron-Irradiation-Induced Crystalline-to-Amorphous Transition in Quartz Single Crystals." *Journal of Non-Crystalline Solids* 116(1):1-15.

Ishimaru M, IT Bae, and Y Hirotsu. 2003. "Electron-Beam-Induced Amorphization in SiC." *Physical Review B* 68(14): Article No. 144102.

Wang LM, and WJ Weber. 1999. "Transmission Electron Microscopy Study of Ion-Beam-Induced Amorphization of $Ca_2La_8(SiO_4)_6O_2$." *Philosophical Magazine A* 79(1):237-253.

Weber WJ and H Matzke. 1986. "Effects of Radiation on Microstructure and Fracture and Fracture Properties in $Ca_2Nd_8(SiO_4)_6O_2$." *Materials Letters* 5(1-2):9-16.

Weber WR, RC Ewing, and A Meldrum. 1997. "The Kinetics of Alpha-Decay-Induced Amorphization in Zircon and Apatite Containing Weapons-Grade Plutonium or Other Actinides." *Journal of Nuclear Materials* 250(2-3)147-155.

Zhang Y, J Lian, CM Wang, W Jiang, RC Ewing, and WJ Weber. 2005. "Ion-Induced Damage Accumulation and Electron-Beam-Enhanced Recrystallization in $SrTiO_3$." *Physical Review B* 72(9):Article No. 094112.

Irradiation Behavior of $SrTio_3$ at Temperatures Close to the Critical Temperature for Amorphization

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Perovskites are the most abundant mineral on earth with a general formula of ABO_3. Strontium titanate ($SrTiO_3$) is a prominent representative of the group that is of technological interest in microelectronics and optoelectronic industries, as well as a potential material for immobilization of nuclear waste.

Irradiation with energetic ions can be used to modify the surface and near-surface properties, inevitably produces defects and lattice disorder, and leads to amorphization. Previous irradiation studies (Zhang et al. 2005; White et al. 1988; Weber et al. 2000; Meldrum et al. 2002) indicate that $SrTiO_3$ undergoes an irradiation-induced crystalline to amorphous phase transition. The mechanism for irradiation-induced amorphization close to the critical temperature is, however, not well documented. To promote a better understanding of damage evolution, damage annihilation, and amorphization processes, this paper quantitatively characterizes damage accumulation on both the Sr and Ti sublattices as a function of dose under Au irradiation at temperatures close to the critical temperature for amorphization.

Ion irradiation, subsequent investigation of damage accumulation by Rutherford backscattering spectrometry (RBS), and cross-sectional transmission electron microscopy (TEM) in the $SrTiO_3$ single crystals were carried out using EMSL research facilities.

For irradiation at 360 K, which is just below the critical temperature (~ 370 K) for amorphization in the bulk, the depth profiles to various ion fluences are shown in Figure 1. The disorder on both the Sr and Ti sublattices increases with ion fluence. A fully amorphous layer is formed around 60 nm, following 1.2×10^{14} cm^{-2} irradiation at 360 K.

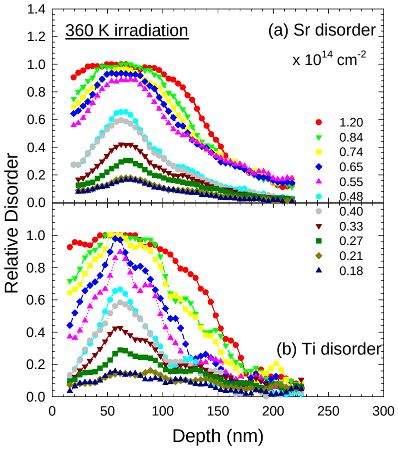

Figure 1. *Disorder profiles on (a) Sr and (b) Ti sublattices under 1.0 MeV Au+ irradiation at 360 K. The lines are smooth curve fits to the data to guide the eye.*

The damage evolution at 400 K, which is above the critical temperature for bulk amorphization in $SrTiO_3$, is unusual as shown in Figure 2. For low ion fluences up to 1.5×10^{14} cm^{-2}, the relative disorder increases with increasing dose over the entire irradiation range, as expected. With further irradiation, the damage peak increases in width, but decreases in height. The damage saturates at a disorder level of ~0.75 under irradiation of 2.8×10^{14} cm^{-2}. For high ion fluence, the maximum damage appears at a deeper depth, where the damage accumulation stage and extended defect stage are delayed because of the nature of ion implantation. In addition, the saturation disorder level at 60 nm decreases. Under higher ion fluence irradiation, the supersaturation of point defects can cause agglomeration and formation of stable planar defects and dislocations (extended defect stage). The nucleation and growth of more complex defects, which act as sinks for point defects, effectively reduce the disorder accumulation rate. As the disorder level decreases at ~60 nm, the local dynamic annealing changes due to extend defect growth acting as a sink for point defects, and a new equilibrium state at lower disorder may eventually be reached. The unusual damage accumulation behavior is attributed to the formation and growth of stable extended defects.

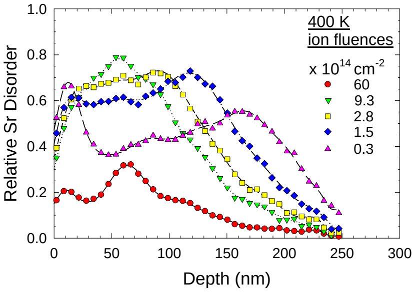

Figure 2. *Disorder profiles on Sr sublattice under 1.0 MeV Au+ irradiation at 400 K.*

Ion beam induced epitaxial crystallization (IBIEC) has attracted much attention over a few decades. The mechanisms of electronic and nuclear energy losses in IBIEC that are controlling the regrowth processes are not yet clear. In this study, electron beam (e-beam)-enhanced recrystallization is clearly observed before and after the electron-beam irradiation, as shown in Figure 3. This recrystallization may be attributed to localized electronic excitations that promote the rearrangement of interfacial atoms. It is worth to pointing out that the e-beam flux during the TEM observation is on the order of 10^{20} cm-$^{2s-1}$, which is eight orders of magnitude higher that the ion flux during the ion irradiation. Based on previous a recrystallization study on e-beam flux, the ion-induced dynamic recovery due to inelastic scattering processes in the current ion-irradiation study is negligible.

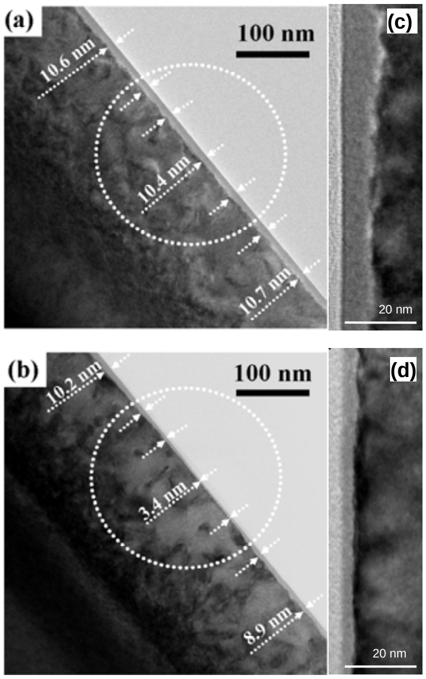

Figure. 3. *TEM images of a) the amorphous layer of ~10 nm as indicated by the arrows. The dashed circle marks the electron irradiation area; b) the crystallization of amorphous layer following the e-beam irradiation; c) higher magnification image of the amorphous layer; and d) higher magnification image after the e-beam irradiation of the same region as shown in c).*

Under current irradiation conditions, nuclear stopping is a few times higher than electronic stopping over the whole irradiation region. During ion bombardment, the nuclear energy losses of the Au ions can efficiently transfer energy to a large number of target atoms in both the crystalline and damaged regions. The deposited energy can create defects, and stimulate defect migration and atomic rearrangement. At lower doses (i.e., the damage accumulation stage), the energy from Au ions is mainly transferred to atoms in the ordered crystalline structure; therefore, the fraction of damaged material increases with dose. As the irradiation dose increases (evolution stage), the probability for energy transfer from the Au ions to already disordered atoms increases, and the dynamic annealing of disordered atoms becomes more probable. When the effect of dynamic annealing is high enough to balance the ion-induced disordering, a saturation level is reached.

In this research, damage accumulation on both the Sr and Ti sublattices in strontium titanate ($SrTiO_3$) has been investigated under 1.0 MeV Au^+ irradiation at 360 and 400 K, close to the critical temperature for amorphization (~ 370 K). Under irradiation at 360 K, the relative disorder on both sublattices follows a nonlinear dependence on ion dose. Amorphization starts from the damage peak region (at a depth of 60 nm) and grows toward the surface and into the bulk. At 400 K, evolution of point defects to extended defects occurs as ion fluence increases. The disorder initially peaks at a depth of 60 nm, saturates at disorder level of ~0.75, and then decreases with further irradiation. At an ion fluence of 6.0×10^{15} cm^{-2}, an amorphous layer of ~10 nm thickness is formed at the sample surface.

Citations

Meldrum A, LA Boatner, WJ Weber, and RC Ewing. 2002. “Amorphization and Recrystallization of the $AB0_3$ Oxides.” *Journal of Nuclear Materials* 300(2-3):242-254.

Weber WJ, W Jiang, S Thevuthasan, RE Williford, A Meldrum, and LA Boatner. 2000. *Defects and Surface-Induced Effects in Advanced Peroskites*. G. Borstel (ed.), p. 317, Kluwer Academic Publishers, The Netherlands.

White CW, LA Boatner, PS Sklad, CJ McHargue, J Rankin, GC Farlow, and MJ Aziz. 1988. “Ion Implantation and Annealiing of Crystalline Oxides and Ceramic Materials.” *Nuclear Instrumentation Methods Physics Research B* 32(1-4):11-22.

Zhang Y, J Lian, CM Wang, W Jiang, RC Ewing, and WJ Weber. 2005. “Ion-induced Damage Accumulation and Electron-beam-enhanced Recrystallization in $SrTio_3$.” *Physical Review B* 72(9):094112-1-8.

Synthesis and Characterization of Lithium-Doped Tin Dioxide Nanocrystalline Powders

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Flat panel liquid crystal displays use degenerated doped indium tin oxide as conductive electrodes, but thin film based transistors on silicon are needed for addressing individual pixels. Processing of silicon thin film transistors increases the cost of fabrication for large-area displays. However, if highly conductive p-type tin oxide (SnO_2) can be realized, oxide-based inexpensive transistors can dramatically alter the production cost and ease material processing. Currently, the “unipolar” doping problem of SnO_2 has been an obstacle. In this research, we examined the prospects of effective p-doping of SnO_2 using lithium as a dopant.

Several structural and functional phenomena in materials science are directly related to particle size. In recent years, studies of nanometer-sized materials have characterized the effects of finite size on thermodynamic and quantum mechanical properties, leading to novel catalytic, optical, and electronic applications. In this regard, corrosion-resistant, tin-oxide (SnO_2) nanoparticles have important niche applications. Some well-known examples include solar energy conversion, catalysis, gas sensing, antistatic coating, and transparent electrode preparations. Another potential application of SnO_2 is for transparent electronics, which would be especially valuable in flat panel liquid crystal displays (LCDs) that already use degenerated-doped indium SnO_2 as conductive electrodes, but need thin film transistors (TFTs) based on silicon for addressing individual pixels. Processing of silicon TFTs increases the cost of fabrication of large-area displays. However, if highly conductive p-type SnO_2 can be realized, inexpensive oxide-based transistors could dramatically alter the production cost and ease material processing. Currently, the “unipolar” doping problem of

SnO_2 has been an obstacle. There are only a few examples of p-doped SnO_2. Theoretically, if effective substitution of tin (Sn) with III-family elements [e.g., cesium (Ce)] or substitution with lithium (Li) is realized, then p-type SnO2 could be synthesized.

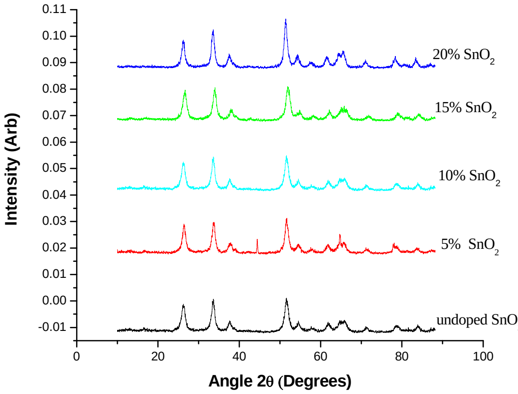

Figure 1. *XRD patterns of Li-doped SnO_2 (numbers indicate the percent of LiCl during synthesis).*

In this paper, we examine the prospects of effective p-doping of SnO_2 using Li as a dopant. Pure and Li-doped SnO_2 nanoparticles were synthesized using the sol-gel precipitation method in the presence of LiCl. There were several potential complications in Li doping SnO_2 especially at high dopant concentration. First, high Li concentration might lead to formation of lithium stannate (Li_2SnO_3), which would effectively phase separate during commonly used high-calcination temperatures. We used a combination of nuclear reaction analysis (NRA) and high-resolution transmission electron microscopy (TEM) studies to probe this possibility. Second, the nature of α or β stannic acid, especially its degree of ionization, might influence whether or not Li is incorporated in the casserite lattice of SnO_2. We employed a wide range of pH conditions during the synthesis to affect the oxo-ionic acid charge. Finally, under these varied reaction conditions, we anticipated that the particle size, particle crystallinity, and occurrence of additional crystalline phases might be influenced. We employed x-ray diffraction (XRD) analysis to quantify these effects. The precipitation pH was found to play an important role when it comes to Li doping. Nuclear reaction analysis NRA) showed that Li is not detected (i.e., <0.005 atomic-percent level) when the solution pH during synthesis is less than 7, while above pH of 7, relatively small amounts of Li are incorporated. Doping level does not appear to alter the lattice structure of casserite. The XRD patterns of the undoped and doped SnO_2 in Figure 1 show only the tetragonal rutile structure. These results agree with results obtained in earlier work, and at least at the level of doping and processing conditions, we were unable to detect measurable quantities of crystalline Li_2SnO_3.

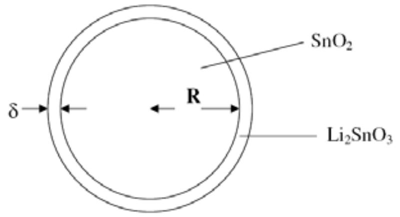

Figure 2. *Shell model.*

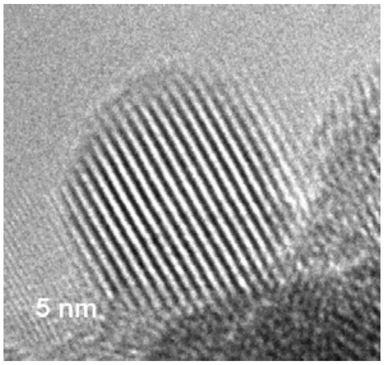

Figure 3. *High-resolution TEM image of 15 percent Li doped SnO_2.*

The crystallite size as determined from XRD analysis decreases with increasing concentration of LiCl used during doping. It is evident from this study that it is possible to control particle size by controlling the LiCl concentration. Although high concentra-tions of LiCl are used during synthesis, the concentration of dopant Li incorporated is small, as determined by NRA. Therefore, we plotted the particle size data as a function of Li incorporated and found that it varies inversely with Li concentration. Although NRA data provide the amount of Li, it does not reveal the spatial distri-bution of Li within nanoparticles. At higher Li doping levels, a chemical complexity may arise because of solid-solid phase separation of conductive amorphous or a thin shell of Li_2SnO_3 from SnO_2. To study this possibility, we considered a crude shell model in which an outer amorphous shell of Li_2SnO_3 surrounds the undoped SnO_2. Using a simple mass balance consideration, the shell model expression can be derived. In the model depicted in Figure 2, the shell thickness depends on the concentration of the Li incorporated in the casserite structure (i.e., the bulk of the nano-particles). Here we assumed shell thickness was zero. As more Li dissolves in the lattice, the thinner the shell becomes. Because we were unable to locate any diffraction peaks within the sensitivity of our x-ray instrument, we conducted search of such thin shell using high-resolution TEM.

The data in Figure 3 allow us to bound the thickness of the amorphous layer at about 0.2 nm. Thus, combined XRD, TEM, and NRA data imply a very thin shell and minimal solubility of Li in the SnO_2 lattice. Recently, we verified the phase-separation model described above using Li-nuclear magnetic resonance studies that revealed two component spectra—one isotropic peak indicating tetrahedral symmetry (for Li dissolved in bulk) and another axially symmetric powder pattern for the surface-bound Li. The latter spectrum exhibited non-zero quadrupolar splitting.

Nanoscopic phase separation, as indicated in our studies, has some interesting consequences for device design. Lithum is believed to convert n-type SnO_x to p-type SnO_x. However to bring about such carrier inversion, intrinsic n-doping resulting from oxygen vacancies must be overcome. Given the high n-type carrier density in SnO_x, a significant concentration of p-type dopant must be introduced in the lattice. Our studies indicate that at a carrier density of approximately 1021 cm^{-3}, about 0.16 atomic-percent of Li can be accommodated. However, a substantial fraction of Li remains on the surface, thus reducing the extent of bulk p-type doping. The observed Li concentration dependence of p-doping in SnO_x by other researchers indicates that increasing the concentration of LiCl in synthesis above 15 percent leads to a reduction in the p-type carrier density. This is consistent with the simple phase-separation model presented above.

In conclusion, a sol-precipitation method was used to prepare SnO_2 and Li-doped nanoparticles. From this work, we managed to show that Li-insertion into SnO_2 is pH dependent and only occurs under alkaline conditions. By varying pH, temperature, and dopant level, we demonstrated that it is possible to control the nanoparticle size. Low particle growth rates were obtained by the introduction of Li particles into the SnO_2.

Crosslinked Enzyme Aggregates in Hierarchically Ordered Mesoporous Silica: A Simple and Effective Method for Enzyme Stabilization

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a -Chymotrypsin (CT) and lipase (LP) were immobilized in hierarchically-ordered mesocellular mesoporous silica (HMMS) in a simple but effective way for the enzyme stabilization, which was achieved by the enzyme adsorption followed by glutaraldehyde (GA) crosslinking. This resulted in the formation of nanometer scale crosslinked enzyme aggregates (CLEAs) entrapped in the mesocellular pores of HMMS (37 nm), which did not leach out of HMMS through narrow mesoporous channels (13 nm). CLEA of a-chymotrypsin (CLEA-CT) in HMMS showed a high enzyme loading capacity and significantly increased enzyme stability. No activity decrease of CLEA-CT was observed for two weeks under even rigorously shaking condition, while adsorbed CT in HMMS and free CT showed a rapid inactivation because of the enzyme leaching and presumably autolysis, respectively. With the CLEA-CT in HMMS, however, there was no tryptic digestion observed, suggesting that the CLEA-CT is not susceptible to autolysis. Moreover, CLEA of lipase (CLEA-LP) in HMMS retained 30 percent specific activity of free lipase with greatly enhanced stability. This work demonstrates that HMMS can be efficiently employed as host materials for enzyme immobilization leading to highly enhanced stability of the immobilized enzymes with high enzyme loading and activity.

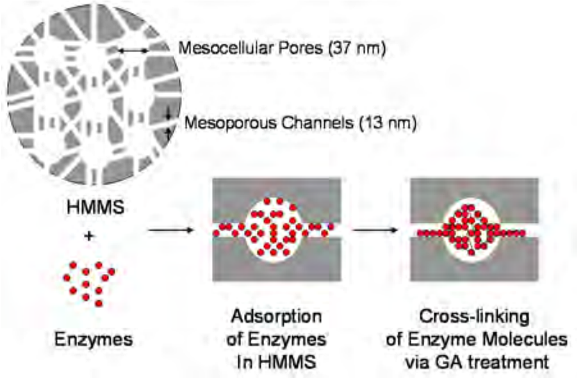

Figure 1. *Preparation of CLEAs in HMMS.*

The preparation scheme of CLEAs in HMMS consists of two simple steps as deicted in Figure 1. The first step is to adsorb enzymes in HMMS, and the second step is to crosslink the adsorbed enzymes via glutar-aldehyde treatment, resulting in nanometer-scale crosslinked enzyme aggregates (CLEAs) in the mesopores of HMMS. The structural properties of the employed HMMS are shown in Figure 1. A SEM image of the HMMS indicates that the component size of HMMS ranges from 200 to 500 nm. TEM image of the HMMS (Figure 2) shows the co-existence of large mesocellular pores (37 nm) and small mesoporous channels (13 nm). The channels are large enough for the enzymes to pass through without considerable diffusion limitation and the mesocellular pores can accommodate CLEAs.

We have demonstrated that the CLEAs entrapped in the mesocellular pores (37 nm) do not leach out through the mesoporous channels (13 nm) like in a ship-in-a-bottle approach, leading to high-enzyme loading with concomitant improved stabilization of enzyme activity. The detailed mechanism of the ship-in-a-bottle approach has been elucidated in this paper.

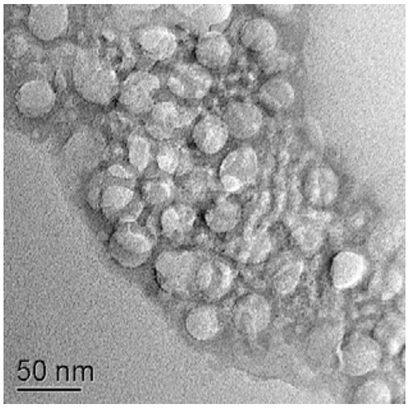

Figure 2. *TEM image of HMMS. Co-existence of large mesocellular pores and small mesoporous channels can be shown.*

Epitaxial Growth and Microstructure of Cu_2O Quantum Dots/Thin Films on $SrTiO_3(100)$

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Cuprous oxide (Cu_2O) is a non-stoichoimetric p-type semiconductor that shows unique electronic structure for applications related, in particular, to chemical and photochemical process such as water splitting under visible light irradiation. Finding an appropriate substrate, such as $SrTiO_3$ (STO), on which Cu_2O thin-film/quantum dots could be grown would help form hetero-junctions and effectively separate electron-hole pairs, thereby enhancing energy conversion efficiency.

In this paper, we report the epitaxial growth of Cu_2O thin films on an STO(100) surface. In the EMSL ultrahigh vacuum (UHV) chamber, the substrates were cleaned using oxygen plasma (1.0 x 10^{-5} torr oxygen partial pressure, 200-W power level) with a sample temperature of 600°C. During growth, Cu was evaporated from an effusion cell in the presence of the oxygen plasma while the substrate was kept at a temperature between 450 and 850°C. The growth rate of the film was controlled by changing the Cu flux, which was monitored by a quartz-crystal oscillator. The growth of the island (specimen A) and film (specimen B) could be obtained at Cu fluxes of 6 x 10^{-4} nm/s and1 x 10^{-3} nm/s, respectively.

Films grown under the two growth rates were similarly dominated by the Cu_2O phase, which showed a preferred orientation with respect to the substrate such that Cu_2O (200)//STO(100) as shown in Figure 1. The core-level Cu 2p x-ray photoelectron spectroscopy (XPS) image of sample A is shown in Figure 2(a). This image indicates that for sample A, the Cu at the very top layer possesses a valence state of +2. After removing approximately 5 nm from the very top layer by sputtering, the Cu^{2+} peak disappears, and instead, as illustrated in Figure 1(a), the Cu^{+} dominates. Cu 2P3/2 and 2P1/2 XPS spectra of sample B for the as-deposited case and after sputtering to remove a surface layer of approximately 5 nm are shown in Figure 2(b). The main peaks of Cu 2P3/2 and 2P1/2 lie at 931.8 and 952.0 eV, demonstrating that Cu in sample B exists only as Cu^{+}. This finding is consistent with the x-ray diffraction (XRD) results, which show a single Cu_2O phase.

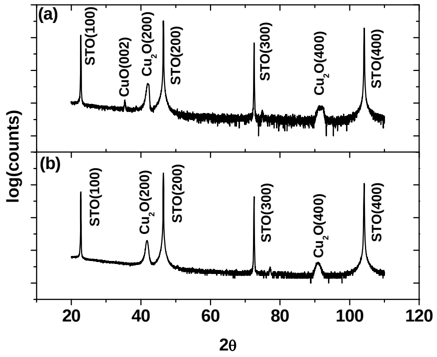

Figure 1. *X-ray diffraction spectra of the samples.*

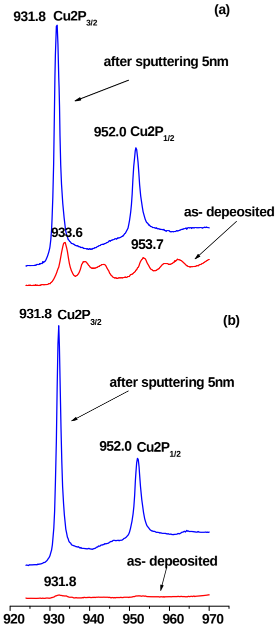

Figure 2. *XPS spectra of the samples.*

Figure 3(a) is an atomic force microscopy (AFM) image of sample A that reveals a very rough surface. The rough surface was morphologically featured by the development of pyramids. The faces and edges of these pyramids are aligned, which indicates a similar crystallographic orientation of all the pyramids relative to the underline STO substrate. The insets shown in Figure 3(a) are two typical Wulff shape constructions of these pyramids. The transmission electron microscopy (TEM) image reveals that the pyramid has a typical height of approximately 200 nm, and all the pyramids are crystallographically aligned along the same direction with respect to the substrate. This point is clearly demonstrated by the selected area electron diffraction pattern shown in Figure 3(c). The overall orientation relationship between the substrate and the pyramid can be written as Cu_2O[001]//STO[001] and Cu_2O(1000//STO(100). This orientation relationship corresponds to a cube-on-cube orientation relationship between the cubic structured Cu_2O and STO. The computed diffraction pattern shown in Figure 3(d) consistently supports this finding.

When compared with sample A, sample B shows a relatively flat surface as is shown in Figure 4(a). Careful scrutiny of the AFM image of sample B reveals that the surface of sample B also consists of very small pyramids, indicating a tendency for faceting of the film surface with the {111} planes. The cross-sectional TEM image shown in Figure 4(b) reveals that sample B indeed indicates growth of a Cu_2O thin film on the STO(100) surface. Both XRD and selected area electron diffraction revealed that, similar to the case of sample A, the thin film in sample B also possesses an epitaxial orientation relationship with the substrate: Cu_2O[001]//STO[001] and Cu_2O (1000//STO(100). This orientation is demonstrated by the electron diffraction patterns shown in Fig. 4(c) and Fig. 4(d).

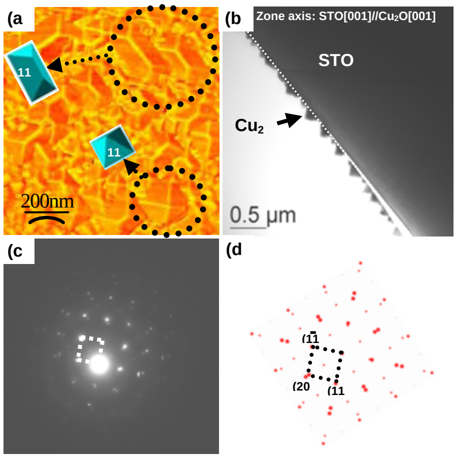

Figure 3. *(a) AFM image, (b) TEM image, (c) electron diffraction pattern, and (d) calculated electron diffraction pattern.*

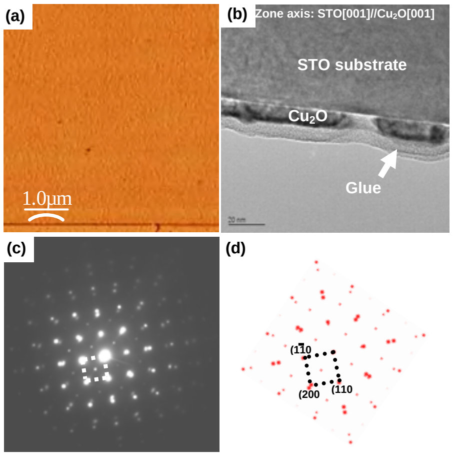

Figure 4. *(a) AFM Image, (b) TEM image, (c) electron diffraction pattern, and (d) calculated electron diffraction pattern.*

The dramatic difference in the morphology of specimen A and specimen B can be examined from the perspective of growth kinetics. For the case of a fast growth (e.g., for sample B), the growth rate is high; therefore, it leaves the system only a relatively short time to reach a configuration by which the overall energy of the system is minimized. On the other hand, in the case of low growth, the atoms will migrate, thereby allowing the system to develop a configuration by which the overall energy of the whole system will be mini-mized. Typically, development of a pyramid structure confined by the {111} planes is energetically more favored than development of a flat surface that is dominated by a Cu_2O(100)-type plane. Energetically, we would expect high-temperature annealing of a Cu_2O thin film, such as that developed in sample B, to pro-mote formation of pyramid-structured quantum dots as shown in the microstructure developed in sample A.

Direct Observation of Adsorption Evolution and Bonding Configuration of TMAA on $TiO_2(110)$

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Trimethyl acetic acid (TMAA) adsorption evolution on the rutile TiO2(110) surface from submonolayer-to-saturation coverages was examined at the atomic level by scanning tunneling microscopy. Upon TMAA deprotonation, no evidence of proton adsorbs on an adjacent bridging O^{2-} site has been found. It has been suggested that uncommon proton bonding configuration is favored instead. Such a configuration is likely to be stabilized by adjacent adsorbed carboxylate (TMA) groups.

The chemical interaction of molecules with titania (TiO_2) surfaces is crucial in a number of important fields, including catalysis and photocatalysis (Diebold 2003). Consistent with the known chemistry of organic acids on titania, TMAA adsorbs dissociatively on $TiO_2(110)$ by O-H bond cleavage at or below 300 K. The TMA bridge-bonds across two Ti^{4+} cations, with the molecular plane oriented normal to the surface and along the Ti rows (the <001> direction). A highly ordered (2×1) TMA monolayer is formed at saturation coverage (Henderson et al. 2003; Onishi 2003). While it has been implicitly assumed that the acid proton adsorbs on an adjacent bridging O^{2-} site, forming an OH^- group (Onishi 2003), there is no unambiguous evidence in the literature for the presence of these hydroxyl species.

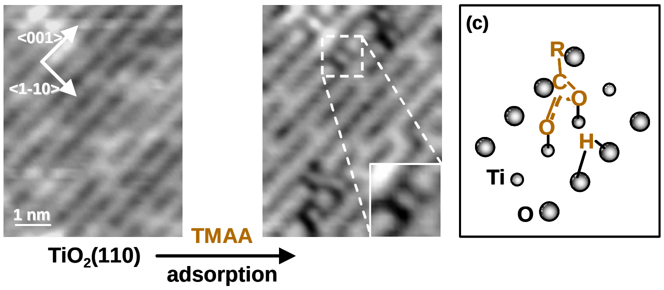

Figure 1. *STM images of the same (5.5×7.5) nm^2 area: (a) before and (b) after TMAA exposure (coverage approximately 0.05 ML). The inset is a magnified view of one feature. Image (c) is a schematic model of the proposed proton bonding configuration.*

Sequences of scanning tunneling microscopy (STM) images showing the same surface area with increasing adsorbate coverages have been acquired for the 260-300 K range (Lyubinetsky et al. 2007). Analysis of the same region during progressive adsorption allows us to monitor changes caused by the adsorption of single TMAA molecules Lyubinetsky et al. 1998). Figure 1 presents the same area images before and after a low-dose TMAA exposure. The adsorbed TMA species appear as a localized dark square-shaped feature with a bright protrusion in the middle. The TMA footprint covers just two neighboring Ti^{4+} atoms, giving additional, direct evidence for the bridge bonded TMA configuration discussed in literature (Onishi 2003).

However, there is no indication of the appearance of OH^- groups in Figure 1b. Because proton abstraction is improbable based on temperature programmed desorption (TPD) results (White et al. 2004), we suggest that the deposited H atom takes on a different bonding configuration, with the proton attaching to a pair of bridging O atoms instead of to a single O atom. Certainly, considering the distance between two O atoms of 0.298 nm, the OH bond in the proton oxygen bridging configuration would be a relatively weak (in the terms of the hydrogen bond strength classification scheme) (Novak 1974). In addition, such a configuration may be stabilized by the proximity of the (negatively charged) TMA group adsorbed symmetrically on adjacent Ti^{4+} sites, as schematically shown in Figure 1c.

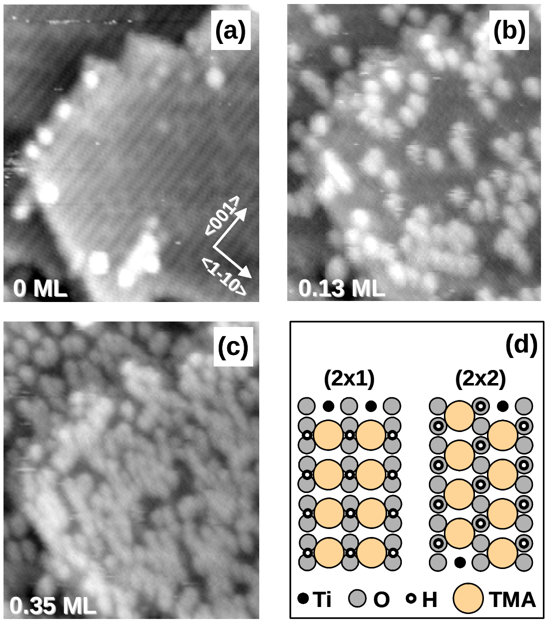

Figure 2. *STM images of the same (16×20) nm^2 area of the TiO_2(110) surface (a) before and after adsorption of 0.13 ML (b), and 0.35 ML (c). Structural models of the TMA monolayer (image [d]) illustrate the favorable (2×1) TMA ordering (left model) by the suggested H bridging a pair of O sites. Alternative atop H attachment to single O ion would rather induce (2×2) ordering (right model).*

Figure 2 illustrates an evolution of the TMAA adsorption throughout its consecutive stages by presenting the STM image snapshots of the same surface region starting from clean TiO_2(110) up to close to saturation of the monolayer. In the image before adsorption (Figure 2a), examples of bridging oxygen vacancies and also of a minor number of OH^- groups are differentiated by their relative contrast (Brookes et al. 2001; Wendt et al. 2005). After dosing with TMAA, the new features that appeared were relatively large bright spots centered on the Ti^{4+} rows (Figure 2b). These features are attributed to the TMA species bridge-bonding to two Ti^{4+} cations as a result of TMAA dissociation through deprotonation (Onishi 2003). (The appearance of TMA groups has changed when compared with the images shown in Figure 1, presumably because of changed STM tip apex conditions). Beginning from approximately 0.1 to 0.15 ML coverages, pairing along the <1-10> direction starts to form, while TMA groups tend to be separated along the Ti rows (<001> direction). This correlates with the tendency of carboxylates to repel each other along the <001> direction (Onishi 2003). Because no significant surface diffusion of TMA has been observed in the studied temperature range, ordering in the <1-10> direction indicates the probable existence of a mobile precursor state. As coverage increases to 0.2 to 0.4 ML, TMA groups are forced to begin accommodating each other on adjacent Ti sites along the <001> direction, as is shown in Figure 2c. Eventually, a (2x1) TMA monolayer develops at nominal saturation coverage of 0.5 ML. Ordering of the TMA groups is possibly assisted by protons bridging between two oxygen sites, which effectively aligns adjacent carboxylates (Onishi 2003). As illustrated in the (2x1) structural model (left part of Figure 2d), such proton bonding is fully symmetric relative to adjacent TMA groups, and they would align the repulsive π-clouds of carboxylates through an electrostatic link by the adjacent protons. Alternative proton bonding (atop single O^{2-} ion) would be less symmetric and provide no apparent explanation for the (2x1) TMA ordering. Should atop proton bonding be present, it would rather favor a (2x2)- or (2xn)-type ordering based solely on a symmetry arguments. In this case, TMA groups would be shifted by a half-unit cell in the <001> direction in every second row in the (2x2) reconstruction, as shown in Figure 2d (right model) for one of the several possible OH configurations.

In summary, TMAA adsorption evolution on the $TiO_2(110)$ surface from submonolayer to saturation coverages was examined at the atomic level by STM using the same area analysis approach. Upon TMAA deprotonation, no evidence of terminal OH group formation has been found. It has been suggested that uncommon geometry associated with a detached hydrogen atom takes place instead, with proton bonding to pair bridging oxygen atoms. Such a configuration is likely to be stabilized by adjacent adsorbed TMA groups and, in turn, be a factor in the formation of TMA (2x1) reconstruction at saturation coverage.

Citations

Diebold U. 2003. "The Surface Science of Titanium Dioxide." *Surface Science* 48(58):53-229.

Henderson MA, JM White, H Uetsuka, and H Onishi H. 2003. "Photochemical Charge Transfer and Trapping at the Interface between an Organic Adlayer and an Oxide Semiconductor." *Journal of the American Chemical Society* 125(49):14974-1495.

Onishi H. 2003. "Carboxylates Adsorbed on TiO_2." In *Chemistry of Nanomolecular Systems,* Springer Series in Chemical Physics 70, ed. T Nakamura, pp. 75-90, Springer, Berlin.

Lyubinetsky I, Z Dohnálek, WJ Choyke, and JT Yates. 1998. "Cl_2 Dissociation on Si(100)-(2x1): A Statistical Study by Scanning Tunneling Microscopy." *Physical Review B* 58(12): 7950-7957.

Lyubinetsky I, ZQ Yu, and MA Henderson. 2007. "Direct Observation of Adsorption Evolution and Bonding Configuration of TMAA on $TiO_2(110)$." *Journal of Physical Chemistry C* 111(11):4342-4346.

White JM, J Szanyi, and MA Henderson. 2004. "Thermal Chemistry of Trimethyl Acetic Acid on $TiO_2(110)$." *Journal of Physical Chemistry B* 108(11):3592-3602.

Novak A. 1974. "Hydrogen Bonding in Solids." In *Structure and Bonding*, Vol. 18, ed. JD Dunitz, pp. 177-216, Springer-Verlag, New York.

Brookes IM, CA Muryn, and G Thornton. 2001. "Imaging Water Dissociation on $TiO_2(110)$." *Physical Review Letters* 87(26): Article Number 266103.

Wendt S, R Schaub, J Matthiesen, EK Vestergaard, E Wahlstrom, MD Rasmussen, P Thostrup, LM Molina, E Laegsgaard, I Stensgaard, B Hammer, and F Besenbacher. 2005. "Oxygen Vacancies on $TiO_2(110)$ and Their Interaction with H_2O and O_2: A Combined High-Resolution STM and DFT Study." *Surface Science* 5989(1-3):226-245.

Oriented ZnO Films Deposited by MOCVD with Low Carbon Concentrations

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Growth of high-purity and carbon-free, wide-band-gap semiconductors is very important for researchers in the optical and semiconductor industries. Carbon contamination is one of the major problems in metal organic chemical vapor deposition (MOCVD) semiconductor growths because the majority of the precursors are carbon dominated. In this report, we show that successful decomposition of Zn(TMHD)2 precursor resulted in low-carbon ZnO films.

The use of environmentally friendly precursors in the MOCVD process is essential because of safety hazards present in commonly used precursors. Because of the popularity and usefulness of ZnO material in transparent conducting oxide coating, spintronics, catalysis, and sensors, literature on ZnO growth by MOCVD is plentiful. Most of the work is based on use of hazardous di-methyl zinc (DMZ), di-ethyl zinc (DEZ), zinc acetate, zinc acetylacetonate-based precursors. In this report, we discuss the relatively uninvestigated Zn(TMHD) precursor for the growth of oriented ZnO films on silicon. The cleanliness of the Zn(TMHD) precursor decomposition was determined by measuring the amount of carbon in the deposited films. We show by x-ray photoelectron spectroscopy (XPS) that despite the high carbon content in the precursor (i.e., C22 in a single Zn(TMHD)2 precursor molecule), much less than 1 atomic (at.) % carbon was present in ZnO films grown with this precursor.

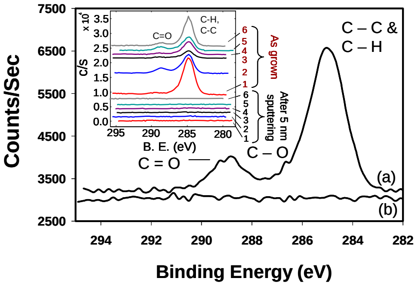

***Figure 1.** High-resolution C 1s spectra of ZnO films before and after sputtering.*

Figure 1 shows high resolution C 1s spectra before and after sputtering. The overall C concentration at the surface was 21 at. %, and was reduced after sputtering to below 1 at. %. Excess oxygen, revealed by an increase in the O to Zn ratio, is attributed to the presence of C-O and C=O functionalities on the surface. Removal of surface C layer appeared to restore the Zn/O ratio to 1:1. The inset in Figure 1 represents the reproducibility of our results. These spectra indicate high-resolution XPS scans of C 1s for ZnO films grown on single crystal silicon and Al_2O_3. The two sets of spectra represent carbon content on as-grown ZnO surfaces before and after 5 nm sputtering of the same position. Sample numbers 1, 3, and 4 are grown on single-crystal silicon, samples 2 and 6 on single-crystal c-plane Al_2O_3, and sample number 5 on r-plane Al_2O_3 under similar conditions.

As expected, we have not detected any substrate relationship to carbon content. The surface carbon concentration in the as-grown films was observed to be in the range of 11 to 34 at. %. However, the carbon was reduced to much less than 1 at. % on all samples after 5 nm of sputtering. Figure 2 indicates low- and high-resolution transmission electron microscope (TEM) micrographs of a typical ZnO film grown on silicon. A columnar structure in low-resolution TEM and the c-axis oriented atomic planar arrangement of ZnO are clearly visible in the images. A paper describing this research was published in the May issue of the *Journal of Materials Research* (Saraf et al. 2007).

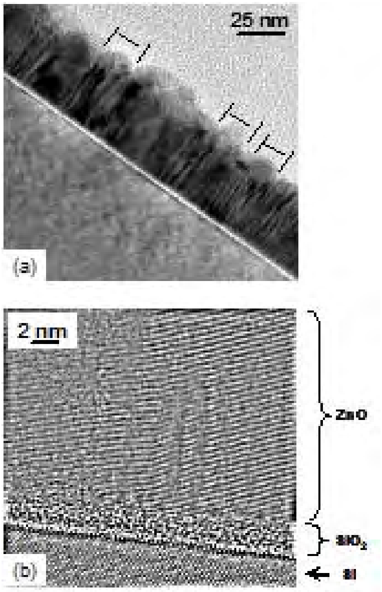

Figure 2. *Low- and high-resolution TEM images of ZnO films.*

Citation

Saraf LV, MH Engelhard, CM Wang, AS Lea, DE McCready, V Shutthanandan, DR Baer, and SA Chambers. 2007. "Metalorganic Chemical Vapor Deposition of Carbon-Free ZnO Using the Bis(2,2,6,6-tetramethyl-3,5-heptanedionato) Zinc Precursor." *Journal of Materials Research* 22(5):1230-1234.

Nucleation and Growth of MOCVD Grown (Cr, Zn)O Films: Uniform Doping vs. Secondary Phase Formation

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Understanding of doping limitations in wide-band-gap semiconductors is crucial before using them for various studies. Zinc oxide (ZnO) is a popular wide-band-gap semiconductor (oxide) studied for its usefulness in light emission, transparency, and doping-assisted, band-gap tuning ability. In this report, we focus on major limitations for chromium as a dopant in ZnO resulting secondary phase formations.

ZnO is a II-VI semiconducting oxide with the bandgap of 3.3 eV. It stabilizes in the hexagonal structure with lattice constants 0.32 nm (a) and 0.52 nm (c). ZnO is a well-known, multi-functional oxide that is useful in thermoelectric, optical, magnetic, dielectric, and sensing applications. Chromium (Cr) is of potential interest as a magnetic and electronic dopant in ZnO. Thus, the aim of this study was to determine the extent to which Cr can be incorporated into the ZnO lattice as a subsitutional cation. From our results, we concluded that little, if any, Cr occupies tetrahedral sites in the ZnO lattice. Instead, the secondary phases and $ZnCr_2O_4$, in which Cr is in octahedral sites, preferentially nucleate. Cr_2O_3 is present predominantly as a disordered phase at the interface. $ZnCr_2O_4$ also is largely segregated at the interface, although some nanocrystalline $ZnCr_2O_4$ may be present in the ZnO matrix.

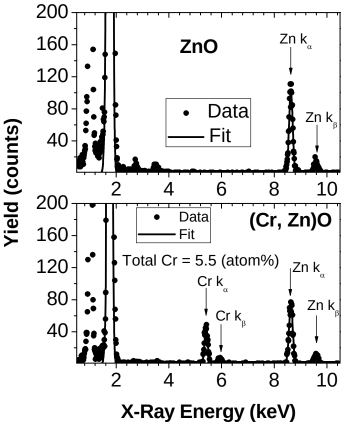

Figure 1. *PIXE spectra of (a) pure ZnO and (b) (Cr, Zn)O films*

Figure 1 indicates particle induced x-ray emission (PIXE) results for ZnO and (Cr, Zn)O films. The experimental PIXE data are shown as solid circles and the solid curve represents K-fitted spectra for pure and (Cr, Zn)O films. The initial peak at 0.7 is from Kβ lines. Peaks representing Cr lines are clearly seen in Figure 1b. The total Cr atomic percentage (at. %) in the film is 5.5 at. %. However, from an x-ray photoelectron spectroscopy depth profile and Rütherford backscattering measurements as shown in Figure 2, very little chromium is observed at the surface. As seen in Figures 1 and 2, a good correlation is observed between the two profiles (i.e., evidence of Cr-rich interface is visible). We have also confirmed from extended x-ray absorption fine structure measurements that Cr indeed occupies octahedral position. X-ray diffraction analysis also was performed to confirm the identity of the secondary spinel phases. The data discussed in this study clearly show that the solid solubility of Cr is significantly less in ZnO.

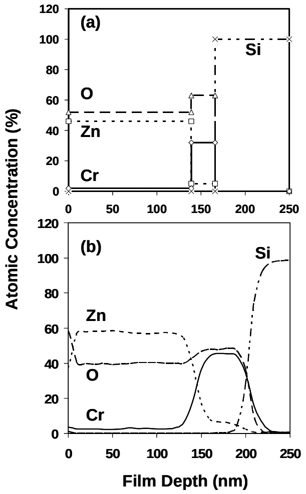

Figure 2. *Rutherford backscattering and x-ray photoelectron spectroscopy depth profiles for (Cr, Zn)O films.*

Citation

Saraf LV, MH Engelhard, P Nachimuthu, V Shutthanandan, CM Wang, SM Heald, DE McCready, AS Lea, DR Baer, and SA Chambers. 2007. "Nucleation and Growth of MOCVD Grown (Cr, Zn)O Films." *Journal of the Electrochemical Society* 154(3):D134-D138.

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.

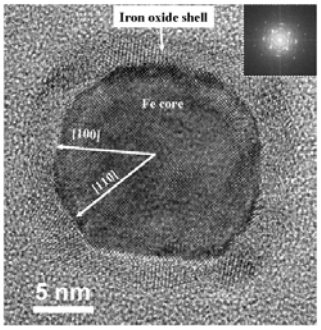

Figure 1. *High-resolution transmission electron microscope image of the core-shell structured iron nanoparticle.*

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.

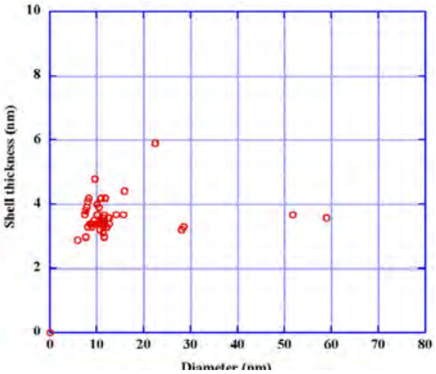

Figure 2. *Measured shell thickness as a function of particle dimension.*

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.

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.

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 tempera-tures 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

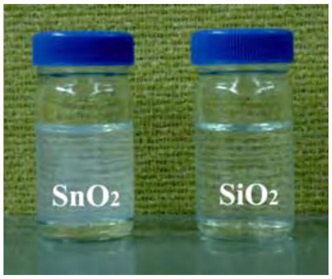

Figure 1. *Transparent nanocrystals.*

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,

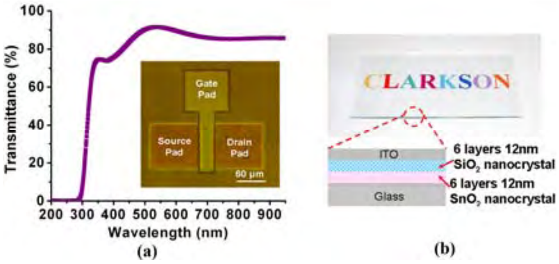

Figure 2. *(a) The optical transmittance of the thickest region of a transistor. The inset is the optical micro---graph of a top-gate transistor. (b) Visual effect of a glass slide with all of the layers of the transistor deposited on the surface.*

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.

User Projects

Field Emission SEM of Anode Supported YSZ Fuel Cells Poisoned by Cr

SP Simner, J Kim, Pacific Northwest National Laboratory, Richland, Washington

J White, Environmental Molecular Sciences Laboratory, Richland, Washington

Surface and Interface Study of Contacts to Carbon-Based Films

TC Droubay, Pacific Northwest National Laboratory, Richland, Washington

LM Porter, PB Kulkarni, Carnegie Mellon University, Pittsburgh, Pennsylvania

Novel Electrochemical Process for Treatment of Perchlorate i(PNNL Scope # 46934)

G Liu, Pacific Northwest National Laboratory, Richland, Washington

The Study of Atomic Gold Clusters in Polyaniline (Summer Research Institute, PNNL Scope #16248)

AH Saheb, M Josowicz, JA Janata, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

The Study of Atomic Gold Clusters in Polyaniline

AH Saheb, M Josowicz, JA Janata, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

Surface Characterization of Ambient Ultrafine Particles

EL Bullock, AM Johansen, C Thomas-Bradley, Central Washington University, Ellensburg, Washington

Routine SEM Analysis of Lysed *Bacillus* Spores

CL Warner, CJ Bruckner-Lea, Pacific Northwest National Laboratory, Richland, Washington

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

Microscopy of Hanford Tank Sludge

EC Buck, Pacific Northwest National Laboratory, Richland, Washington

Electron Microscopy Investigation of Bacterial Outer Membrane Vesicles

MJ Kuehn, Duke University, Durham, North Carolina

TEM Study on SOFC Interconnects

Z Yang, Pacific Northwest National Laboratory, Richland, Washington

TEM Study on SOFC Interconnects and Interfaces

Z Yang, Pacific Northwest National Laboratory, Richland, Washington

Characterization of Mesoporous SiO_2 Particles for the Characterization of Non-Ideal Sorption Behavior

DR Yonge, DL Washington, Washington State University, Pullman, Washington

Electrochemical Detection of Lead in Saliva

TG Carter, University of Oregon, Eugene, Oregon

W Yantasee, A Cinson, D Choi, Pacific Northwest National Laboratory, Richland, Washington

K Hongsirikarn, T Sangvanich, K Pattamakomsan, Chulalongkorn University, Bangkok, Thailand

A Combinatorial Sputtering Approach to Magnetic Properties Modification of FeCoB

DP Pappas, National Institute of Standards and Technology, Boulder, Colorado

RR Owings, Applied Materials, Boise, Idaho

Controlling the Thermal and Non-Thermal Reactivities of Metal Oxide Structures Through Nanoscaling - Controlling Reactivities of Metal Oxide Strcutures(Mike Henderson's BES Project - 43626)

MA Henderson, KM Rosso, NI Iordanova, SA Chambers, M Dupuis, AG Joly, JE Jaffe, Pacific Northwest National Laboratory, Richland, Washington

IV Lyubinetsky, KM Beck, Environmental Molecular Sciences Laboratory, Richland, Washington

MS Gutowski, Heriot-Watt University, Edinburgh, United Kingdom

G Xiong, Rn Shao, unknown, Washington

Electrochemical and TEM Characterization of Metal Nanoparticles Deposited in Carbon Nanotubes

CM Wai, Y Lin, University of Idaho, Moscow, Idaho

Chemical Characterization of Sub-Micrometer Mineral Phases in Extraterrestrial Materials that have Previously been Characterized by NanoSIMS Isotope Imaging

FJ Stadermann, C Floss, Washington University in St. Louis, St. Louis, Missouri

Tn Yada, Institute of Astronomy and Astrophysics, Academia Sinica, Taipei, Taiwan, Province of China

Advanced Electrode Concepts for CdZnTe Radiation Detectors

CE Seifert, G Dunham, Pacific Northwest National Laboratory, Richland, Washington

J White, Environmental Molecular Sciences Laboratory, Richland, Washington

Energetic Ion Studies of Key Future Technological Materials

MI Laitinen, University of Jyvaskyla, Jyvaskyla, Finland

HJ Whitlow, V Touboltsev, University of Jyväskylä, Jyväskylä, Finland

Investigation of the Surface Characteristics of Chemically Modified Natural Fibers

LS Fifield, JD Holbery, Pacific Northwest National Laboratory, Richland, Washington

Stability of Ceria and Other NanoParticles

S Kuchibhatla, S Seal, D Bera, University of Central Florida, Orlando, Florida

KH Pecher, Pacific Northwest National Laboratory, Richland, Washington

DR Baer, Environmental Molecular Sciences Laboratory, Richland, Washington

SEM/EDS of Solid Oxide Fuel Cell Seal Materials

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

JS Vetrano, US Department of Energy, Washington, DC, Washington, Wash DC

XPS Studies of Self-Assembling Monolayers

BJ Tarasevich, Pacific Northwest National Laboratory, Richland, Washington

Understanding the Properties of Oxide and Metal Nanostructures

S Sivarajah, K Ahilan, University of Jaffna, Jaffna, Sri Lanka

Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone (PNNL Scope # 30948 Bryan/Hubler EMSP)

AS Del Negro, TL Hubler, SA Bryan, Z Wang, Pacific Northwest National Laboratory, Richland, Washington

WR Heineman, CJ Seliskar, University of Cincinnati, Cincinnati, Ohio

Surface Migration of Additives in Polymers

LA Archer, VS Minnikanti, Cornell University, Ithaca, New York

Surface Migration of Additives in Polymers

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Determination of Nanoporous Material Oxidation States

DM Wellman, A Karkamkar, Z Hontz, E Richards, Pacific Northwest National Laboratory, Richland, Washington

Characterization of Pure and Doped ZnO Nanoclusters

J Antony, Y Qiang, University of Idaho, Moscow, Idaho

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TOF-SIMS and Auger Studies of Ozone Oxidation of Unsaturated Self Assembled Monolayers on Silicon Surfaces

BJ Finlayson-Pitts, TM McIntire, University of California, Irvine, Irvine, California

PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

XPS Analysis of Fabric Chars to Determine the Phosphorous - Nitrogen Synergism in Flame Retardants

S Gaan, G Sun, University of California, Davis, Davis, California

Stabilization of Polar Oxide Interfaces: Integrated Experimental and Theoretical Studies of Atomic Structure and Electronic Properties

S Cheung, Pacific Northwest National Laboratory, Richland, Washington

M Gajdardziska-Josifovska, University of Wisconsin, Milwaukee, Milwaukee, Wisconsin

Ion Beam Characterization of Nanocomposite Tribological Coatings

RJ Smith, PE Gannon, Montana State University, Bozeman, Montana

Surface Texture of Zircon Grains from the Sierra Madera Impact Structure, West Texas

SA Huson, MC Pope, Washington State University, Pullman, Washington

Thrust 4: Model Hematite Thin Films and Bacterial Iron Reduction (LDRD: Cytochrome and Whole Cell Interactions with Iron Oxides)

TC Droubay, Z Wang, L Shi, BH Lower, Pacific Northwest National Laboratory, Richland, Washington

TW Wietsma, Environmental Molecular Sciences Laboratory, Richland, Washington

Characterization of Manganese Cobalt Oxides Using XPS

G Xia, Pacific Northwest National Laboratory, Richland, Washington

Molecularly Organized Nanostructural Materials (Greg Exarhos's BES Project - 12152)

Y Shin, G Exarhos, C Windisch, AR Teodoro-Dier, Pacific Northwest National Laboratory, Richland, Washington

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

Nuclear Reaction Analysis of Biotite Minerals

CV Ramana, E Essene, University of Michigan, Ann Arbor, Michigan

Preparation of ZnO Thin Films by MOCVD

KR Kittilstved, DR Gamelin, University of Washington, Seattle, Washington

Characterization of GaN/InGaN/GaN Thin Film Structures

F Ohuchi, E Venkatasubramanian, K Poochinda, University of Washington, Seattle, Washington

Compositionally Graded Co and Cr doped TiO_2 Rutile for Optimum Thermoelectric Power

L Saraf, V Shutthanandan, Environmental Molecular Sciences Laboratory, Richland, Washington

A Yamamoto, AIST, Ibaraki, Japan

F Ohuchi, S Iwanaga, University of Washington, Seattle, Washington

Adhesion of Polymer Sphere to Modified Natural Fiber Via AFM

JD Holbery, Pacific Northwest National Laboratory, Richland, Washington

Systematical Study of Novel Nano-Magnetic Materials

D Li, Y Liu, X Wang, Alfred University, Alfred, New York

J Helfer, Biophan Technologies, Inc., West Henrietta, New York

Determination p-Dopant Concentration in Wide Band Gap SnO_2 Semiconductor, using RBS Technique

SB Rananavare, A Chaparadza, Portland State University, Portland, Oregon

The Microstructural Influence on Fatigue Crack Growth in Rene 88DT

E Sackmann, KO Findley, Washington State University, Pullman, Washington

Depth Profiles of Isotopic Oxygen in Cerium Oxide Catalysts

DA Berry, National Energy Technology - Laboratory, Morgantown, West Virginia

Norovirus TEM Proposal, Straub

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B Mayer, C Nickerson, Arizona State University, Tempe, Arizona

Host Cell Interactions with Human Infectious Diseases, Straub

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J Vinje, Center for Disease Control Prevention, Atlanta, Georgia

S Fout, Environmental Protection Agency, Cincinnati, Ohio

Rhenium and Technetium Uptake by Iron-Based Materials

KM Krupka, Pacific Northwest National Laboratory, Richland, Washington

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Electron Microscopy Imaging of Cyanobacteria *Synechcystis* sp

C Gassman, Columbia Basin College, Pasco, Washington

A Dohnalkova, B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

Electron Energy Loss in Radiation Detection

B Cannon, EC Buck, Pacific Northwest National Laboratory, Richland, Washington

C Wang, Environmental Molecular Sciences Laboratory, Richland, Washington

Electron Microscopy of Novel Metal-Transforming Bacteria from Extreme Environments

TS Magnuson, Idaho State University, Pocatello, Idaho

Characterization of Tungsten Carbide Synthesized by Controlled Template Method

J Kwak, Pacific Northwest National Laboratory, Richland, Washington

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

Investigation Cellulose Phase Change and Interaction with Other Molecules by DSC

H Zhao, Pacific Northwest National Laboratory, Richland, Washington

Study of the Ferromagnetic Activation in ZnO Diluted Magnetic Semiconductors

CR Johnson, KR Kittilstved, DR Gamelin, University of Washington, Seattle, Washington

Transient Kinetics Experiments for Studying Catalytic Reactions for H_2 Production

Y Yang, RS Disselkamp, Pacific Northwest National Laboratory, Richland, Washington

VM Lebarbier, University of New Mexico, Albuquerque, New Mexico

CT Campbell, RJ Chimentao, Ln Cameron, IM Jensen, University of Washington, Seattle, Washington

Scanning Electron Microscopy of *Corynebacterium glutamicum*

H Yukawa, Research Institute of Innovative Technology for the Earth, Kyoto, Japan

Ecophysiological Investigation of Cyanobacteria using Controlled Cultivation

KM Rosso, EA Hill, Pacific Northwest National Laboratory, Richland, Washington

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YA Gorby, J. Craig Venter Institute, La Jolla, California

Optical Properties of Ag Nanoparticles Embedded in Polymer Matrices

TD Pounds, MG Norton, Washington State University, Pullman, Washington

Controlling Field Emission from HV Structures

M Zhu, BC Holloway, College of William and Mary, Williamsburg, Virginia

Structural Characterization of Complex Electrodes

SA Towne, JD Holbery, Pacific Northwest National Laboratory, Richland, Washington

Characterization of Oxide Based Diodes

GS Herman, WF Stickle, Hewlett-Packard Company, Corvallis, Oregon

SEM-EDS Elemental Mapping of Weymouth Soils

KJ Cantrell, Pacific Northwest National Laboratory, Richland, Washington

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Segregation on Annealed R-Cut Sapphire Surfaces

SB Rivers, RJ Lad, University of Maine, Orono, Maine

Nanoengineered Electrochemical Sensor for Mixed Wastes (PNNL Scope# 45409)

J Wang, Pacific Northwest National Laboratory, Richland, Washington

Structure of the *Shewanella* Cell Surface

AL Neal, University of Georgia, Aiken, South Carolina

Epitaxial Growth and Properties of Candidate Diluted Magnetic Oxide Semiconductors - Chemistry and Physics of Ceramic Surfaces (Scott Chambers' BES Project - 10122)

TC Kaspar, SA Chambers, TC Droubay, AR Teodoro-Dier, Pacific Northwest National Laboratory, Richland, Washington

SM Heald, Argonne National Laboratory, Argonne, Illinois

Evaporative Co-Deposition of Fluoride Materials

DW Matson, Pacific Northwest National Laboratory, Richland, Washington

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

Measurement of Band Gap, Band Offset, and Thickness for Ultra-Thin SiO_2, SiON and High-k Films on Si

Z Chen, CB Samantaray, University of Kentucky, Lexington, Kentucky

High-Resolution Ion Scattering Studies of Nano-Scale Oxide Films and Thermal Stability of Oxide-Semiconductor Interfaces

S Ramanathan, C Chang, Harvard University, Cambridge, Massachusetts

Test Mass Characterization for Precision Gravitational Tests

CD Hoyle, TS Cook, EG Adelberger, University of Washington, Seattle, Washington

Use of Wet Chemical Facilities in the EMSL 1310 Laboratory - Protein Pipeline (Marvin Warner's DHS Project - 47443)

C Dutton, Washington State University, Richland, Washington

MG Warner, AM Pierson, Pacific Northwest National Laboratory, Richland, Washington

AJ Tyler, Utah State University, Logan, Utah

Synthesis of Sub-Micron Cuprous Oxide Films on a Silicon Nitride Membrane for Study using Time-Resolved X-Ray Techniques

PB Hillyard, Stanford University, Stanford, California

KJ Gaffney, Stanford Synchrotron Radiation Laboratory, Menlo Park, California

Synthesis of Photoactive Metal Oxide Films for Study using Time-Resolved X-Ray Techniques

PB Hillyard, Stanford University, Stanford, California

KJ Gaffney, JR Bargar, Stanford Synchrotron Radiation Laboratory, Menlo Park, California

Investigation of Electron Emission from Nano-Structures

AY Wong, J Chen, University of California, Los Angeles, Los Angeles, California

R Wang, Nonlinear Ion Dynamics, LLC, Van Nuys, California

Molecular Beam Scattering Measurements on Anatase TiO_2(001) and Rutile TiO_2(110)

U Burghaus, North Dakota State University, Fargo, North Dakota

Fabrication of Si Templates for the Construction of Monolithic Multi-Electrospray Emitters

RT Kelly, K Tang, RD Smith, Pacific Northwest National Laboratory, Richland, Washington

Olefins by High-Intensity Oxidation (Scope 46868)

Y Wang, D Kim, RA Dagle, J Hu, Pacific Northwest National Laboratory, Richland, Washington

X Wang, New Jersey Institute of Technology, Newark, New Jersey

Hydrogen Production - (Steam Reforming of Biomass Scope 46621)

Y Wang, D Kim, J Hu, CM Fischer, R Kou, G Li, Pacific Northwest National Laboratory, Richland, Washington

Z Zou, Xiamen University, Fujian, China

X Wang, New Jersey Institute of Technology, Newark, New Jersey

Integrated Automated Analyzer for Groundwater Monitoring - (Yuehe's SERDP Work Scope 42177)

Y Lin, G Liu, J Wang, W Yantasee, Pacific Northwest National Laboratory, Richland, Washington

A Lee, National University of Singapore, Singapore, Malaysia

J White, Environmental Molecular Sciences Laboratory, Richland, Washington

Kiln Phosphoric Acid Process (Scope 47245)

T Hart. Pacific Northwest National Laboratory, Richland, Washington
JA Megy, JDC, Inc, New Cumberland, West Virginia

Mechanisms of Sulfur Poisoning of NOx Adsorber Materials (Chuck Cummins CRADA Work Scope 43315)

CH Peden, Pacific Northwest National Laboratory, Richland, Washington

J White, Environmental Molecular Sciences Laboratory, Richland, Washington

Trace Impurities in Graphite Crucible used for Advanced Detector Materials Synthesis

M Bliss, Pacific Northwest National Laboratory, Richland, Washington

JB Cliff, unknown, Washington

High Resolution TEM Analysis of CuInS2 Nanoparticles and XRD analysis of CuInS2 Thin Films

JJ Pak, L Lau, JS Gardner, Idaho State University, Pocatello, Idaho

Site Specific Valence Above and Below the Verwey Transition in Magnetite

TC Droubay, TC Kaspar, SA Chambers, Pacific Northwest National Laboratory, Richland, Washington

JO Cross, Argonne National Laboratory, Argonne, Illinois

X-Ray Analysis of Quantum Well Films

PM Martin, Pacific Northwest National Laboratory, Richland, Washington

TGA Analysis of Synthesized Organic Components of Self-Assembled Monolayers on Mesoporous Silica

RJ Wiacek, RS Addleman, A Cinson, J Davidson, Pacific Northwest National Laboratory, Richland, Washington

The Use of FESEM

X Zhou, Pacific Northwest National Laboratory, Richland, Washington

Ion Beam Modification of Advanced Titanium Alloys

KO Findley, CP Norby, KC Dallavis, KJ Stephenson, Washington State University, Pullman, Washington

Center of Excellence for Chemical Hydrogen Storage (Scope #46385)

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Technetium (Tc) Reduction by Chemically and Biologically Reduced Smectite Clay

H Dong, Miami University, Oxford, Ohio

Applications of Nanostructured Materials and Electrodes in Electrochemical Sensors and Fuel Cell

X Cui, Fudan University, Shanghai, China

Computational and Experimental Nanoparticle Dosimetry for Nanomaterial Safety

JG Teeguarden, SM Varnum, Pacific Northwest National Laboratory, Richland, Washington

Micro-fabrication of Miniaturized Solid Oxide Fuel Cell (SOFC) on Silicon Chip

P Singh, O Marina, Pacific Northwest National Laboratory, Richland, Washington

L Saraf, T Thevuthasan, Environmental Molecular Sciences Laboratory, Richland, Washington

Development of Wet Chemical Etching Methods to Create Chalcogenide Glass Film Structures

A Qiao, NC Anheier, K Krishnaswami Pacific Northwest National Laboratory, Richland, Washington

Trace Signatures in Particles

JB Cliff, unknown, Washington

Environmental Photochemical Fate of Manufactured Carbon Nanomaterials
I Hua, Purdue University, West Lafayette, Indiana

High Surface Area Nanocrystalline SiC Material Analysis

Y Wang, J Kwak, J Hu, D Howe, Pacific Northwest National Laboratory, Richland, Washington

DM Ginosar, Idaho National Engineering and Environmental Laboratory (INEEL), Idaho Falls, Idaho

Characterization of Microstructure and Composition of Magnetostrictive Nanobars for Bio-Sensor Application

S Li, Z Cheng, Auburn University, Auburn, Alabama

Surface-Modified Iron Oxide Nanoparticle Characterization by Transmission Electron Microscopy

JW Gunn, N Bhattarai, M Zhang, University of Washington, Seattle, Washington

Development of a Catalyst for the Steam Reformation of JP-10

RA Dagle, Pacific Northwest National Laboratory, Richland, Washington

D Nguyen, Energia Technologies, INC, Castro Valley, California

Spectroscopic Study of the Bioactivity of Nanoparticles by Exposure to Human Lung Cells (Summer Research Institute, PNNL Scope #16248)

D Dutta, BM Moudgil, University of Florida, Gainesville, Florida

SK Sundaram, Pacific Northwest National Laboratory, Richland, Washington

X-Ray Photoelectron Spectroscopy and Expert Consulting on Thermal Stabilization of Multi-Component Inorganic Oxide Materials

GE Spanner, LR Pederson. Pacific Northwest National Laboratory, Richland, Washington

J White, Environmental Molecular Sciences Laboratory, Richland, Washington

H Gysling, AirFlow Catalysts Systems, Inc., Rochester, New York

Examine the Compositions of the Black Sands in Northern Oregon

JS Young, David Heil Associates Corporation, Portland, Oregon

Equilibrium-Induced Decomposition of Nitrates on a Nox Storage/Reduction Catalyst
WS Epling, University of Waterloo, Waterloo, Ontario, Canada

X-Ray Photoemission Study of Graphite

S Azad, UCAR Carbon Company Inc., Parma, Ohio

The *in vivo* Localization and Interactions between Structural Components of the *Shewanella oneidensis* MR-1 Metal Reducing System by High Resolution Transmission Electron Microscopy

MJ Marshall, Pacific Northwest National Laboratory, Richland, Washington

A Dohnalkova, Environmental Molecular Sciences Laboratory, Richland, Washington

The Biogeochemical Mechanisms Controlling Reduced Radionuclide Particle Formation Properties and Stability

MJ Marshall, Pacific Northwest National Laboratory, Richland, Washington

Radionuclide Reduction by *Anaeromyxabacter dehalogenans*

FE Loeffler, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

Chromium Diffusion Kinetics in Nano-Ceria and Doped Ceria Coatings: An UCF-PNNL Collaboration

S Seal, RK Thanneeru, Sn Kuchibhatla, SA Deshpande, AS Karakoti, University of Central Florida, Orlando, Florida

Spectroscopic and Microscopic Characterization of Graphite

S Azad, UCAR Carbon Company Inc., Parma, Ohio

Non-Destructive SEM-Based Analysis of Complex Functional Structures in Insects: Development of Tools for Rapid Species Diagnosis in Tropical Biodiversity Surveys

NO Pellmyr, University of Idaho, Moscow, Idaho

High-Resolution Interfacial Studies of Nano-Scale Oxide Films

S Ramanathan, C Chang, Harvard University, Cambridge, Massachusetts

Effects of Temperature and Time (130 Years) on Surface Charges and Chemical Properties of Black Carbon

C Cheng, JC Lehmann, BT Nguyen. Cornell University, Ithaca, New York

Molecular Beam Scattering Measurements on Anatase TiO_2(001) and Rutile TiO_2(110)

U Burghaus, North Dakota State University, Fargo, North Dakota

Characterization of Novel DNA/Semiconductor Nanoconjugates

F Zhou, D Jiang, California State University, Los Angeles, Los Angeles, California

Fundamental Investigations of Heterogeneous Catalysis Using Isotopic Transient Kinetic Analysis

S Chuang, University of Akron, Akron, Ohio

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CT Campbell, L Cameron, IM Jensen, University of Washington, Seattle, Washington

J Goodwin, Clemson University, Clemson, South Carolina

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Characterization of High Surface Area Tungsten Carbide Synthesized by Templated Synthesis Methods Electrocalytic Applications

J Kwak, Pacific Northwest National Laboratory, Richland, Washington

Post Growth Analysis of Compositionally Graded InGaN Grown with MOCVD

F Ohuchi, E Venkatasubramanian, K Poochinda, C Lu, University of Washington, Seattle, Washington

Compositionally Graded V2O5 for Improved Thermoelectric Power

A Yamamoto, AIST, Ibaraki, Japan

F Ohuchi, S Iwanaga, University of Washington, Seattle, Washington

Novel Catalytic Materials for the Hydrodesulfurization and Water-Gas Shift Processes

ME Bussell, AW Burns, Western Washington University, Bellingham, Washington

Amorphous Semiconductor Analysis using Ion Beam Tools

CH Henager, J Ryan, BR Johnson, Pacific Northwest National Laboratory, Richland, Washington

Fundamental Studies of Nitrogen Oxide Surface Chemistry: A Model System Approach

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J Szanyi, CH Peden, Pacific Northwest National Laboratory, Richland, Washington

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Post Growth Analysis of GaN and InGaN Grown with MOCVD

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Hydrogen Materials Compatibility Studies

CH Henager, JD Holbery, Pacific Northwest National Laboratory, Richland, Washington

Model Oxide Defects with Vicinally Stepped NiO(100) Substrates

Y Du, IV Lyubinetsky, Environmental Molecular Sciences Laboratory, Richland, Washington

MA Langell, University of Nebraska, Lincoln, Nebraska

MBE Growth and Properties of Model TiO_2 Surfaces for Fundamental Studies of Heterogeneous Photocatalysis

SA Chambers, MA Henderson, T Ohsawa, Pacific Northwest National Laboratory, Richland, Washington

C Wang, P Nachimuthu, Y Du, Environmental Molecular Sciences Laboratory, Richland, Washington

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MBE Growth and Properties of N-doped TiO_2 for Enhanced Visible Light Absorption and Water Splitting

SA Chambers, S Cheung, MA Henderson, Pacific Northwest National Laboratory, Richland, Washington

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J Rodriguez, Brookhaven National Laboratory, Upton, New York

C Wang, P Nachimuthu, V Shutthanandan, Environmental Molecular Sciences Laboratory, Richland, Washington

CS Fadley, Lawrence Berkeley National Laboratory, Richland, West Virginia

Epitaxial Growth and Properties of Magnetically Doped ZnO Prepared by Pulsed Laser Deposition of Nanoparticle Targets

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SA Chambers, TC Droubay, TC Kaspar, Pacific Northwest National Laboratory, Richland, Washington

KM Whitaker, CR Johnson, KR Kittilstved, DR Gamelin, SA Santangelo, PI Archer, Y Li, ST Ochsenbein, University of Washington, Seattle, Washington

Real-Time FTIR Measurements of Fe-Oxide Transformation in Presence of Dissimilatory Fe-Reducing Bacteria

GG Geesey, Montana State University, Bozeman, Montana

TC Droubay, Pacific Northwest National Laboratory, Richland, Washington

Visualization of a Pd-Au{100} Catalyst: a Scanning Tunneling Microscopy Study

P Han, DW Goodman, Texas A&M University, College Station, Tennessee

Directed Self-Assembly of Metal Oxide Island Nanostructures

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Structure-Property Relationships in Thin Film Energy Conversion Materials and Coatings

DW Matson, PE Burrows, LC Olsen, PM Martin, ME Gross, WD Bennett, CC Bonham, G Graff, ES Mast, SN Kundu, AB Padmaperuma, L Sapochak, PK Koech, H Qiao, J Ryan, Pacific Northwest National Laboratory, Richland, Washington

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Nerve Agent Detection Using Enzyme-Coated Nanowires

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J Lee, Chosun University, Gwangju, Korea South, Republic of

D Lee, Korea Institute of Industrial Technology, Cheonan, Korea South, Republic of

Elemental Characterization of Ionizer Filaments for Thermal Ionization Mass Spectrometry (TIMS)

MD Engelmann, Pacific Northwest National Laboratory, Richland, Washington

JB Cliff, unknown, Washington

Molecular-Level Understanding of Transport and Optic Properties of Doped Oxide Nanoclusters

Y Qiang, J Antony, M Faheem, A Sharma, University of Idaho, Moscow, Idaho

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Molecular Level Construction of Functional Surfaces

PL Gassman, Environmental Molecular Sciences Laboratory, Richland, Washington

SM Gorun, New Jersey Institute of Technology, Newark, New Jersey

Selective Heterogeneous Catalysis

LS Fifield, JT Bays, Pacific Northwest National Laboratory, Richland, Washington

Ion Beam Analysis of Components for Solid Oxide Fuel Cells

RJ Smith, Montana State University, Bozeman, Montana

Early Transition Metal Oxides as Catalysts: Crossing Scales from Clusters to Single Crystals to Functioning Materials

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CH Peden, J Hu, J Kwak, J Liu, Y Wang, X She, G Xia, D Kim, J White, Pacific Northwest National Laboratory, Richland, Washington

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VM Lebarbier, University of New Mexico, Albuquerque, New Mexico

J White, Environmental Molecular Sciences Laboratory, Richland, Washington

DA Dixon, University of Alabama, Tuscaloosa, Tuscaloosa, Alabama

NOx Adsorber Materials: Fundamental Studies, and Investigations of Sulfur Poisoning and Thermal Deactivation

CH Peden, RS Disselkamp, D Kim, J Kwak, J Szanyi, RG Tonkyn, CM Verrier, D Tran, J Male, Pacific Northwest National Laboratory, Richland, Washington

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Metal-Induced Crystallization via Sputtering Deposition on Flexible Substrates and its Applications

ST Dunham, C Shih, H Guo, University of Washington, Seattle, Washington

Development of Room Temperature Ferromagnetism in Wide-Band-Gap Oxide Semiconductor Nanostructures

A Punnoose, AP Thurber, Boise State University, Boise, Idaho

Fundamental Studies of Heterogeneous Photocatalysis on Model TiO_2 Surfaces

MA Henderson, Pacific Northwest National Laboratory, Richland, Washington

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Using Metallic Interlayers to Stabilize Metal-Metal Interfaces

RJ Smith, WA Priyantha, A Comouth, H Chen, Montana State University, Bozeman, Montana

Chemistry of Outer Solar System Materials

TB McCord, GB Hansen, University of Washington, Seattle, Washington

An Experimental and Data Analysis Investigation into the Trapped Gases and Non-Ice Material in the Surfaces of the Outer Planets Icy Satellites and Our Moon

CA Hibbitts, Johns Hopkins University, Laurel, Maryland

J Szanyi, Pacific Northwest National Laboratory, Richland, Washington

Photochemical Studies on N-Doped TiO_2 Single Crystals - Fundamental Investigations of Water Splitting on Model TiO_2 (Mike Henderson's BES Project - 48526)

VH Lam, University of Central Florida, Orlando, Florida

MA Henderson, SA Chambers, S Cheung, T Ohsawa, Z Dohnalek, Pacific Northwest National Laboratory, Richland, Washington

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MK Bowman, University of Alabama, Tuscaloosa, Tuscaloosa, Alabama

R Shao, SC Andrews, unknown, Washington

Biomineralology and Ultrastructure of Neutrophilic Iron-Oxidizing Bacteria

KJ Edwards, University of Southern California, Los Angeles, California

CS Chan, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

Study of Thermal Decomposition of Polyester Fibers Treated with Phosphorus Flame Retardants

S Gaan, G Sun, University of California, Davis, Davis, California

Enhanced Ionic Conductivity of Samaria Doped Ceria Thin Films through Tailoring the Dopant Concentration and Microstructures

LM Bauder, S Michael, S Morrison-Smith, Pacific Northwest National Laboratory, Richland, Washington

Z Yu, Nanjing Normal University, Nanjing, China

Z Jaquish, unknown, Washington

Biocompatible, Engineered Surfaces of Mixed Chemistry

V Hlady, University of Utah, Salt Lake City, Utah

Cryo-EM Investigations of Interfacial Bacterial Extracellular Polymeric Substance (EPS) in Vanadium Interactions

MJ Marshall, Pacific Northwest National Laboratory, Richland, Washington

The Role of PdZn Alloy Formation and Particle Size on the Selectivity for Steam Reforming of Methanol

AM Karim, A Datye, TR Conant, VM Lebarbier, University of New Mexico, Albuquerque, New Mexico

Characterization of Chemistry and Physics at Metal-Polythiophene and Metal-Carbon Interfaces

LM Porter, KA Singh, PB Kulkarni, Carnegie Mellon University, Pittsburgh, Pennsylvania

J White, Environmental Molecular Sciences Laboratory, Richland, Washington

Model System Surface Science Approach to Study Photochemistry at Adsorbate-Substrate Interfaces: The Trimethyl Acetate, Silver, Titania System

MA Henderson, Z Dohnalek, Pacific Northwest National Laboratory, Richland, Washington

IV Lyubinetsky, Environmental Molecular Sciences Laboratory, Richland, Washington

JM White, University of Texas at Austin, Austin, Texas

SC Andrews, unknown, Washington

Bone Growth on Tailored Biomimetic Surfaces

MI Laitinen, HJ Whitlow, University of Jyvaskyla, Jyvaskyla, Finland

Defects and Defect Processes in Ceramics

WJ Weber, W Jiang, I Bae, BD Milbrath, Pacific Northwest National Laboratory, Richland, Washington

L Boatner, Oak Ridge National Laboratory, Oak Ridge, Tennessee

X Xiang, University of Michigan, Ann Arbor, Michigan

Y Zhang, Environmental Molecular Sciences Laboratory, Richland, Washington

Cryogenic XPS Study of Metal Oxide/Water Interfaces

J Boily, Pacific Northwest National Laboratory, Richland, Washington

Catalytic and Optical Properties of Surface Attached and Matrix Embedded Quantum Dots

G Duscher, North Carolina State University, Raleigh, North Carolina

Electron Energy Loss in Radiation Detection Materials

B Cannon, AJ Carman, Pacific Northwest National Laboratory, Richland, Washington

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Thin Film Electrolyte/Electrode Development and Enhanced Ionic Transport in Miniaturized Solid Oxide Fuel Cells on Silicon Chips

P Singh, O Marina, Pacific Northwest National Laboratory, Richland, Washington

Surface and Bulk Characterization of Ambient Ultrafine Particles

EL Bullock, AM Johansen, C Thomas-Bradley, JM Johnston, TK O'connell, JK Wells, Central Washington University, Ellensburg, Washington

Surface Characterization of Calcium Phosphates

WJ Shaw, BJ Tarasevich, Pacific Northwest National Laboratory, Richland, Washington

Mixed Oxide Films for Gas Sensing and Photo-Catalytic Applications

KR Padmanabhan. Wayne State University, Detroit, Michigan

Spin Electronic Phenomena in Magnetically Doped Perovskites and Complex Oxide Interfaces

TC Kaspar, SA Chambers, TC Droubay, Pacific Northwest National Laboratory, Richland, Washington

C Wang, V Shutthanandan, T Thevuthasan, J White, Environmental Molecular Sciences Laboratory, Richland, Washington

D McCready, unknown, Washington

Toward Preparation and *Operando* Characterization of Nanostructured Heterogeneous Photocatalysts

Y Shin, GE Fryxell, XS Li, RE Williford, K Parker, Pacific Northwest National Laboratory, Richland, Washington

Near Real-Time Alkene Sensor for Atmospheric Aerosol Chemistry Monitoring

JW Grate, Pacific Northwest National Laboratory, Richland, Washington

R Shekarriz, MicroEnergy Technologies, Inc., Portland, Oregon

Design of Micro-Cantilever Actuators for Measuring Surface Tension of sub Microliter Volumes Applied towards Monitoring Interfacial Processes

DW Britt, BA Henrie, Utah State University, Logan, Utah

Microfabrication of Electrospray Emitter Arrays for Improved Sensitivity IN Electrospray Ionization-Mass Spectrometry

RT Kelly, RD Smith, K Tang, Pacific Northwest National Laboratory, Richland, Washington

Surface and Interface Studies of Photochemically Initiated Immobilization

S Chada, M Yan, L Liu, DJ Henry, RR Bard, K Wang, Y Miao, SN Uppalapati, X Wang, Portland State University, Portland, Oregon

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Characterization of Mixed Monolayers with X-Ray Photoelectron Spectroscopy (XPS)

L Liu, M Yan, Portland State University, Portland, Oregon

D Hu, Pacific Northwest National Laboratory, Richland, Washington

The Thickness Measurement of Electrolyte Cast on Mylar Film

S Hong, VL Sprenkle, Pacific Northwest National Laboratory, Richland, Washington

Thin Film X-ray Diffraction Studies of Calcium Phosphate Films and XPS Studies of Self-Assembling Monolayers

BJ Tarasevich, Pacific Northwest National Laboratory, Richland, Washington

Reforming of Hydrocarbons on Solid Oxide Fuel Cell Anodes

JJ Strohm, DL King, Y Wang, Pacific Northwest National Laboratory, Richland, Washington

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Structural and Chemical Properties of Catalysts

ME Bussell, AW Burns, Western Washington University, Bellingham, Washington

Structure and Composition of Electrochemically Active Mixed Metal Oxides

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Response of Radiation Detector Materials to Ions

BD Milbrath, Pacific Northwest National Laboratory, Richland, Washington

Y Zhang, Environmental Molecular Sciences Laboratory, Richland, Washington

Response of Radiation Detector Materials to Ions

BD Milbrath, Pacific Northwest National Laboratory, Richland, Washington

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Low Angle X-Ray Characterization of Catalyst Porosity

XS Li, Pacific Northwest National Laboratory, Richland, Washington

Mechanisms of Environment-Assisted Degradation in Reactor Materials

S Bruemmer, C Windisch, Pacific Northwest National Laboratory, Richland, Washington

JS Vetrano, US Department of Energy, Washington, DC, Washington, Wash DC

Gold Hollow Nanostructures: Synthesis and Optical Properties

X Lu, Y Xia, University of Washington, Seattle, Washington

Characterization of Metal Nanoparticles for Optimization of Process Parameters to Support Synthesis of Well-Defined Carbon Nanotubes

LS Fifield, Pacific Northwest National Laboratory, Richland, Washington

A Gupta, VB Mikheev, Battelle Columbus, Columbus, Ohio

Cellular Internalization Studies of Semiconductor Nanoparticles in Bacteria

A Punnoose, MR Kongara, Boise State University, Boise, Idaho

ICP Analysis of Ionic Liquids

JE Holladay, H Zhao, T Hart, Pacific Northwest National Laboratory, Richland, Washington

Transparent Circuits

F Hua, Clarkson University, Potsdam, New York

Understanding Particle Generation and the Risk of Occupational Exposure and Environmental Release of Nanoparticles during Processing of Nanocomposite Materials

DJ Gaspar, TJ Johnson, Z Wang, Pacific Northwest National Laboratory, Richland, Washington

MG Yost, University of Washington, Seattle, Washington

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Implications of U Sequestration in U-Al-SO_4-Si Grain Coatings for Remediation and Stewardship

AS Madden, BP Spalding, Oak Ridge National Laboratory, Oak Ridge, Tennessee

D Phillips, Queen's University Belfast, Belfast, Ireland

DE Watson, ElSohly Laboratories, Inc., OXFORD, Mississippi

Zinc Oxide: A Material for Efficient Light Emission

MD Mccluskey, W Hlaing Oo, Washington State University, Pullman, Washington

C Wang, Environmental Molecular Sciences Laboratory, Richland, Washington

Deep Desulphurization of Hot Coal Gas for Production of Liquid Fuels

L Li, J Male, R Vedula, Pacific Northwest National Laboratory, Richland, Washington

Characterization of Nanostructured Catalysts and Nanostructured Materials

J Liu, D Wang, Q Huo, Pacific Northwest National Laboratory, Richland, Washington

High Pressure VLS Synthesis of Silicon Nanowires

JC Chan, SB Rananavare, Portland State University, Portland, Oregon

Ion Beam Methods for the Synthesis, Modification, and Characterization of Radiation Detection Materials

L Boatner, JS Neal, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Fate and Transport of Titanium Dioxide through Freshwater Ecosystems

DJ Gaspar, A Miracle, AL Bunn, JA Ward, Pacific Northwest National Laboratory, Richland, Washington

Investigating the Correlation among Properties, Morphology and Composition of Multimetallic Alloy and Core-shell Nanoparticles and Novel Nanostructures

C Zhong, P Njoki, D Mott, S Lim, State University of New York at Binghamton, Binghamton, New York

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Community-Based Biosignatures of Exposure and Functional Response in the Sediment-Water Interface of the Hyporheic Zone and Periphyton Community in River Systems

J Small, AL Bunn, Pacific Northwest National Laboratory, Richland, Washington

Incorporation of Cellulose Nanocrystals Into PHB/PHV Copolymer

MP Wolcott, Washington State University, Pullman, Washington

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Synthesis of Highly Uniform Magnetic Nanoparticles with Enhanced Moment Density

J Yang, X Gao, University of Washington, Seattle, Washington

Characterization of Nanomaterials in Support of the NTP Nanotechnology Safety Initiative

TA Cristy, Battelle Columbus, Columbus, Ohio

Mossbauer and XPS Characterization of Fe-Based Fischer-Tropsch Catalysts

RK Kukkadapu, Environmental Molecular Sciences Laboratory, Richland, Washington

V Subramani, Research Triangle Institute, Research Triangle Park, North Carolina

Biqing Liang's Proposal

B Liang, JC Lehmann, Cornell University, Ithaca, New York

Propane Reforming Process Development

J Hu, DR Palo, RA Dagle, B Roberts, Pacific Northwest National Laboratory, Richland, Washington

Immiscibility Features between Silica-Rich and Carbonate-Rich Material in Breccia from the Sierra Madera Impact Structure

SA Huson, MC Pope, Washington State University, Pullman, Washington

Maria Salazar-Villalpando's Proposal

MD Salazar-Villalpando, DA Berry, National Energy Technology - Laboratory, Morgantown, West Virginia

Structure, Composition, and Phase Behavior of Mixed Biphenylthiol Self-Assembled Monolayers

EL Bullock, Central Washington University, Ellensburg, Washington

Evaluation of Multicomponent Proous Oxide Films

XS Li, Pacific Northwest National Laboratory, Richland, Washington

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

Spectroscopy and Microscopy of Doped TiO_2 Nanocrystalline Materials

DR Gamelin, JD Bryan, NS Norberg, KM Whitaker. University of Washington, Seattle, Washington

Hydrogen Production-(Steam Reforming of Hydrocarbons including Methane, Propane, Gasoline, Jet Fuel and Biomass Derived Products)

J Hu, RA Dagle, D Howe, B Roberts, CM Fischer, G Whyatt, Pacific Northwest National Laboratory, Richland, Washington

J White, Environmental Molecular Sciences Laboratory, Richland, Washington

Nanomaterials for Chelation Therapies and Sensing Applications

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T Sangvanich, K Pattamakomsan, Bn Charnhattakorn, V Koonsiripaiboon, J Kanlayanatham, V Sukwarotwat, Chulalongkorn University, Bangkok, Thailand

Ion Beam Implantation of Titanium Alloys to Improve Durability in Structural and Biomedical Applications

KO Findley, MP Carroll, Washington State University, Pullman, Washington

Composition Analysis of Surface-Bound Nanoparticle Monolayers

ML Jespersen, JE Hutchison, JA Dahl, University of Oregon, Eugene, Oregon

Functional Interfaces at the Nanoscale

JW Grate, MG Warner, G Exarhos, LM Bauder, Pacific Northwest National Laboratory, Richland, Washington

AJ Tyler, Utah State University, Logan, Utah

Radiation Induced Defects in Nanostructured Polymer-Derived Ceramics

L An, University of Central Florida, Orlando, Florida

Study of Interfacial Phenomena of Novel-Layered Thin Film Structure

Y Zhang, Environmental Molecular Sciences Laboratory, Richland, Washington

Y Liu, X Wang, Alfred University, Alfred, New York

An Integrated Approach to Quantifying the Coupled Biotic and Abiotic Mechanism, Rates and Long-Term Performance of Phosphate Barriers for *in situ* Immobilization of Uranium

DM Wellman, A Miracle, EM Pierce, Pacific Northwest National Laboratory, Richland, Washington

Assessment of Functionalization of Gold Nanoparticles

JA Dahl, JE Hutchison, ML Jespersen, University of Oregon, Eugene, Oregon

Edgar Buck's Proposal

EC Buck, RN Wittman, Pacific Northwest National Laboratory, Richland, Washington

Preparation and Analysis of I-III-VI2 Nanomaterials for the Solar Energy Conversion and Radiation Sensing Applications

JJ Pak, L Lau, JS Gardner, Idaho State University, Pocatello, Idaho

Lirong Zhong's Proposal -- TEM/SEM-Microprobe Study on Carbon Dioxide Flooding Sandstone Core

L Zhong, Pacific Northwest National Laboratory, Richland, Washington

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Nanoparticles-Based Biosensors for Detection of Environmental Biomarkers

CM Wai, K Shimizu, University of Idaho, Moscow, Idaho

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A Lee, National University of Singapore, Singapore, Malaysia

J White, Environmental Molecular Sciences Laboratory, Richland, Washington

X Kang, Guangdong Ocean University, Guangdong, China

Todd Allen's Proposal

TR Allen, L Tan, AM Kruizenga, University of Wisconsin-Madison, Madison, Wisconsin

Biological Templates for Synthesis of Ordered Ceramic Nanostructures

Y Shin, G Exarhos, C Windisch, Pacific Northwest National Laboratory, Richland, Washington

J White, Environmental Molecular Sciences Laboratory, Richland, Washington

Nanoscale Enzyme Reactors (NERs) for Biofuel Cells

P Wang, University of Minnesota, Minneapolis, Minnesota

SY Ha, MB Fischback, Washington State University, Pullman, Washington

J Kim, Pacific Northwest National Laboratory, Richland, Washington

S Shin, K Kwon, H Park, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea South, Republic of

Development of Alternative and Durable High Performance Cathode Supports for PEM Fuel Cells

P Kumar, Washington State University, Pullman, Washington

Y Wang, J Liu, J Kwak, Z Zhang, VV Viswanathan, Y Shao, R Kou, Pacific Northwest National Laboratory, Richland, Washington

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Course in Nanoscience and Nanotechnology

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DR Baer, Environmental Molecular Sciences Laboratory, Richland, Washington

F Ohuchi, University of Washington, Seattle, Washington

Investigating Electrochemical Properties, Composition and Oxidation States of Nanoparticles and Catalysts Using Electrochemistry and XPS

C Zhong, State University of New York at Binghamton, Binghamton, New York

Mechanisms of Laser and Electron Beam Modifications of Wide Band-Gap Single Crystal Surfaces

JT Dickinson, E Khan, Washington State University, Pullman, Washington

WP Hess, Pacific Northwest National Laboratory, Richland, Washington

Single Enzyme Nanoparticles

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S Shin, H Park, H Chang, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea South, Republic of

S Kim, Pennsylvania State University, University Park, Pennsylvania

Ceria Nanomonitors for Trace Oxygen Monitoring in Portable Energy Systems

S Prasad, RK Reddy, S Gupta, YS Yadav, VL Venkatraman, DB Mek, Portland State University, Portland, Oregon

J White, Environmental Molecular Sciences Laboratory, Richland, Washington

Kiln Phosphoric Acid (KPA) Process

T Hart, Pacific Northwest National Laboratory, Richland, Washington

JA Megy, JDC, Inc, New Cumberland, West Virginia

Structural Analysis of Ion-Beam-Induced Amorphous SiC by Advanced Electron Microscopy

M Ishimaru, A Hirata, M Naito, Y Hirotsu, Osaka University, Ibaraki, Japan

Non-Destructive Evaluation of Damaged Ancient Scrolls using NMR and PIXE Scanning to Separate Text from the Scroll Background Combined with 3D Virtual Unrolling

WB Seales, University of Kentucky, Lexington, Kentucky

E Iuliano, Edward M. Iuliano, D.O., Richland, Washington

Contribution of Biosorption Processes to the Sustained Removal of Uranium from Groundwater in the Absence of Added Electron Donor

LA N'guessan, DR Lovley, University of Massachusetts Amherst, Amherst, Massachusetts

Adhesion of Polymer Spheres to Modified Natural Fibers

JD Holbery, D Howe, Pacific Northwest National Laboratory, Richland, Washington

PL Gassman, J White, Environmental Molecular Sciences Laboratory, Richland, Washington

Degradation of Lignin Using Homogeneous Catalysis in Ionic Liquids

G Li, SD Burton, ZC Zhang, JE Amonette, Pacific Northwest National Laboratory, Richland, Washington

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JM White, University of Texas at Austin, Austin, Texas

Investigation of Arsenic and Lead Migration at Former Phosphate Fertilizer Plants

KJ Cantrell, W Deutsch, Pacific Northwest National Laboratory, Richland, Washington

B Arey, Environmental Molecular Sciences Laboratory, Richland, Washington

Analysis of Self-Assembled Monolayers on Mesoporous Supports (SAMMS) Materials

JT Bays, RJ Wiacek, RS Addleman, A Cinson, J Davidson, CA Fernandez, Pacific Northwest National Laboratory, Richland, Washington

Characterization of Protein Confinement in Functionalized Nanoporous Supports

C Lei, Pacific Northwest National Laboratory, Richland, Washington

Irradiation Induced Nanostructures

L Wang, X Xiang, H Xiao, University of Michigan, Ann Arbor, Michigan

High Resolution Electron Microscopy Study of Nanostructured Materials

J Liu, K Zhu, Pacific Northwest National Laboratory, Richland, Washington

Characterization of Solid Oxide Fuel Cell Electrodes after Exposure

O Marina, LR Pederson, GW Coffey, X Zhou, CD Nguyen, Pacific Northwest National Laboratory, Richland, Washington

J White, Environmental Molecular Sciences Laboratory, Richland, Washington

Michael Knoblauch's Proposal: Molecular Structure and Interaction of Forisome Filaments

M Knoblauch, Washington State University, Pullman, Washington

Fabrication of a Carbon Nanotube Thermionic Cathode

KJ Bunch, Pacific Northwest National Laboratory, Richland, Washington

Addressing Challenges in Nanoscale Characterization

DC Johnson, SL Golledge, University of Oregon, Eugene, Oregon

DJ Gaspar, A Miracle, AL Bunn, BJ Tarasevich, GE Fryxell, XS Li, RJ Orth, DW Matson, CR Yonker, K Wallace, JG Teeguarden, J Liu, D Wang. Pacific Northwest National Laboratory, Richland, Washington

J White, Environmental Molecular Sciences Laboratory, Richland, Washington

A Gupta, Battelle Columbus, Columbus, Ohio

Undoped and n-Type Doped TiO_2 Anatase Surface Structures and Reactivity with Water

S Chamberlin, University of Wisconsin, Milwaukee, Wisconsin

CJ Hirschmugl, University of Wisconsin, Milwaukee, Milwaukee, Wisconsin

Gregory Szulczewski's Proposal

GJ Szulczewski, University of Alabama, Tuscaloosa, Tuscaloosa, Alabama

Role of Surface and Interface on Transport Properties in Nanoscale Conducting Oxides

X Zhou, Pacific Northwest National Laboratory, Richland, Washington

Material Homogeneity Studies on 3D Microfabricated Ceramic Structures using Nanoparticle Building Blocks

SV Atre, Oregon State University, Corvallis, Oregon

Interfacial Phenomena in Cu Plating

VM Dubin, Y Tao, J Blanchard, X Xu, eMAT Technology LLC, Moses Lake, Washington

Doping inorganic Wide-Band-Gap Semiconductors for Future Energy Devices

W Jiang, Pacific Northwest National Laboratory, Richland, Washington

Molecular Interfaces to Single-Crystal Anatase Surfaces

RJ Hamers, University of Wisconsin-Madison, Madison, Wisconsin

Characterization of Amorphous Oxide Transparent Semiconductors

GS Herman, WF Stickle, CE Otis, CM Mcconica, RL Hoffman, SD Leith, Hewlett-Packard Company, Corvallis, Oregon

Experimental Validation of Multiscale Modeling Approach to Materials Discovery for Radiation Detection Materials

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Y Li. Pennsylvania State University, State College, Pennsylvania

Tuning the Chemistry and Configuration of Oxide Nanostructures for Energy and Environmental Applications

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T Thevuthasan, DR Baer, L Saraf, V Shutthanandan, C Wang, J White, P Nachimuthu, Environmental Molecular Sciences Laboratory, Richland, Washington

Fundamental Understanding of Charge Transfer from a Ru-Based Dye Adsorbate to a TiO_2(110) Surface

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BA Parkinson, Colorado State University, Fort Collins, Colorado

T Thevuthasan, P Nachimuthu, Environmental Molecular Sciences Laboratory, Richland, Washington

Bradley Tebo's Proposal

BM Tebo, Oregon Health Sciences University/Oregon Graduate Institute, Portland, Oregon

Cryo-TEM Investigation of Polyketide Synthase Megacomplexes in *Candidatus Endobugula sertula* and *Teredinibacter turnerae*

MG Haygood, AE Silva, Oregon Health Sciences University/Oregon Graduate Institute, Beaverton, Oregon

Development of a Scalable Solution-Based Catalyst Fabrication Process using Microreaction Technology

C Chang, S Han, Oregon State University, Corvallis, Oregon

Reaction Specificity of Nanoparticles in Solution (PNNL Scope # 42184/44076, Baer/Amonette Nano-Fe BES/EMSP Project)

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Experimental and Theoretical Studies of Reaction Pathways for the Breakdown of Chlorinated Hydrocarbon Molecules by Metal and Metal Oxide Nanoparticles(including PNNL Scope # 42184/44076, Baer/Amonette/Tratnyek Nano-Fe BES/EMSP Project)

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3-Dimensional Reconstruction and Modeling of Bacterial Extracellular Polymeric Substances (ExPS)

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Determining Mechanisms of Nonlinear Photo Response and Transport Properties in Scintillating Materials

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Use of Inductively Coupled Plasma Atomic Emission Spectrometer for Determining Metal Ion Uptake by New Extraction Chromatography or Ion Exchange Resins

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Determination of Changes in Surface Chemistry of SOFC Seal Materials

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Using Ni-Ion Irradiation for the Development of Advanced Materials for the Next Generation Nuclear Reactor

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Site-Specific Sample Preparation of Surfaces and Buried Interfaces for TEM and Atom Probe Analysis

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Medical Plastic Surface Characterization

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What is this Stuff?

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Molecular-Level Mechanisms of Microbial Basalt Alteration

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Detailed Characterization of Arsenic Adsorptive Media

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Observation of Biogenic Nano-scaled Wire-like Arsenic Sulfide Mineral

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Grape Berry Shrivel: A Study of Anatomical and Ultrastructural Changes

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Cryo-TEM Investigation of Polyketide Synthase Megacomplexes in *Candidatus Endobugula sertula* and *Teredinibacter turnerae*

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Photodesorption of Organic Radicals from TiO_2(110)

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Exploration of the Cell Parameter and Thermal Expansion Behavior in Au and ZrW_2O_8 Nanoparticles

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Growth of Ti-Doped Epitaxial Alpha-Fe_2O_3(0001) Thin Films

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Growth of Single Crystal $La_2CuO(^{4+}$delta) Films

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The Oxidation of Self Assembled Organic Monolayers by Nitrate Radicals using Time of Flight Secondary Ion Mass Spectrometry

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Secondary Ion Mass Spectroscopy Study of Transitions Metals Doped ZnO Nanowires

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Characterization and Method Development for Back-End of the Line Wafer Processing Concepts

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Oxidation Studies of Coatings for Interconnect Plates in Solid Oxide Fuel Cells

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SEM and SIMS Analysis of Organic Semiconductor Films Grown using Liquid Crystal Solvents

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Fabrication and Characterization of Carbon Nanotube-Based Composites

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Synthesis and Characterization at Atomic Level of Novel Nanocrystalline Metal Oxide Structures

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Sulfur Absorbents for Emission Control

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Hydrogenation of Pyrolysis Oils to Create Gasoline
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Characterization of Lithium Aluminate Powders

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Influence of Gd and Sm Doping on Atomic and Ionic Transport Properties of Novel Nanostructured Ceria-Zirconia Multilayers

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Early Transition Metal Oxides as Catalysts: Crossing Scales from Clusters to Single Crystals to Functioning Materials - Catalysis Science (Chuck Peden's BES Project - 45385)

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Nanotemplated Electrodeposition

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Molecular Science Computing Facility

The Molecular Science Computing Facility (MSCF) supports a wide range of computational activities in environmental molecular research, from benchmark calculations on small molecules to reliable calculations on large molecules, from solids to simulations of large biomolecules, and from reactive chemical transport modeling to regional cloud climate modeling. Recently, aerosol modeling and bioinformatics of various sorts have been added to the computational mix. MSCF provides an integrated production computing environment with links to external facilities and laboratories within the U.S. Department of Energy (DOE) system, collaborating universities, and industry.

Capabilities

MSCF provides computational resources for Computational Grand Challenges in environmental molecular science and basic and applied research areas that address the environmental problems and research needs facing DOE and the nation with an emphasis on combining theory with experiment. Computational grand challenge projects typically involve multiple investigators from universities, national laboratories, and industry working collaboratively as teams. These projects fit within the EMSL Science Themes and are usually granted computer time allocations for three years. MSCF supported 23 three-year grand challenge projects during 2007. The average annual computer time allocation for grand challenge projects in 2007 was 477,530 central processor unit (cpu) hours, with individual project allocations ranging from 180,000 to 1,650,000 cpu-hours. In 2007 the MSCF supported 37 EMSL Science Theme projects, which are 1- to 3-year allocations averaging 102,325 cpu-hours with 12 involving use of experimental capabilities within EMSL

Instrumentation & Capabilities

- **MPP2**. Production cluster of 980 HP rx2600 nodes, 1960 1.5-gigahertz IA64 processors, 450-terabytes local disk, 9.7-terabytes memory, and 11.8-teraflops theoretical peak performance
- **Dtemp**. Shared parallel high-performance filesystem on MPP2, 53 terabytes
- **NWfs**. EMSL long-term data store, 726 terabytes
- **Network**. 10 GBit/sec internet connection, 10 Gigabit Ethernet MSCF backbone
- **NWVisus**. Visualization server, SGI Onyx 350, 16 processors, 32-GB RAM, three graphics heads, 860-GB disk, with 3-D display and projection capability.
- **Molecular Science Software Suite**. NWChem, Ecce, GA Tools

MSCF also supports smaller, shorter-term projects called MSCF Pilot Projects. Pilot Projects are limited to a maximum of 75,000 processor hours and a 1-year duration that can be submitted at any time. MSCF supported 47 Pilot Projects during 2007, with an average allocation of 61,744 cpu-hours. Pilot Projects are typically directed at developing the capability to submit a Computational Grand Challenge proposal in the future (e.g., a combination of theory/method or code development activities, or calculations that provide the initial scientific basis of a Computational Grand Challenge proposal). Pilot Projects are also awarded for computer support of experimental research taking place within other W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) facilities.

A fourth category of MSCF computer projects are provided to the Office of Science via the INCITE program. In 2007, there was one such project with 750,000 cpu-hours allocated.

User Computing in MSCF. To optimally address the complex environmental problems facing DOE and the nation and to best use limited staff resources, EMSL follows the recommendation of the EMSL Science Advisory Committee to use a Computational Grand Challenge approach to provide large blocks of resources to the user community. A call for proposals is usually issued annually, and teams of computational scientists respond with peer-reviewable proposals for system time allocations. Access for the grand challenge teams is granted for periods of one to three years. In 2007, a Computational Grand Challenge call was not made because of the large number of EMSL Science Theme projects (37) that reviewed well and received computer time. Instead, the five CGC projects that were scheduled to complete their third year were given an opportunity to extend into a fourth year with allocations based on their third-year progress. Principal investigators from all five projects accepted.

Projects Using Computation and Experiment, One great advantage of performing research at EMSL is the opportunity to run experiments and interact with computational chemists, theoreticians and computer scientists. By combining experiment with significant computer power, scientific advances are more readily obtained. In 2007, there were 15 EMSL Science Theme projects with both an experimental and computational component in EMSL.

MSCF Resources

MSCF provides a combination of production computing hardware and software resources and visualization tools to support the scientific research activities of the Computational Grand Challenge, EMSL Science Themes, and Pilot Projects. The hardware and visualization resources are the High-Performance Computing System-2 (MPP2), NWfs, the Graphics and Visualization Laboratory (GVL), and the Molecular Science Software Suite (MS^3). These resources are discussed below.

MPP2. MPP2 provides a balanced supercomputer. Since becoming operational in July 2003 with a theoretical peak performance of 11.8 teraflops, 9.7 terabytes of RAM, and 450 terabytes of disk, the Hewlett-Packard supercomputer (Figure 1) has been tailored to meet the operational needs of EMSL users.

***Figure 1**. EMSL's 11.8-teraflop HP supercomputer.*

NWfs. NWfs, which is the EMSL archive system located in MSCF, uses a groundbreaking approach to disk storage that clusters many low-cost commodity disks to provide fault-tolerant, scalable, long-term storage. Such large-capacity archive systems usually rely on tape for mass storage, but NWfs distinguishes itself by having all its data instantly accessible on disk-based storage. NWfs currently has a capacity of 726 terabytes and the ability to grow as needed to over a petabyte.

GVL. GVL provides production graphics and visualization facilities for the display and analysis of complex datasets from both experiments and simulations. GVL contains three high-performance graphics stations based on Silicon Graphics Incorporated (SGI) technologies with high-speed Gigabit Ethernet connections to the production supercomputers and to NWfs, a digital video system integrated with the workstations to facilitate the display and capture of scientific data, and digital video editing equipment for the preparation of scientific presentations.

MS^3. Software resources include MS^3, which is a comprehensive, integrated set of tools that enables scientists to understand complex chemical systems at the molecular level. MS^3 couples the power of advanced computational chemistry techniques with existing and rapidly evolving high-performance massively parallel computing systems with extensible problem-solving capabilities. The suite consists of three components: 1) the Northwest Computational Chemistry Software (NWChem), 2) the Extensible Computational Chemistry Environment (Ecce), and 3) the Global Array Tools (GA Tools). These three components are briefly described below.

- ***NWChem***. Documentation and information are available on the NWChem Website (http://www.emsl.pnl.gov/docs/nwchem). NWChem provides many methods for computing the properties of molecular and periodic systems using standard Gaussian and planewave-based quantum mechanical descriptions of the electronic wave function or density. In addition, NWChem can perform classical molecular-dynamics and free-energy simulations. These approaches may be combined to perform mixed quantum-mechanics and molecular-mechanics simulations.

  NWChem is available on almost all high-performance computing platforms, workstations, PCs, and clusters of desktop or workgroup servers. NWChem development provides maximum efficiency on massively parallel processors. Among the new features that will be available in the 5.1 version:

  – Coupled cluster linear response properties will be used to accurately model frequency dependent polarizabilities.
  – The new spin-orbit zeroth-order relativistic approximation (ZORA), available in both the Gaussian and plane wave density functional theory, will enable users to better model heavy element chemistry.
  – The constrained density functional theory method developed and contributed by the Van Voorhis Group will be available. In addition, the Truhlar group will make their latest M06 density functional available in NWChem.

- ***Ecce***. Ecce, which is composed of a suite of client/server Unix-based applications, is a domain-encompassing, problem-solving environment for computational chemistry. Applications for setting up, running, and analyzing the results of computational chemistry studies are built on top of a Web-based data management and inter-application messaging server framework. A computational code registration capability supports several underlying chemistry codes and the ability to integrate new ones without reworking core Ecce applications. Running jobs through industry standard remote communications, like secure shell, and a batch queue management system registration capability allows transparent access to high-performance compute resources from users' desktop workstations. A simple installation procedure and extensive online help combine to make Ecce a preeminent user environment for computational chemistry. There are six major application components:

  1. Calculation Manager aids in the organization and manipulation of computational chemistry studies. This tool allows an at-a-glance overview of the status of every calculation and easy access to key setup parameters and run statistics.
  2. Molecule Builder is an intuitive point-and-click tool that enables the building, visualization, modification, and manipulation of three-dimensional representations of chemical systems.
  3. Basis Set Tool enables users to select from nearly 300 predefined Gaussian basis sets or the ability to create new ones for use in *ab initio* electronic structure calculations.
  4. Calculation Editor allows the user to choose input options using point-and-click interfaces for different chemistry codes, and then generates the code-specific input.

5. Job Launcher is used for submitting a calculation to a computer for processing. The user may submit a calculation to any computer that has been registered within Ecce and for which the user has an account.
6. Calculation Viewer provides convenient access to current information for a single calculation during execution or after completion. It has many features for viewing and visualizing chemical system properties.

- ***GA Tools***. GA Tools (also known as ParSoft) includes high-performance computing libraries and tools for applied parallel computing focused on inter-processor communications through the aggregate remote memory copy interface, high-performance input/output through the Parallel I/O tools, and programming models for hierarchical memory systems through the Global Arrays and Memory Allocator libraries. The development of these tools is driven by needs of real scientific application codes on the high-end parallel systems. Development of Aggregate Remote Memory Copy has been supported by EMSL operations and by the DOE Center for Programming Models for Scalable Parallel Computing.

MSCF Organization

MSCF is organized into three project groups: 1) the Visualization and User Services Group, 2) the High-Performance Software Development Group, and 3) the Computer Operations Group.

Visualization and User Services Group (VisUS). This group provides an extremely diverse set of services for all users of the MSCF high-performance computers and GVL. Scientists who need access to high-end computing equipment frequently have difficulty getting started. Difficulties encountered range from logging in to getting user codes to run and scale efficiently. VisUS handles user proposal applications, follows user progress during computational projects, manages proposal reviews for both Computational Grand Challenge projects and Pilot Projects, helps with user accounts, provides general consulting support for MSCF software packages, supports and maintains software, manages the GVL, conducts training and user workshops, develops visualization software and high-quality visualizations, and maintains Websites.

The group manages the Computational Grand Challenge and EMSL Science Theme proposal process for the MSCF. This activity includes receiving proposals, providing preliminary review for EMSL missions, assigning external peer reviewers, evaluating peer reviews, granting project allocation, and managing the allocations by using GOLD, a dynamic-reservation-based allocations management system originally developed at PNNL.

Consultants have various roles, including those of administrator, scientific point of contact, tutor, programmer, or research scientist, and field a variety of requests for support. Consultants also work directly with MS^3 development teams to give customer feedback and to test functionality.

Information about the use and configuration of the MSCF computational resources is critical to the user base and is provided efficiently to users via the Internet through the MSCF home page. The MSCF Website contains all necessary information about how to establish accounts and get started, and about computer configurations as well as documentation and Web-based tutorials for MS^3. Scientists generate enormous amounts of data either from computational resources or from EMSL instruments. These data are usually complex and difficult to understand. The capabilities and expertise available in the GVL, including its high-performance graphics compute servers and state-of-the-art multimedia equipment, help scientists visualize these complex data. The real-time digital video capture capability from the graphics compute servers allows fast, yet high-quality, video production. Users can generate presentation media in any form—from video (including all international video standards) to Web-based animations. The group also provides basic video production services.

High-Performance Software Development Group. This group has the primary responsibility for developing and supporting MS^3. This effort includes:

- developing high-performance versions of the software and new high-performance algorithms
- continually refreshing the underlying software architecture to stay current with new hardware and software technology and standards
- responding to user requests for additional features
- supporting and maintaining the software
- diagnosing MS^3 problems associated with computer vendor hardware and software
- consulting on specific MS^3 problems
- distributing MS^3 to remote sites
- porting software to new architectures
- conducting training and user workshops.

The MS^3 project group focuses on developing next-generation molecular modeling software for newly evolving computer technologies, especially massively parallel computers. The project group is composed of computational chemists and computer scientists (with external collaborations to mathematicians) who work together to develop the MS^3 software. This software is used by many of the MSCF Grand Challenge projects and has been distributed to almost 1900 sites worldwide. In addition to the development activities, this group is also responsible for training software users, conducting tutorial workshops, and providing user support. Several resources have been developed to facilitate user support and training. These resources include MS^3 Websites with user and reference manuals, download information, release notes, FAQs, a list of known bugs, tutorials, and benchmark information, Web-based context-sensitive help available from within the software, as well as a mailing list where users can post support-related questions and get answers either from experienced users or from the NWChem developers.

Computer Operations Group. This group operates, maintains, and advances the capabilities of the MSCF scientific computing systems. The group is responsible for the operation and implementation of the various production supercomputers in the MSCF and has developed unique system management, monitoring, allocation management, and scheduling capabilities. The primary focus is on providing high-quality, reliable production computing cycles and storage capabilities in the MSCF to support very large parallel calculations for Computational Grand Challenge projects.

Upgrades and Activities

In Fiscal Year 2007, the following activities occurred in the MSCF:

- HP was selected to deliver a **$24M supercomputer** that will support the scientific research of EMSL users. The new system, named Chinook, will allow users to conduct a broad range of cutting-edge research, such as discovering safe and effective materials in which to produce and store hydrogen; studying chemical processes in bacteria's behavior to address bioremediation and energy production issues; and developing computer simulation tools to aid in environmental cleanup. The new system will include 4620 quad-core AMD Barcelona processors, 37 terabytes of memory and an expected peak performance of about 163 teraflops. It will allow scientists to study complex scientific problems with larger and more realistic models and get answers faster by scaling computational models to larger numbers of processors. The system will be delivered and tested in two phases starting in January 2008, and is expected to be fully operational in September 2008. It will replace the current supercomputer, which went online in 2003.

- An informal ribbon cutting of the new supercomputing raised floor in the Molecular Science Computing Facility was held on January 10, 2007, to give staff and users a sense of celebration as well as knowledge that the facility is growing and will continue to grow during the next decade. The new ~ 4000-square-foot raised floor constitutes the first-ever permanent expansion of EMSL. One hundred and seventy-five people attended the ceremony. Cabling and cooling capabilities will be located under the floor, and the room itself will provide space for expansion of the MSCF's data archive capabilities as well as house at least a portion of the next-generation supercomputer, which is scheduled for operation in 2008.

- The **NWChem** meeting, "NWChem Meeting on Science Driven Petascale Computing and Capability Development at EMSL," was held at EMSL on January 25 – 26, 2007. Sixty-five experts in software development and computational chemistry attended the meeting to discuss status and future direction of NWChem, how to contribute to the growth of NWChem related to its scientific capability and computational performance by 2022, and parallel implementation and natural linear scaling of coupled-cluster theory of large molecule applications. The information generated by the participants' discussions is being rolled into a strategic plan for further development of NWChem. The report is available online at http://www.emsl.pnl.gov/docs/nwchem/nwchem.html .

A Quantitative Account of Quantum Effects in Liquid Water

GS Fanourgakis,(a) **GK Schenter,**(a) **and SS Xantheas**(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

Since the first electrostatic interaction potential introduced by Bernal and Fowler in 1933 and the first computer simulations for its liquid state by Baker and Stillinger in 1969 and Rahman and Stillinger in 1971, water still remains an active field of research.

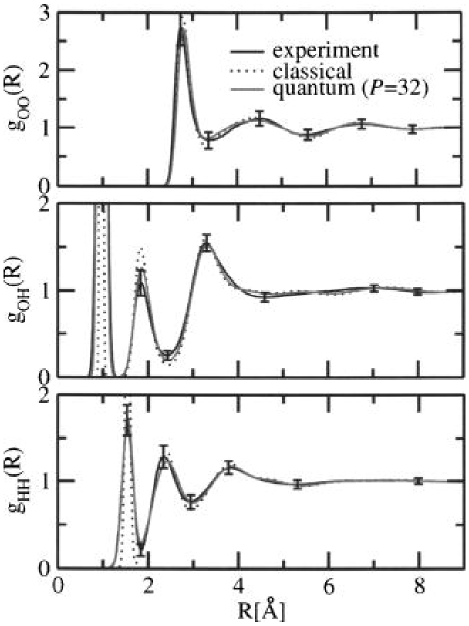

Figure 1. *Calculated quantum statistical mechanical and experi-mental RDFs for oxygen-oxygen, oxygen-hydrogen, and hydrogen-hydrogen at T=298.15 K. The error bars correspond to the experimental uncertainty.*

A comprehensive model describing water and its anomalous properties has yet to be developed. Most existing potentials for water have been parametrized to reproduce its macroscopic structural and thermodynamic properties using classical molecular dynamics simulations. These models are, however, appropriate for classical molecular dynamics simulations only for the particular phase that was included in the training set. Truly "transferable" models require an accurate representation of underlying Born-Oppenheimer potential energy surface and explicit account of zero-point-energy effects.

An alternative to classical potentials is evaluation of the electronic energy and forces from first principles. The authors report converged quantum statistical mechanical simulations of liquid water with the Thole model, flexible, polarizable (TTM2.1-F) interaction potential for water. The quantum statistical mechanical radial distribution functions (RDFs) and average energy of the system were sampled using centroid molecular dynamics. Simulations with a total duration of 600 ps with 0.05-fs time steps for a periodic unit cell of 256 molecules with up to 32 replicas per atom suggest that the quantum effects contribute 1.01 ±0.02 kcal/mol to the liquid enthalpy of formation at 298.15 K. They furthermore demonstrate a first-time quantitative agreement with experimental results for the heights and broadening of the intramolecular OH and HH peaks in the radial distribution functions (see Figure 1). The results presented in this paper clearly identify a path for obtaining accurate structural and thermodynamic information of complex, many-body systems, and lay the foundation for forthcoming studies of other thermodynamic states of water and the examination of its anomalous properties (Fanourgakis et al. 2006; Thole 1981; Kuharski and Rossky 1985).

Citations

Fanourgakis GS, GK Schenter, and SS Xantheas. 2006. "A Quantitative Account of Quantum Effects in Liquid Water." *Journal of Chemical Physics* 125(14): Article No. 141102.

Kuharski RA and PJ Rossky. 1985. "A Quantum-Mechanical Study of Structure in Liquid H_2O and D_2O." *Journal of Chemical Physics* 82(11):5164.

Thole BT. 1981. "Molecular Polarizabilities Calculated with a Modified Dipole Interaction." *Chemical Physics* 59(3):341-350.

Asymptotic Extrapolation Scheme for Large-Scale Calculations with Hybrid Coupled-Cluster and Molecular Dynamics Simulations

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While high-level coupled cluster (CC) calculations currently are possible for small- and medium-size molecular systems, the development of accurate, excited-state methods for larger, biologically relevant systems pose a significant challenge for theory.

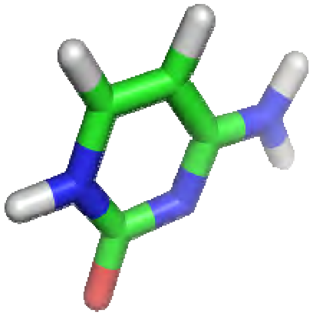

***Figure 1.** The structure of excited states of the cytosine molecule plays an important role in understanding photo-stability of DNA.*

Usually, the size of biologically important systems prohibits the use of highly correlated *ab initio* methods and extensive basis sets that include diffuse functions or functions of triple- or quadruple-ζ quality. On the other hand, these factors are imperative in understanding photophysical and photochemical properties of nucleic acids, especially those related to the ultraviolet (UV)-protection mechanism based on the ultrafast conversion of excited electronic states. Recently, the authors developed, using NWChem capabilities, a suite of programs that combines classical molecular dynamics with high-level *ab initio* methods for excited states (Kowalski and Valiev 2006). The main goal of this effort was to create a framework for realistic, temperature-dependent, excited-state calculations for biochemical systems with an approximate description of the effects of the native environment, including its dynamical fluctuations. Because thermal averaging involves multiple calls to rather expensive *ab initio* procedures, the low-scaling extrapolation schemes may play a pivotal role in further advancing this area. The main purpose of this paper is to address, on a very basic level, these important issues. A very simple τ-parameter dependent cut-off scheme was used for the virtual orbitals, with orbital energies lying above the cut-off factor. Based on this scheme, simple heuristic formulas were derived for the excitation energies as a function of the τ-parameter, subsequently used in the extrapolation procedures that describe an asymptotic dependence of τ-dependent energies. The performance of the asymptotic extrapolation scheme for completely re-normalized equation-of-motion approach with singles, doubles, and noniterative triples (CR-EOMCCSD(T)) methods is illustrated on the excited-state calculation of cytosine (see Figure 1) base in its native DNA environment. We have clearly shown that:

1. Errors resulting from the extrapolation procedure are negligible when compared to standard fluctuations in the excitation-energy values caused by a fluctuating environment.

2. Use of the asymptotic extrapolation scheme results in more than two orders of magnitude speedups of the CR-EOMCCSD(T) codes with insignificant loss of accuracy on the order of few hundreds of electron volts. Further development of the asymptotic extrapolation scheme in the context of high-level *ab initio* methodologies should lead to the routine use of the highly correlated methods in studies of photoinduced processes in biologically relevant systems.

Citation

Kowalski K and M Valiev. 2006. "Asymptotic Extrapolation Scheme for Large-Scale Calculations with Hybrid Coupled Cluster and Molecular Dynamics Simulations." *Journal of Physical Chemistry A*, 110(48):
13106-13111.

Cycloaddition Functionalizations Preserve or Control Carbon Nanotube Conductance

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Carbon nanotubes continue to show promise for new materials with unique properties. By adding the right small molecules to a carbon nanotube, the ability to conduct electrons is modified. This could lead to a method of controlling a carbon nanotube's electrical properties.

An extensive theoretical study on the energetics and quantum conductance of armchair carbon nanotubes functionalized with carbenes or nitrenes was performed (Figure 1). The groups are attached to neighboring carbon atoms forming a three-membered ring. The diameter of the tubes, relative angle of the sidewall carbon-carbon bond, and the chemical nature of the groups, determine the stability of the bond between the two sidewall carbons. This is radically at variance with the damage permanently induced by other common ligands, where a single covalent bond is formed with a sidewall carbon. Chirality, curvature, and chemistry determine bond cleaving, and in turn the electrical transport properties of a functionalized tube. A well-defined range of diameters can be found for which certain addends exhibit a bistable state, where the opening or closing of the sidewall bond, accompanied by a switch in the conductance, could be directed with chemical, optical, or thermal means. Two conclusions can be drawn. First, even with a large number of functional groups, the conductance remains high when cycloadditions break the sidewall bond. Second, a subclass of substituents can be found (e.g., $C(CN)_2$) that stabilizes two tautomeric forms on the same tube, separately displaying high and low conductance.

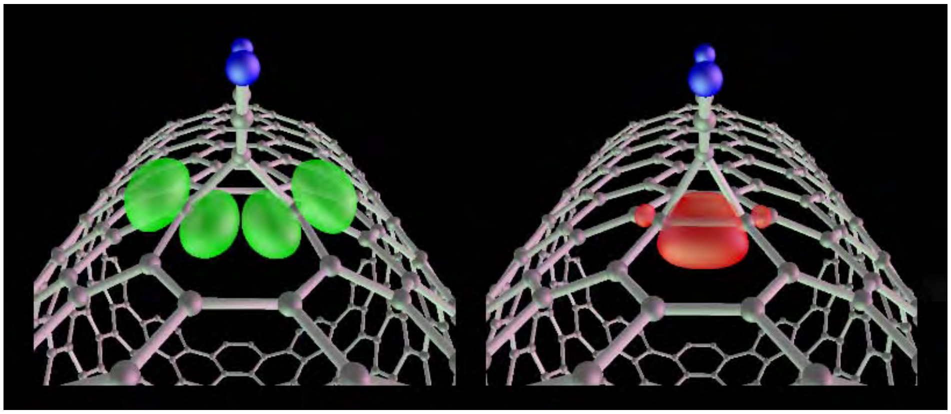

Figure 1. *Two tautomeric states show different conductance states suggesting a novel conductance-control mechanism. Orbital rehybridization through bond breaking and forming can be applied to both semiconducting and metallic nanotubes.*

Lattice Strain Effects on Carbon Monoxide Oxidation on a Platinum(111) Surface

L Grabow,[(a)] Y Xu,[(b)] and M Mavrikakis[(a)]

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(b) Oak Ridge National Laboratory, Oak Ridge, Tennessee

Carbon monoxide is very toxic and odorless. Understanding how carbon monoxide is oxidized on a catalytic surface by oxygen can lead to better, more efficient ways to remove this molecule from internal combustion engine and other sources.

Strain can significantly affect binding energies of adsorbed species and activation energy barriers of surface reactions. Density functional theory was used in combination with microkinetic modeling to establish the foundations of the qualitative analysis presented by Cirak et al. 2003 and provide insights for a deeper understanding of the effect of surface strain on catalytic reactions in general. Accordingly, the first-ever quantitative analysis of chemo-mechanical coupling as it manifests itself on surface reactivity was carried out. The results of our first principles calculations are summarized in a potential energy surface (PES) given in Figure 1. The rate limiting step can be changed by manipulating the strain. When the platinum surface is compressed the barrier is higher, but when the platinum surface is stretched the barrier is lower than a relaxed platinum surface.

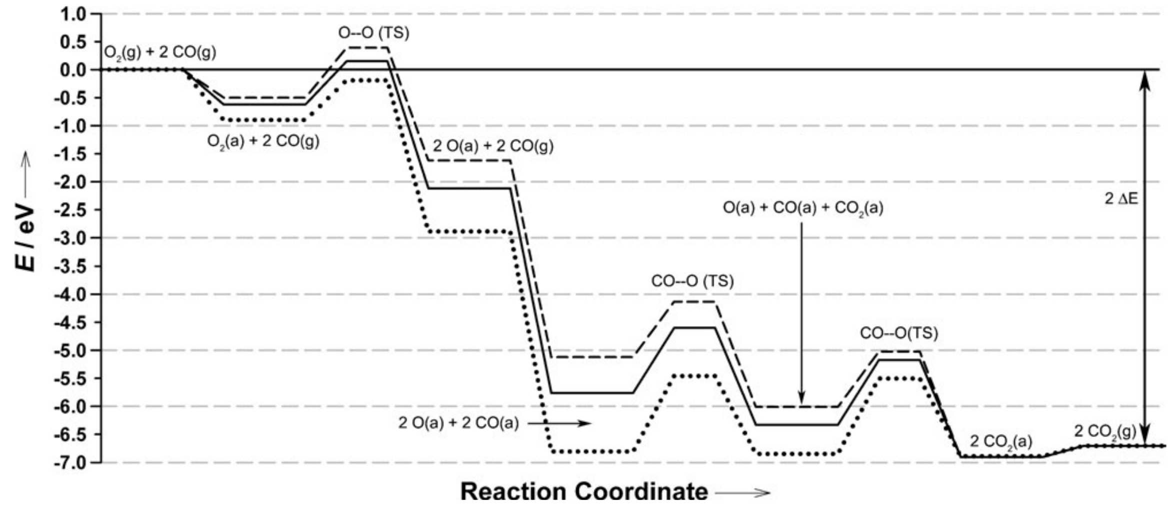

*Figure 1. Overall PES for carbon monoxid oxidation on Pt(111) for equilibrium lattice constant (—), 2%-compressed (--), and 4%-stretched (···). (2*ΔE) represents the heat of the overall reaction: $O_2(g) + 2CO(g) \rightarrow 2CO_2(g)$, where (g) indicates gas phase species. In the graph, TS indicates the transition state of the respective elementary step.*

Citation

Cirak F, JE Cisternas, AM Cuitino, G Ertl, P Holmes, IG Kevrekidis, M Ortiz, HH Rotermund, M Schunack, and J Wolff. 2003. "Oscillatory Thermomechanical Instability of an Ultrathin Catalyst." *Science* 300(5627):1932-1936.

De Novo Structure-Based Molecular Design

***BP Hay*[a] *and VS Bryantsev*[a]**

(a) Pacific Northwest National Laboratory, Richland, Washington

An important theme in supra-molecular chemistry is the formation of anion complexes using synthetic host molecules; however, identification of suitable hosts is not a trivial task. To address this issue, we have developed the de novo structure-based design software, HostDesigner, which is specifically tailored to discover molecular structures that are organized to complex with small guest molecules.

In a previous study, we identified bis-urea podands that are structurally organized for binding tetrahedral oxyanions (Bryantsev and Hay 2006). However, whether 1) any of the candidates will exhibit a significant steric preference for a tetrahedral guest or 2) some of the candidates will accommodate other anion shapes with equal facility remained to be determined. The current study represents the first step in an effort to explore the possibility of achieving anion shape selectivity—that is, the design of bis-urea tweezers that are structurally organized for binding tetrahedral ClO_4^-, trigonal NO_3^-, and spherical Cl^- anions.

Bis-urea host molecules were constructed using the *de novo* structure-based design software, HostDesigner, as described previously by Bryantsev and Hay (2006). Structures were built by connecting two N-methylurea-anion (nitrate and chloride) fragments with a hydrocarbon fragment taken from the library. Subsequent molecular mechanics analysis was applied to provide a more accurate prioritization of the top candidates. The top 500 candidates from each run are placed in order of increasing the relative binding energy, ΔG_{rel} to yield the final candidate ranking. The following expression was used to determine the ordering of relative binding energies:

$$\Delta G_{\mathrm{rel}} = \Delta E_1 + \Delta E_2 + 0.31 \mathrm{x} N_{\mathrm{rot}},$$

where ΔE_1 = E(binding form) – E(global minimum), ΔE_2 = E(complex) – E(host, binding form) – E(guest), and N_{rot} is the number of freely rotating bonds restricted on complexation.

The results revealed that many bis-urea podands complementary for one anion shape can also accommodate other anion shapes. This finding is not surprising because the optimal placements for two urea groups around the spherical Cl^-, trigonal planar NO_3^-, and tetrahedral ClO_4^- are similar (Figure 1) (Hay et al. 2005), and if the host is flexible enough, it can easily adopt a conformation suitable for a particular anion geometry.

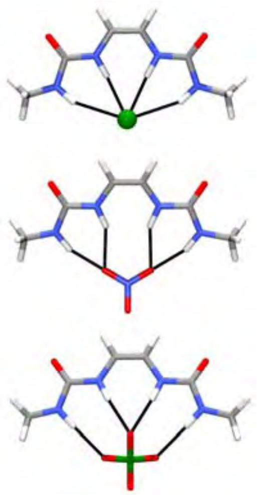

***Figure 1**. Geometries obtained for complexes of one candidate architecture with Cl^-, NO_3^-, and ClO_4^- reveal that this host can form four hydrogen bonds with all three anion shapes.*

Citations

Bryantsev VS and BP Hay. 2006. "*De Novo* Structure-Based Design of Bisurea Hosts for Tetrahedral Oxdoanion Guests." *Journal of the American Chemical Society* 128(6):2035-2042.

Hay BP, TK Firman, and BA Moyer. 2005. "Recognition through the Complementary Placement of Urea Donor Groups." *Journal of the American Chemical Society* 127(6): 1810-1819.

Atomistic Simulations of Hydrated Nafion and Temperature Effects on Hydronium Ion Mobility

A Venkatnathan,(a) ***R Devanathan,***(a) ***and M Dupuis***(a)

(a) Pacific Northwest National Laboratory, Richland, Washington

Polymer electrolyte membrane fuel cells (PEMFCs) can generate power with high efficiency and minimal greenhouse gas emissions. They have the potential to revolutionize power generation for the transportation, residential, and aerospace sectors. The polymer membrane is the heart of the fuel cell. Desired membrane properties are high proton conductivity; thermal, mechanical, and chemical stability; and low cost. None of the existing membranes meet all these requirements. There is a pressing need to design and optimize fuel cell membranes based on a molecular-level understanding of proton transport in polymer membranes.

In this study, molecular simulations are employed to study nanostructure and molecular transport in the widely used polymer membrane, Nafion™ (Dupont). The results reveal that the extent of membrane hydration specifically affects the sulfonate groups on the polymer chains where protons tend to reside. Figure 1 shows a snapshot of a Nafion membrane at low hydration and radial distribution functions at various hydration levels.

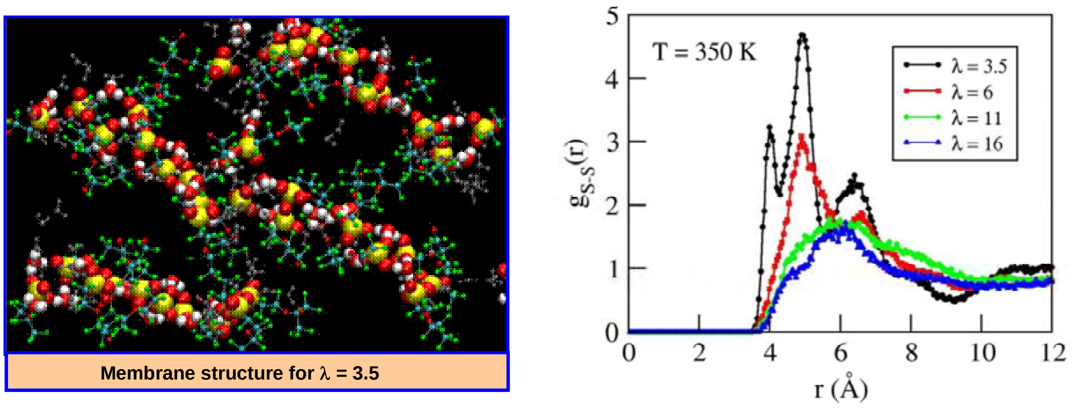

Figure 1. *Left: Snapshot of hydrated Nafion membrane at low hydration. Right: Radial distribution functions of sulfur atoms in hydrated Nafion.*

At low hydration levels of a Nafion membrane, the sulfonate groups aggregate, which diminishes proton transport through the membrane. At higher membrane hydration levels, the distance between the sulfonate groups increases, thereby enhancing proton transport. The dynamical properties of proton and water transport, such as diffusion at fuel cell operating temperatures, also have been examined. This work was recently published as a cover article in the *Journal of Physical Chemistry B* (Venkatnathan et al. 2007). More recently, a detailed examination of the nanostructure of Nafion and the dynamics of proton and water using a different force-field model was performed. The local structure of Nafion membrane around the acidic sulfonate groups that are critical for proton transport is shown in Figure 2. Details of this work appeared in the *Journal of Physical Chemistry B* (Devanathan et al. 2007).

The results, which are in good agreement with experimental measurements of the water diffusion coefficient in hydrated Nafion, help in the interpretation of results obtained from recent neutron scattering experiments.

Citations

Devanathan R, A Venkatnathan and M Dupuis. 2007. “Atomistic Simulation of Nafion Membrane: I. Effect of Hydration on Membrane Nanostructure.” *Journal of Physical Chemistry B* 111(28):8069-8079.

Venkatnathan A, R Devanathan, and M Dupuis. 2007. “Nanostructure of Proton Exchange Membrane Under Low Hydration and Hydronium Mobility: Atomistic Simulation and Characterization.” *Journal of Physical Chemistry B* 111(25):7234-7244.

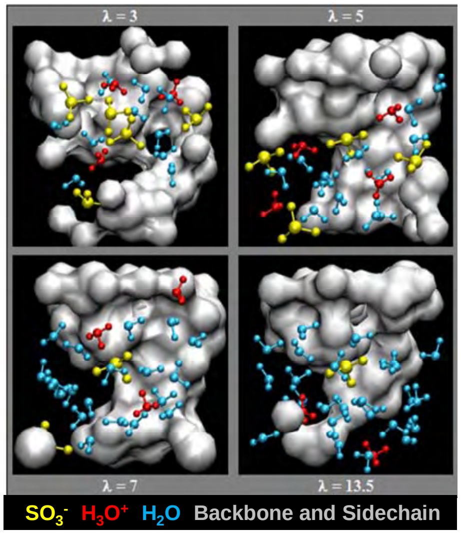

Figure 2. *Snapshot of local structure of hydrated Nafion membrane at various level of membrane hydration ( ).*

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

M Liu[(a)] *and J-H Wang*[(a)]

(a) Georgia Institute of Technology, Atlanta, Georgia

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.

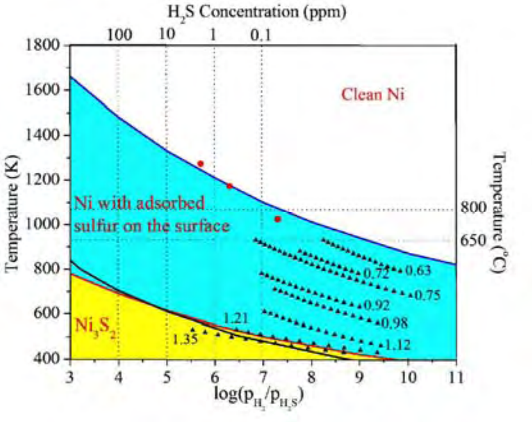

Figure 1. *The new predicted phase diagram for the S-Ni system in H_2S/H_2 fuel mixtures. The black line is from the bulk phase diagrams. The red dots are related to the sulfur tolerance experiment. The black symbols are related to the experiment of chemisorbed S(a) with different coverage as indicated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

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.*

User Projects

Collaborative Development of Software for Electronic Structure Calculations

MF Guest, CCLRC Daresbury Laboratory, Warrington, United Kingdom

Correlation of Structure and Function of Zinc Metalloproteins via Solid-State NMR Methods

G Parkin, Columbia University, New York, New York

ER Kantrowitz, Boston College, Chestnut Hill, Massachusetts

AS Lipton, PD Ellis, R Heck, Pacific Northwest National Laboratory, Richland, Washington

Sub-Grid Modeling of Diesel Particulate Filtration Using the Lattice-Boltzmann Method

ML Stewart, Pacific Northwest National Laboratory, Richland, Washington

MP2/CBS Pair Corrrelation Function of Liquid Water

RH Wood, University of Delaware, Newark, Delaware

Quantification of the Ligand Effects in Transition Metal Coordination Compounds using Electronic Structure Calculation Methods

CA Tsipis, C Kefalidis, Aristotle University of Thessaloniki, Greece

Real-Time Atomistic Simulation Studies of Light Harvesting and Charge Transport for Hydrogen Production in Solar Cells

EJ Bylaska, Pacific Northwest National Laboratory, Richland, Washington

DS Kilin, SV Kilina, K Tsemekhman, O Prezhdo, BF Habenicht, University of Washington, Seattle, Washington

WR Duncan, unknown, Seattle, Washington

Comparative Protein Structure Modeling: From Protein Sequence to High-accuracy Protein Structure

J Guo, University of Georgia, Athens, Georgia

TP Straatsma, Pacific Northwest National Laboratory, Richland, Washington

X Xu, eMAT Technology LLC, Moses Lake, Washington

Comparative Molecular Trajectory Analysis

SK Wurstner, TP Straatsma, M Singhal, Pacific Northwest National Laboratory, Richland, Washington

Wet Electrons at Metal Oxide Surfaces

H Petek, J Zhao, University of Pittsburgh, Pittsburgh, Pennsylvania

The Unoccupied Electronic Structure of Surface Adsorbates

H Petek, J Zhao, University of Pittsburgh, Pittsburgh, Pennsylvania

Thrust Area #2: Molecular Modeling of Electron Transfer in Fe(III) Oxides

KM Rosso, SN Kerisit, X Wang, Pacific Northwest National Laboratory, Richland, Washington

FN Skomurski, University of Michigan, Ann Arbor, Michigan

DM Smith, Whitman College, Walla Walla, Washington

M Valiev, Environmental Molecular Sciences Laboratory, Richland, Washington

MC Wander, State University of New York at Stony Brook, Stony Brook, New York

JD Kubicki, Pennsylvania State University, University Park, Pennsylvania

Joint Application of Theory and Experiment to the Chemistry of Environmentally Important Organic Peroxides

GB Ellison, University of Colorado, Boulder, Colorado

BK Carpenter, A Litovitz, Cornell University, Ithaca, New York

JF Stanton, University of Texas at Austin, Austin, Texas

High Performance Sequence Analysis for Data-Intensive Bioinformatics

CS Oehmen, L Mccue, HJ Sofia, Pacific Northwest National Laboratory, Richland, Washington

EA Welsh, Washington University in St. Louis, St. Louis, Missouri

DJ Baxter, Environmental Molecular Sciences Laboratory, Richland, Washington

Proton Transport in Polymer Electrolyte Membranes

R Devanathan, M Dupuis, A Venkatnathan, Pacific Northwest National Laboratory, Richland, Washington

De novo Structure-Based Molecular Design

V Bryantsev, California Institute of Technology, Pasadena, California

BP Hay, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Nanostructured Catalysts for Fuel Cells

CH Turner, CK Acharya, University of Alabama, Tuscaloosa, Tuscaloosa, Alabama

DFT Studies of Size and Structure Effects of IR Nanoparticles on Their Catalytic Activities for Methane Dissociation

L Wang, Southern Illinois University, Carbondale, Illinois

Computational Study of Oxygen Reduction on SOFC Cathode Surfaces

M Liu, J Wang, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

Architectural Rendering of EMSL Office Expansion

MC Perkins, Pacific Northwest National Laboratory, Richland, Washington

Defect Processes, Phase Transformations, and Nanoscale Phenomena in Complex Ceramics

R Devanathan, F Gao, WJ Weber, Pacific Northwest National Laboratory, Richland, Washington

Energy and Entropy Effects in Dissociation of Non-Covalent Complexes: Experimental and Theoretical Investigation of the Structures and Interactions of Glycopeptide Antibiotics-Cell Wall

Z Yang, J Laskin, Pacific Northwest National Laboratory, Richland, Washington

Investigation of DNA Structural Perturbations Induced by the Guanine Oxidation Products Spiroiminohydantoin and Guanidinohydantoin

ND Priestley, KD Sugden, University of Montana, Missoula, Montana

Asynchronous File System Experiments

MI Seltzer, CA Stein, Harvard University, Cambridge, Massachusetts

Computational Atomic and Molecular Physics for Advances in Astrophysics, Chemical Sciences, and Fusion Energy Sciences

JP Colgan, Los Alamos National Laboratory, Los Alamos, New Mexico

P Krstic, T Minami, CO Reinhold, Oak Ridge National Laboratory, Oak Ridge, Tennessee

MS Pindzola, SD Loch, FJ Robicheaux, Auburn University, Auburn, Alabama

NR Badnell, University of Strathclyde, Glasgow, Scotland, United Kingdom

DC Griffin, CP Balance, Rollins College, Winter Park, Florida

Theoretical Investigations of Chiral Self-Assembly at Solid Surfaces

M Ratner, Northwestern University, Evanston, Illinois

I Paci, University of Victoria, Victoria, British Columbia, Canada

Virtual Tools for Cardiac Remodeling

JM Guccione, University of California, San Francisco, San Francisco, California

DR Einstein, Pacific Northwest National Laboratory, Richland, Washington

Molecular Dynamics of Aqueous $NaNO_3$ and NaCl Solutions: The Surface Propensity and Thermodynamic Properties of Aqueous Anions (Summer Research Institute, PNNL Scope #16248)

JL Thomas, BJ Finlayson-Pitts, DJ Tobias, University of California, Irvine, Irvine, California

LX Dang, Pacific Northwest National Laboratory, Richland, Washington

First-Principles Calculations of $La(1-x)Sr(x)Fe(1-y)Co(y)O_3$ Solids and Surfaces (Summer Research Institute, PNNL Scope #16248)

C Lee, SB Sinnott, University of Florida, Gainesville, Florida

R Devanathan, Pacific Northwest National Laboratory, Richland, Washington

Theoretical Characterization of H_3O^+ on the Water - Vapor Interface (Summer Research Institute, PNNL Scope #16248)

LX Dang, Pacific Northwest National Laboratory, Richland, Washington

J Cui, KD Jordan, University of Pittsburgh, Pittsburgh, Pennsylvania

Molecular Recognition at the Electronic Level

JJ Stezowski, University of Nebraska, Lincoln, Nebraska

PA Karr, Wayne State College, Wayne, Nebraska

High Performance Sequence Alignment: OMB Software Effectiveness Metric Studies for FY06

CS Oehmen, Pacific Northwest National Laboratory, Richland, Washington

KJ Roche, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Investigations into Sulfur Poisoning Mechanisms in Solid-State Oxide Fuel Cells Using Quantum-Chemical Computations

M Liu, J Wang, Y Choi, Georgia Institute of Technology, Georgia Tech Research Corporation, Atlanta, Georgia

Molecular Dynamics Study of an Actin Septamer: Testing the Holmes Model and the Hydrophobic Plug Loop Hypothesis

GC Schatz, KM Barrett, MJ McCullagh, JT Paci, Northwestern University, Evanston, Illinois

KC Holmes, Max Planck Institut fur medizinische Forschung, Heidelberg, Germany

Design Criteria for Organic Charge Transporting Materials through Computational Modeling

L Sapochak, AB Padmaperuma, PE Burrows, Pacific Northwest National Laboratory, Richland, Washington

M Valiev, N Govind, Environmental Molecular Sciences Laboratory, Richland, Washington

Oxide Surface Structure and Acidity

KM Rosso, SN Kerisit, Pacific Northwest National Laboratory, Richland, Washington

BR Bickmore, Brigham Young University, Provo, Utah

DM Smith, Whitman College, Walla Walla, Washington

Nucleation, Growth and Evaporation Rates of Aerosols

SM Kathmann, CJ Mundy, Pacific Northwest National Laboratory, Richland, Washington

TL Windus, MS Gordon, EA Hull, LD Crosby, HM Netzloff, Iowa State University, Ames, Iowa

Hydrogen Bonding in Inhomogeneous Environments

SI Sukharev, AG Anishkin, University of Maryland, College Park, Maryland

ME Green, VS Znamenskiy, S Liao, City College of New York, New York, New York

M Mezei, Mount Sinai School of Medicine, New York, New York

Absorption and Emission of Radiation in Materials

SH Garofalini, Rutgers University, Piscataway, New Jersey

SM Kathmann, R Devanathan, RM Van Ginhoven, Pacific Northwest National Laboratory, Richland, Washington

JD Musgraves, LR Corrales, OA Monti, B Potter, MH De Silva, H Chandra, University of Arizona, Tucson, Arizona

Computational Design of Catalysts: The Control of Chemical Transformation to Minimize the Environmental Impact of Chemical Processes

JM Caruthers, KA Novstrup, JM Switzer, Purdue University, West Lafayette, Indiana

MA Barteau, AC Lukaski, University of Delaware, Newark, Delaware,

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Computational Study of Protein-Protein Interaction Dynamics at Single Molecule Level

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Accurate *ab initio* Determinations of Thermochemistry of Novel Molecular Radicals, Cations and Neutrals of Relevance to Combustion, Environmental, and Atmospheric Chemistry

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Capture and Reduction of Metal Ions out of the Environment by Biomolecular Systems

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Computational Chemical Dynamics of Complex Systems

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Correlation of Structure and Function of Zinc Metalloproteins via a Combined NMR/Molecular Theory Approach

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Advanced Peta-Scale Molecular Dynamics Simulations

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Complex Enzymatic Reactions

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Interfaces and Interactions: Non-ideal Behavior of Biological Molecules

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Molecular Computational Studies in Geochemistry and Environmental Chemistry

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Reliable Electronic Structure Prediction of Molecular Properties

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First Principles Multiscale Analysis of Biochemical Processes: Signal Transduction and Spectroscopic Analysis of Local Structure-Folding Relations in Membrane Proteins

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Scaling Up for Large Metagenomic Computations with ScalaBLAST

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Lustre Scalability Research

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Calculation of the Vibrational Frequencies and Intensities of Monolayer and Submonolayer Water Adsorbed on Pt(111)

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SGI Altix Allocation for Advanced Computing Technology Lab

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Excited States of DNA Hairpins

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Development and Application of Advanced Tools for Computational Fluid Dynamics

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Infrared Adiabatic Rapid Passage Spectroscopy of Small Gas Phase Molecules

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Computational Rheology of Dense Suspensions

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Conceptual Animations of Efficient Enzymes within Functionalized Mesoporous Silica

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IO Benchmarking and Testing in Support of the Global Cloud Resolving Model and Data Subsetting and Analysis

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Hybrid Numerical Methods for Multiscale Modeling of Subsurface Biogeochemical Processes

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Petascale Institute Virtualized Lustre Scalability Research

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Calculation of Oxygen Surface Diffusion on Bulk Oxygen Ion Conductors

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Computational Investigation of Metal Clusters on Doped Carbon Supports

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Computational Studies of the Heterogeneous Production of Molecular Chlorine by OH Oxidation of Chloride in Sea Salt

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Modeling of Polymer Membrane Nanostructure and its Effect on Proton and Small Molecule Transport

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First Principles Adaptive Kinetic Monte Carlo Calculations of Catalytic Reactions at Supported Nanoparticles

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Exploring the Mechanisms and Kinetics of Small Peptides towards the Search for the Global Minimum through Molecular Dynamics Simulations

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Investigation of the Metal Binding Octarepeat Region from the Human Prion using Nanoscale Computer Simulations

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***Ab initio* Studies on Voltage Gating of Ion Channels**

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Glycolipid Structure, Dynamics and Recognition in a Membrane Environment

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Development of Novel Electrolyte and Electrode Materials for a New Generation of Low-Temperature SOFCs Using First-Principles Atomistic Thermodynamics

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Parameterization of Subsurface Flow and Transport Models for Multi-Scale Simulation

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Non-Empirical Simulations of Nuclear Fuel Materials

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Hybrid Numerical Methods for Multiscale Modeling of Subsurface Biogeochemical Processes

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Global Cloud Resolving Model: Benchmarking, Data Access, and Model Testing

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Modeling Multiscale-Multiphase-Multicomponent Subsurface Reactive Flows using Advanced Computing

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Mechanistic Studies of Protein Allostery at the Atomistic Scale

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The Aerosol Modeling Testbed

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Thermodynamic and Chemical Properties of La1-xSrxCoxFe1-xO3 from First-Principles Calculations: Implications for Use as SOFC Cathodes

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Benchmark Modeling of Aerosol-Cloud Interactions

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On Improving Current Colloid Filtration Theory Models

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Computational and Experimental Investigations on NMR Properties of Actinide Compounds

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Structural Criteria for the Design of Anion Receptors: The Interaction of Halides with Nitrogen-Containing Heterocyclic Compounds

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High Accuracy Modeling of Frequency Dependent Polarizabilities: Exploring the Cutting Edge Limits of NWChem

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Enabling PVFS2 Support over Quadrics for MPP2 Cluster

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Computer Simulation of Defects and Interfaces in Nuclear Fuel Materials

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Improving the Execution Time of NWLang

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A Grid-Based Exact or High-Accuracy Solution of The Electronic Schrudinger Equation

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Computer Simulation of Radiation Effects in Zircon

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Superparameterization: A New Paradigm for Climate Modeling

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Molecular Computational Studies In Environmental Chemistry, Geochemistry, and Biogeochemistry

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Direct Dynamics Simulations: From Molecules to Macromolecules and Condensed Phases

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Multifluid Flow and Multicomponent Reactive Transport in Heterogeneous Subsurface Systems

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Enabling Quantitatively Predictive Understanding of Multifluid Flow and Multicomponent Biogeochemical Reactive Transport in Complex, Subsurface Systems

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Image Processing, Modeling and Simulation of Complex Biological Systems Using Volume Filling and Boundary Fitted Mesh Based Methods

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Ab initio Calculations on a Proposed Gating Mechanism for the KcsA Channel

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Computational Study of Protein-Protein Interaction Dynamics

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Multi-Region Reactive Transport Due To Strong Anisotropy in Unsaturated Soils with Evolving Scales of Heterogeneity

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EGFR Dimerization

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A Combined Approach for Protein Structure Prediction and Protein-Protein Docking

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Multimedia for Investigator Training

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Aerosol Model Data Storage

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Investigating 3D Coupled Geophysical Processes of the Subsurface

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Oxidation and Radiation Damage in Nucleic acid Bases

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Electronic Structure Study of Platinum Clusters

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PNNL Next Generation Chemistry-Meteorology-Aerosol Model

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Accurate *ab initio* Determinations of Thermochemical Properties of Environmental and Biological Molecular Systems for Benchmarking with Experiments

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Studies of Long Time Scale Processes of Environmental Importance

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Structure and Recognition in Microbial Membranes Proteins, and DNA

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New Theoretical Developments and Computational Studies of Complex Processes in Environmental Chemistry, Waste Containment, and Biochemistry

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Reliable Relativistic Quantum Chemistry Calculations for Molecules with Heavy Elements

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Bioinformatics Tools to Define the Proteomic State of the Cell

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Immune Response to Environmental Factors: MD Simulations of Antibody Structure

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Simulation of the Conformation of Single Conjugated Polymer Molecules with Varying Conjugation Length in a Nematic Liquid Crystal

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Computing and Networking Services

The primary mission of Computing and Networking Services (CaNS) is to provide the infrastructure and computing services within the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) for an advanced computing environment that enables staff, visitors, and collaborators to effectively use computer and network resources for their scientific and business requirements. In supporting growing business and research needs of EMSL in the area of information sciences, CaNS secures global information access to our facilities by providing online remote access to both computing resources and scientific equipment. A large portion of the efforts undertaken by CaNS staff members involves providing customer support to EMSL researchers and offsite users. For offsite users, CaNS provides secure information access and dissemination among EMSL researchers and a global scientific user community.

Capabilities

One of the primary roles of CaNS is to provide computer support to all EMSL users and visitors, including scientists, technicians, and support staff. Computing support includes computer procurement assistance, setup, delivery, connection, and upgrade installation. System administration services include configuration management, software upgrades, security standards, account setup, and automated backup. CaNS is responsible for the design and implementation of EMSL's computing infrastructure, software, and Internet application development and support; conference room support; and management of computer maintenance contracts.

Expert Support and Services

- Security
- Desktop computing
- Scientific computing
- Instrument control systems
- Compute clusters and servers
- Infrastructure design and upgrade
- Web hosting and services
- Software application development and deployment
- Auditorium and conference room support

In Fiscal Year 2007, CaNS staff responded to approximately 5,440 formal requests for assistance (a decrease of 21% percent over the 6,789 requests made in 2006) and ~1,500 informal requests. Demonstrating consistency and responsiveness, CaNS staff members resolve 74.6 percent of support

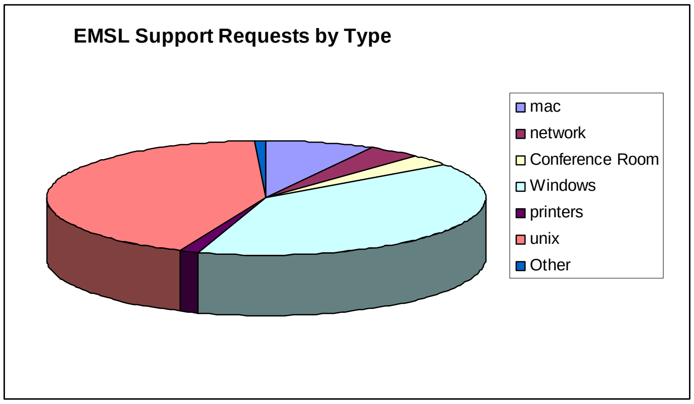

Figure 1. *EMSL Support Requests by Type*

requests within a day and 88.6 percent within a week, giving priority to visiting scientists. Figure 1 shows a breakdown of computer support requests in 2007.

EMSL has a history of growth in the number and variety of computer systems used by its staff members (Figure 2). In Fiscal Year 2007, 228 systems were added to the support scope, and 315 systems were released, yielding a net decrease of 87 systems (4.2%) and leaving a total of 1963 systems in use in EMSL.

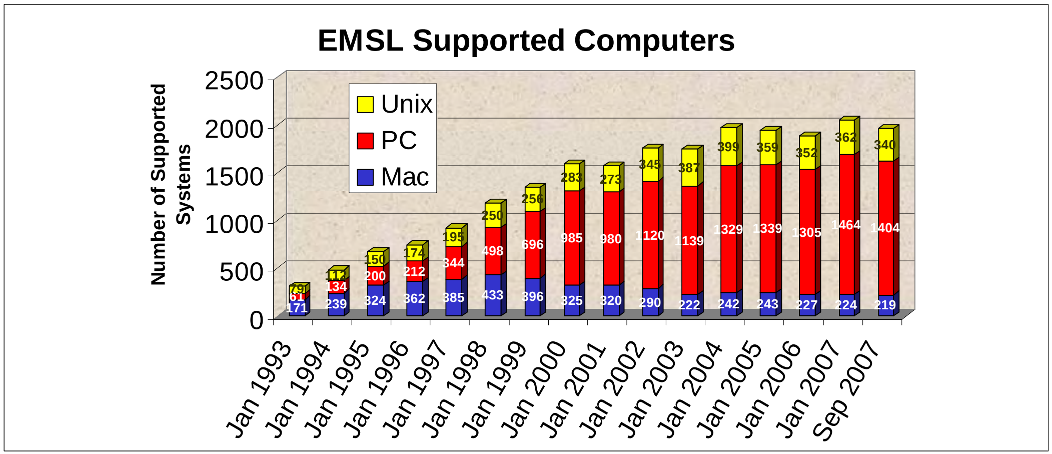

Figure 2. *EMSL computer use trends.*

In Fiscal Year 2007, CaNS added 172 new scientific users, increasing its support scope to 1050 active users. Of this total number of users, 490 use EMSL capabilities from offsite.

Support Queues. CaNS uses a web-based software-support request application (Footprints) to store and reply to submitted requests, and to record all dialogue surrounding problems. Users benefit by receiving a more thorough response, faster service, and an improved tracking system to ensure their problems are solved expeditiously. CaNS helps staff members benefit from the ability to better organize their work and identify chronic problems. CaNS also provides its support-request system to other projects in EMSL, such as NWChem and Ecce developers.

Data from Fiscal Year 2007 show that the 32 help queues were staffed by 146 administrators and experts, who together handled 11,936 support requests. Figure 3 shows historical use of the primary EMSL support queue, support@emsl.pnl.gov.

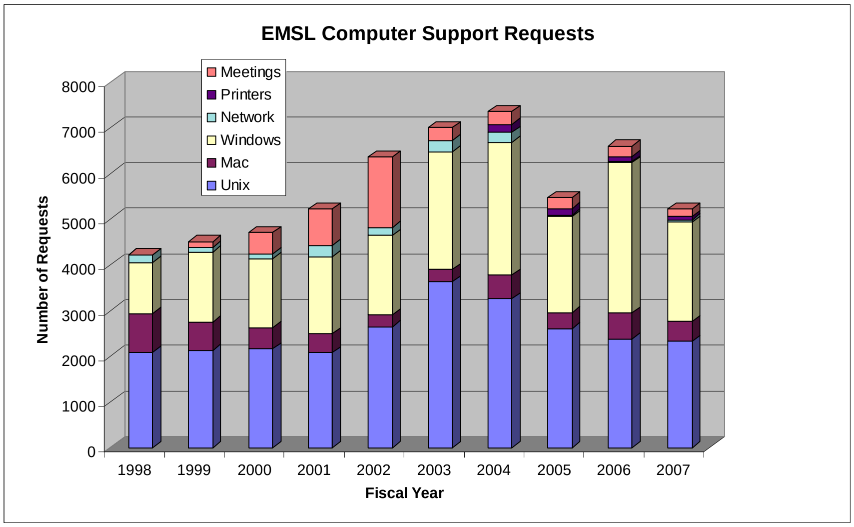

***Figure 3**. Computer support request history.*

CaNS has implemented an automatic support request satisfaction survey. Approximately one third of completed requests generate a survey query to the item's requestor. The requestor completes a simple survey rating our response and performance. The results are automatically recorded in a database and reviewed to identify areas for improvement. In Fiscal Year 2007, 257 customers replied. Average satisfaction with the service performed was 4.89 out of 5.0; average satisfaction with our response time was 4.89 out of 5.0. Three responses reported unsatisfactory service or response. These have been followed up on and corrective actions taken where necessary.

Security

A major CaNS focus involves infrastructure and application upgrades designed to increase the security of EMSL's computing resources while continuing to provide open access for visitors and collaborators. This is an increasingly difficult task as new and more sophisticated security threats arise. Major project areas focused on the formation of the CaNS Cyber Security team. The focus of this team is to unify the efforts of the CaNS and Molecular Science Computing Facility (MSCF) cyber security teams, reduce redundancy, increase collaboration, and build greater trust and peer interaction between the projects. This team spans both server and client along with UNIX, Linux, PC and Macintosh platforms. Some of the security tasks that have come out of the formation of this team include development of a management network in the form of the Secure Collaborative Zone (SCZ), CaNS brown bags, expanded scanning for vulnerabilities, unified UNIX sign-on, and PointSec deployment.

SCZ. The SCZ is an internet-accessible network for the purpose of allowing external collaborators access and storage of raw data files for experiments and analysis via web applications.

Center for Internet Security (CIS) Benchmarks. Expansion of the CIS benchmarks was carried out for EMSL server infrastructure. CIS benchmarks enumerate security configuration settings and actions that "harden" systems. They are unique, not because the settings and actions are unknown to any security specialist, but because consensus among hundreds of security professionals worldwide has defined these particular configurations. See http://www.cisecurity.org/ for further detail. When vulnerabilities are detected from the scans, corrections are made in a timely manner due to the use of the EMSL support queue, to track and triage service requests. This expanded scanning assisted in EMSL's "outstanding" rating from the DOE Site Assist Visit auditors on network and system security.

Unified UNIX Sign-On. In Fiscal Year 2006, work began to create a unified UNIX sign-on, providing users of Pacific Northwest National Laboratory (PNNL) resources the need to remember just a single user ID and password pair. Integrating UNIX authentications with PNNL Active Directory, thereby reducing UNIX password maintenance effort and auditing to that of the central AD service the lab already uses for Microsoft Windows based systems. This activity was completed in Fiscal Year 2007 and has been in production since mid-year.

Tracking of Security Bulletins. To better reduce duplication of effort, a CaNS Security Bulletin queue was established. This support queue is shared by all CaNS security task leads. Currently, the MSCF security task lead is responsible for triaging all incoming vendor and government (i.e., CIAC) cyber security bulletins and then determining to which platforms the notice applies, who is responsible for responding to the notice, and what action is needed. Previously, each security function within EMSL managed security bulletins autonomously. This centralized system greatly reduces and concentrates effort.

Oracle Upgrade. EMSL-managed UNIX systems were patched for Oracle vulnerabilities. A primary application server was patched along with two other managed PNNL infrastructure systems.

PointSec Deployment. CaNS Linux staff were instrumental in developing a Linux standard configuration. PointSec combines a required log in along with strong encryption (AES) to create an advanced security solution. When the user logs in, the laptop is unlocked and the single log-in can also unlock the other tasks (e.g., operating systems, networks, PKI, or digital signing). PointSec:

- allows only authorized users to access information stored on mobile computing devices
- enforces automatic mobile security practices (i.e., transparent encryption)
- allows mobility without compromising security
- minimizes financial losses and mitigates legal and regulatory risks associated with exposing sensitive information.

CaNS Brown Bags. In Fiscal Year 2006, "CaNS Presents" was established as a monthly mechanism to share technical capabilities with EMSL users. The primary presenters are CaNS staff, though the presenters have come from across PNNL in an effort to exchange ideas, raise awareness and create a more secure computing infrastructure. Twelve presentations were given during Fiscal Year 2007 on topics ranging from configuring system administration tools such as PointSec to safe use of wireless. All presentations were very well received, often standing room only. A complete listing can be found at http://emslweb.emsl.pnl.gov/ops/comphelp/web/html/presentations.html.

Desktop Computing

Windows/Macintosh Desktop Support. The EMSL Office Computer Support team provided primary computer support services to more than 1400 Windows and 210 Macintosh computer systems. While the majority of these systems reside on user desktops, some systems are connected to specialized electronic instruments and devices that support the EMSL research mission. Most Windows systems are primarily Windows XP with the Office 2003 suite. This configuration provides EMSL users with increased reliability and capabilities, such as the ability to connect remotely to a desktop computer located in EMSL. We still have legacy Windows systems such as Windows 95, 98, 2000, and NT 4.0, along with Windows XP, that are used as instrument controllers and data collectors. Windows XP systems are running Service Pack 2 with about 100 patches and updates to implement needed security enhancements. Macintosh systems in EMSL are primarily G3, G4, G5 and Intel models running OS X 10.4.114 and the Office 2004 suite.

Along with numerous support requests from PC and Macintosh users for Application troubleshooting, peripheral device setups, personal digital assistant support, wireless configurations, remote access, and domain account administration, the team responded to increased requests Pointsec full hard drive encryption for laptops, and the upgrade or removal of Windows 2000 systems. This year the EMSL Enclave was removed and systems were reconfigured accordingly.

Unix Desktop Support. Linux continues to grow in popularity and is now the dominant Unix desktop operating system, increasing from a 47 percent share in 2005, to a 53 percent share in 2006, to a 57 percent share in 2007 (Figure 4). We anticipate that Linux will continue to dominate the Unix desktop environment in the future.

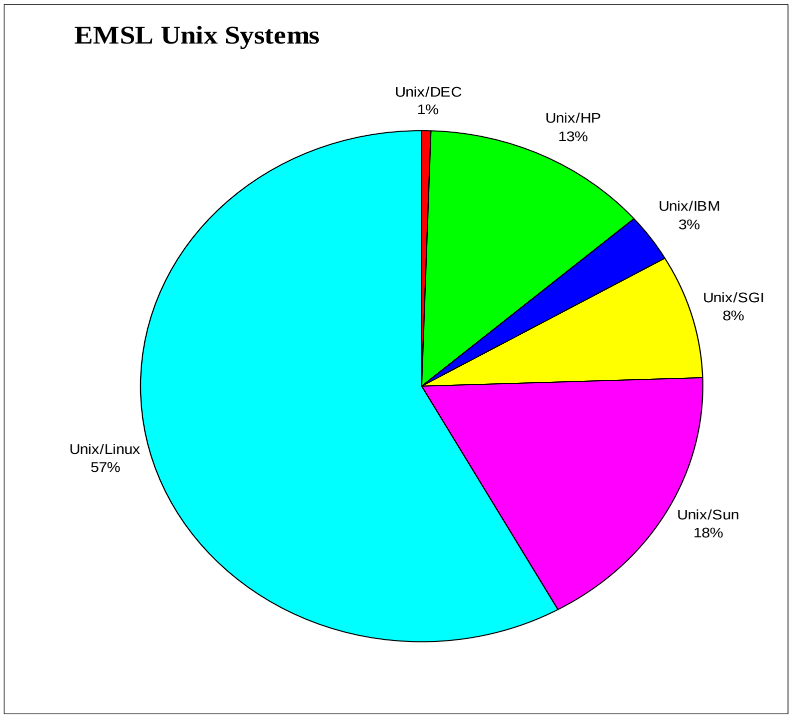

***Figure 4**. Distribution of Unix operating systems.*

With the increase in the use of Linux, an effort was made to standardize a Linux version, and 400 licenses were purchased for Red Hat Enterprise Linux (RHEL). CaNS played a major role in the testing and deployment of RHEL Linux, with team members maintaining the central Linux installation server. This new server allows EMSL staff members to easily install Linux and subscribe their system to an update service that automatically updates their computer when new operating system patches are released. The RHEL update service is analogous to the Microsoft Windows Update service.

Scientific Computing

Windows Scientific Computing Support. CaNS supports computers used to control scientific instruments during experiments or to collect data from experiments. A variety of Windows, Macintosh, and other operating systems are installed on these computers. The estimated distribution is detailed in Figure 5.

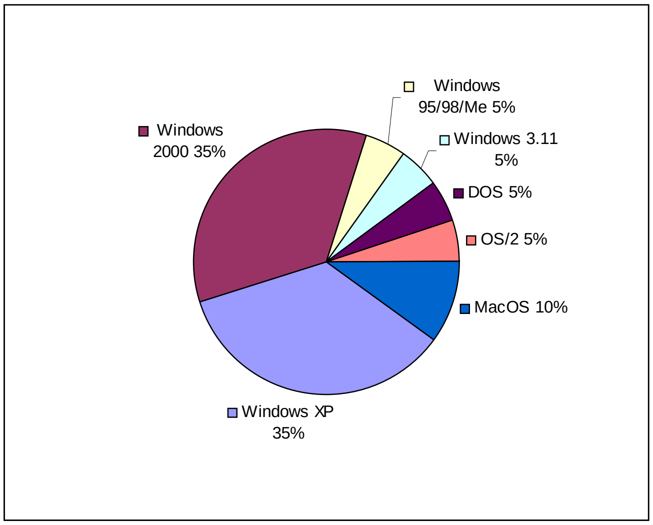

***Figure 5**. Distribution of Windows/Macintosh operating systems installed on computers used to control research instruments or collect data (excluding office systems).*

Bionet is the CaNS-created private instrumentation network that provides computer network connectivity between laboratories and storage resources. This network is isolated from the PNNL network connectivity that is available in every office and laboratory, and it allows instrument control and data acquisition equipment to be connected to a network and available from specific gateways while protecting the equipment from all of the systems on the PNNL network. The number of machines on this network now totals 116. There are additional instruments and controllers that do not have entries in DNS.

Cluster Support. During Fiscal Year 2007, four clusters were added to the set of CaNS-managed systems.

- **Texas** is a 24-node cluster used for NWChem development. This cluster has a total of 96 CPUs and uses an Infiniband network for high-speed, low-latency communications.

- **Mitcluster** was built as a capability replacement for PNNL researcher and EMSL scientific user Michel Dupuis's aging 64-CPU IBM P4 server. The new cluster provides much more processing power at a reduced annual cost to his group. This was the first cluster to use the Qlogic brand of Infiniband network cards.

- **Vancouver** was another capability replacement cluster consisting of 24 nodes (dual CPU, quad core) for a total 192 CPUs. The cluster uses Infiniband as a high-speed network and employs a 3-node Lustre file system running over the Infiniband fabric as a global scratch area.

- **Gnode1** is an 18-node cluster representing our first resource available for use outside the firewall and is intended to display high-performance computing capabilities developed at PNNL, including the application ScalaBLAST.

At the end of 2007, CaNS managed 18 Linux clusters with approximately 1700 CPUs. All of the clusters were procured via the PNNL Managed Hardware Program, where CaNS staff work with the vendor to ensure availability of appropriate components.

CaNS continues to be the primary resource in cluster-computing solutions at PNNL.

Infrastructure Design and Upgrades

File System Consolidation. With the dissolution of the EMSL Enclave, CaNS continues to work to consolidate services that were once split out. One of the largest consolidation undertakings was removing the Windows-based distributed file system service and using file services managed by PNNL. This task was accomplished in a staged rollout with no loss of scientific data.

Unix Infrastructure Backup System. The EMSL disk-based infrastructure backup system continues to perform well. Its disk arrays were upgraded in capacity to 20 terabytes, and it provides for recovery of infrastructure and shared file system files for a 1-year window.

Windows Server Backup Services. The backup system used by the Windows Server team, Symantec Backup Exec, has become the model for other backup services being used at PNNL. Additionally, the Windows Server team continues to successfully back up all infrastructure and project servers to a single backup server. The system has been successfully used to restore data and, in one case, an entire server system, saving countless hours and data.

Unix/Linux Backup Services. The desktop Unix/Linux team replaced the PNNL standard subscription backup service for more than 200 CaNS-managed Unix/Linux systems with the implementation of the backup system built around the Amanda open-source backup software. The highly successful project has saved EMSL-supported systems about $75K in Fiscal Year 2007 and is expected to save more in upcoming years.

Remote Installation Services (RIS). The RIS project continues to grow, with additional installation services continuing to be offered. The system can be used to configure new Windows or Linux installations all the way down to wiping a machine to be excessed.

Thin Client Project. This project continues to grow, with several of the clients being deployed to laboratory spaces where the footprint of the client was a bonus for the users. Additional installations are planned, and the Windows Server team has been asked to participate and bring experience to the PNNL Thin Client Project.

Distributed File Services. The CaNS strategy for high availability in its distributed file services (Andrew File System or AFS) configuration paid off several times in Fiscal Year 2007, as hardware component failures were repaired without disruption of service to users. Besides high availability, the EMSL distributed file system provides uniform access for users to their personal and project areas from any Windows, Macintosh, or Unix system; enhanced and secure file-sharing capability; consistent file backups; access to shared software; access to website content; and consistent tools across platforms. Of the 3.5 terabytes of available space, 1.5 terabytes are in use, which leaves plenty of space for both transient files and long-term storage. Figure 6 shows the historical usage versus capacity.

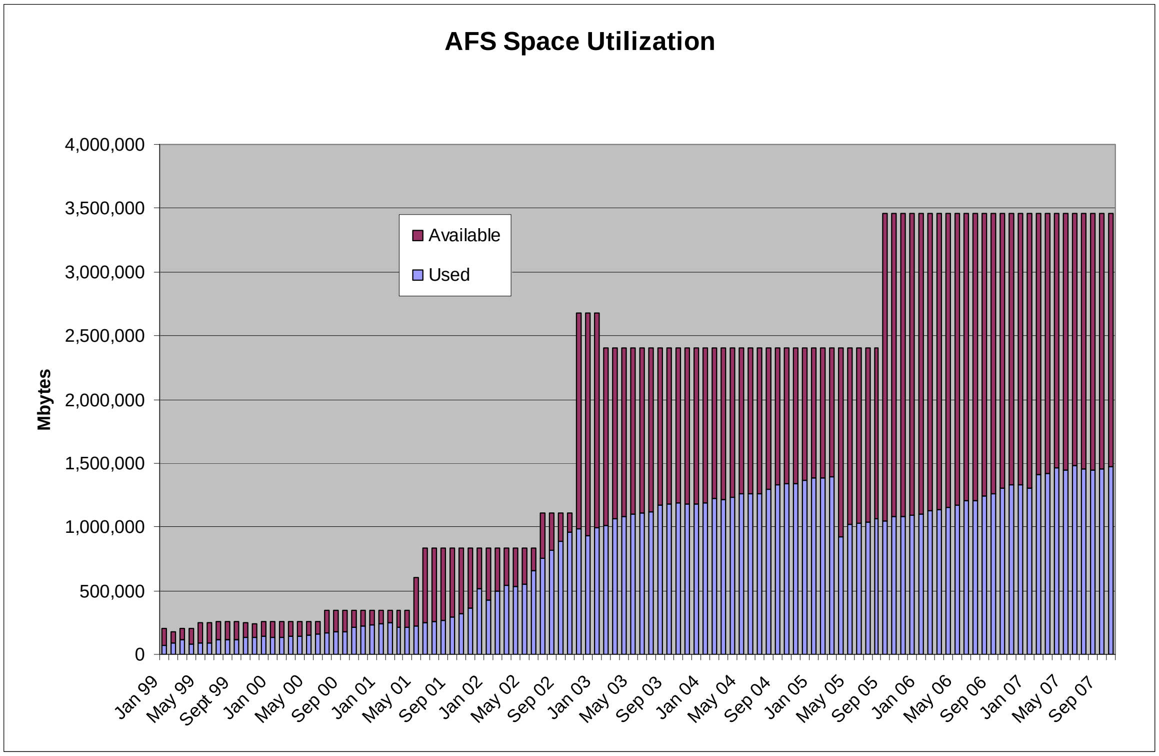

***Figure 6**. AFS capacity utilization.*

Web Hosting and Services

EMSL Web Services. Increased security concerns required EMSL to split its web server and move the server with external access to a more secure configuration. To accomplish this upgrade, the layout of the server configurations was redesigned, and the redesigned layout was implemented. A new server was purchased and deployed to house the external server, and the internal web server was moved to its own system. The external server was put behind proxy servers in 2005 to manage secure internal and external access. In Fiscal Year 2006, a second web server, linux based, was also deployed behind the proxy servers. In Fiscal 2007 both web servers continued to run as deployed.

The EMSL website continues to be moderately busy with about 1,156,000 visits in 2007, up from 1,109,000 visits in 2006. The website absorbed well over 10 million hits during the year. Figure 7 shows the history of user visits.

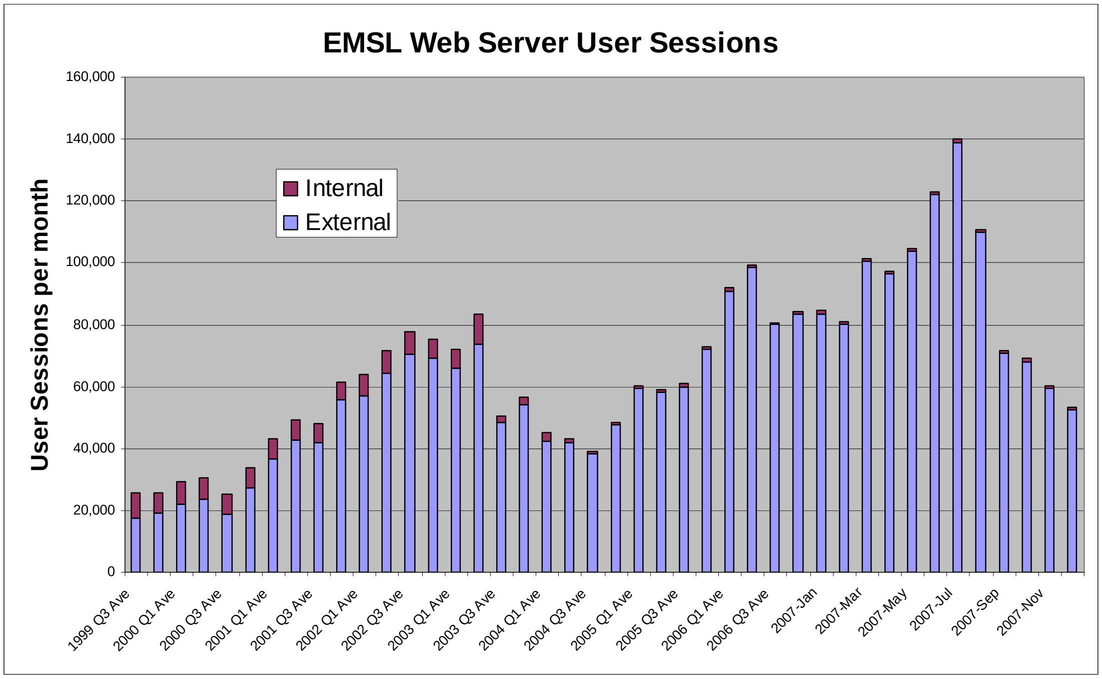

***Figure 7**. History of user visits.*

Software Application Development and Deployment

Unix Software Repositories. Software repositories provide shared access to frequently used software including freeware and floating license managers for commercial scientific applications. Applications in the repository include computer languages and interpreters; editors and debuggers; configuration management tools; documentation tools and pre-viewers; communication and collaborative tools; visualization, plotting, and graphing tools; numerical tools and libraries; data acquisition tools; and data management, structure, and format conversion. More than 150 applications available via this repository have been built and compiled to operate over the various operating systems that CaNS supports. The repository is made available via the AFS distributed file system and provides the benefit of consistent applications that users do not have to build themselves.

Auditorium and Conference Room Support

CaNS supported approximately 450 symposia, conferences, and meetings throughout the year. CaNS also worked in conjunction with Streaming Video Services to provide internet streaming for several meetings through the year, the "Director Lecture Series Seminars" being one example. These seminars put on by the PNNL Director's Office host both PNNL and some external lecturers. The recorded meeting is hosted on the Director's website for on-demand viewing.

CaNS staff are also working to upgrade equipment in the Battelle Auditorium. A new projector was installed, along with computers, a remote monitor to the podium, and some audio equipment. This will aid in video taping and live streaming from the Battelle Auditorium.

CaNS supported the following major events in Fiscal Year 2007:

- **October** – Regional Visualization and Analytics Center Consortium, National Visualization and Analytics Center, Radiation Portal Monitor Project (RPMP) all-hands meeting, Pacific Supply and Safety Vendor Show, Administrative Development Forum, Computational and Information Sciences Directorate Innovation

- **November –** Department of Energy (DOE) Corporate Operating Experiences Program, Fundamental Sciences Directorate (FSD) "O" Vision, ASFME Seminar, Laboratory Advisory Council Committee, Director Lector Forum (Live Stream), Woman of Achievement brown bag

- **January –** NWChem, DOE Review of PNNL

- **February –** DOE Office of Basic Energy (BES) Sciences Review dry run (videotape), Administrative Development Forum

- **March –** Administrative Development Forum, BES Review, Battelle Columbus Operations visit, RPMP training, National Center for Research Resources Advisory Committee, private sector open house, vendor showcase

- **April –** Woman of Achievement, Chinese delegation visit, Energy Conservation Initiative midyear review, Lehman Review, B2B Vendor Show, Jean Futrell recognition award, Fitzner-Eberhardt Award

- **May –** Independent Oversight Forum, Laboratory-Directed Research and Development Program, Office Professional Conference, MT Thomas Award for Outstanding Post-Doctoral Achievement

- **June –** FSD Review, Management Skills Development Program graduation, Science and Engineers Development Program graduation, Energy Science and Technology Directorate Peer Review, Managed Hardware Program Vendor Show, B2B Vendor Show, Executive Council Red Team Review

- **July –** Science Alive Workshop, Lab Fellows Seminar, Republic of Georgia Institute of Physics visit, Information Sciences and Engineering all-hands staff meeting, Catalysis midyear review, Senate Meeting, Communications and External Relations all-staff meeting, Tokyo Institute of Technology Visit, Lab Fellow annual review, Biomolecular Systems Initiative Review

- **August –** Radiation Detection Material Discovery Initiative Review, DOE Advanced Scientific Computing Research Visit, *Shewanella* Federation Project Meeting, Environmental Biomarkers Initiative Annual Review, PNNL MTLS Initiative External Advisory Review, First LEGO League Kickoff, Homeland Security Research Center visit, Commercial Partnership Meeting

- **September –** Director's Lecture Series (live stream) Woman of Achievement Award Seminar (live stream), Pacific Northwest Microscopy Society, Lab Fellow and Science and Engineering Award Event, EMSL 10-Year Anniversary celebration.

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Instrument Development Laboratory

The Instrument Development Laboratory (IDL) designs, builds, and deploys advanced state-of-the-art instrument systems and custom application software in support of ongoing experimental research efforts in the W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL). As depicted in Figure 1, IDL staff members support EMSL researchers and users by providing a wide variety of design and fabrication services for hardware and software, custom engineered solutions to research problems, and experience in the interface and control of commercial instrumentation. IDL staff members are especially skilled in the rapid integration of commercial and custom hardware/software packages to suit the exact specifications of specific research projects.

***Figure 1**. IDL and its staff members provide a wide variety of technical support to EMSL staff and users.*

Capabilities

Some of the IDL's most recognizable expertise and capabilities fall into the following areas:

- **Engineering**
    - Design from circuits to systems
    - Custom electronics and instrumentation
    - Embedded systems
    - Robotics
- **Software Development**
    - Image processing and pattern analysis
    - Laboratory automation
    - Remote operation
    - Data acquisition
    - Large-scale data management

- **Fabrication**
    - Circuit boards
    - Component integration
    - Custom enclosures

The IDL staffs a fully equipped electronics and fabrication shop for EMSL researchers and facility users. IDL customers will find a fully stocked parts supply, electronic components and small hardware, test and measurement equipment available for checkout, and ready assistance during business hours. For immediate hardware assistance, customers may access the IDL electronics laboratory and receive assistance from any IDL staff member. For work that is limited in scope and not time-consuming, there usually is no charge to EMSL staff for services. For larger projects, staff may wish to schedule time with an IDL staff member, who will diligently assist the customer in defining the work to be done and begin the process of designing solutions.

Custom Software Design, Development, and Support are critical services offered to IDL customers. IDL staff members specialize in several key capabilities related to research: data acquisition, instrument control, laboratory automation, systems integration, data analysis and visualization, data management and archiving, and handheld and embedded systems. Using a modular code design model as their basis, IDL software developers can efficiently develop software in a number of languages, tools, and scripts (e.g., Visual Basic .NET, C# .NET, Java, C, C++, .National Instrument's Labview, and Microsoft SQL Server). In addition, software developers are skilled in a number of instrument control strategies, including General Purpose Interface Bus, serial (RS-232), infrared, Transmission Control Protocol/Internet Protocol, Analog and Digital I/O, and high-speed event counting and timing.

The IDL Support Queue is accessible by customers via e-mail (idl-support@emsl.pnl.gov). The queue is monitored daily, and customers are encouraged to submit their requests for any type of service offered by the IDL.

The IDL Website at http://idl.emsl.pnl.gov provides a full description of IDL capabilities, access to the support queue, team highlights, recent projects, statement-of-work access, and a downloadable business plan.

IDL Technical Support is readily available to assist research by providing software modifications, troubleshooting, equipment fabrication, and research instrumentation support.

Fiscal Year 2007 Activities

IDL activities in Fiscal Year 2007 spanned across technologies and across EMSL. Significant hardware development activities included advancement of the second-generation Single Particle Mass Spectrometer (SPLAT II), an instrument which EMSL's User Advisory

Committee recommended as one of the five capabilities successfully developed and deployed to the user community, meeting a Department of Energy stretch goal. Further, IDL staff fabricated and/or upgraded additional automated liquid chromatography carts for mass spectrometry. IDL also fabricated and programmed a data station for the 6-T Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. Finally, IDL hardware development staff supported numerous user projects in various science themes through the development of a variety of smaller-scale custom control and data acquisition devices.

IDL software development staff supported a number of significant EMSL user projects. In proteomics, IDL developers continued to advance the state-of-the-art in informatics through the creation and upgrade of algorithms and tools to facilitate analysis. To further empower users, the IDL released software applications both internally and externally to the proteomics community. This included tool suites such as Decon2LS and MTDBCreator which were demonstrated to the user community at the U.S. Human Proteomics Organization meeting in March 2007. Additional tools such as Multialign were released to the EMSL users for analysis of data from metabolomics and proteomics projects. Also, a novel, formal statistical framework was developed to characterize results generated by the AMT tag pipeline in use at EMSL and is in the process of being finalized in 2008. A novel method of amino acid sequence assignment to tandem mass spectra through *de novo* sequence tag measurements was implemented as the USTags program, providing significantly reduced risk of false assignments of peptide sequences in comparison with industry standard algorithms such as SEQUEST, X!Tandem, or MASCOT. In addition, members of IDL created the first generation of tools to analyze data generated by the ion mobility mass spectrometer system being developed here at PNNL. This included both extending current software (Decon2LS) and developing new methods and software for the analysis. IDL staff also upgraded the SEQUEST peptide identification system and began development of a data distribution portal to provide external collaborators access to proteomics data. Finally, IDL software development staff implemented an imaging application for visualizing protein abundances in tissue and organs utilizing data obtained from a mouse brain.

Maintenance of the electronics and fabrication laboratory remained an important ongoing effort for IDL staff. This includes managing parts inventories and the instrument checkout system, support of walk-in EMSL users, and general lab upkeep.

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Publications

Publications by EMSL staff members and from users where the publication resulted from research carried out at EMSL are listed below.

Abstracts

Dohnalkova A, R Mendoza, C Gassman, and CL Bilskis. 2007. "Creating 3D Reconstruction of Cyanobacterium Cyanothece Sp. by Alignment of Serial TEM Tomograms from Consecutive Plastic Sections." Abstract submitted to Microscopy & Microanalysis 2007 Meeting, Ft. Lauderdale, FL. PNNL-SA-53972. Published in *Creating 3D reconstruction of cyanobacterium Cyanothece sp. by alignment of serial TEM tomograms from consecutive plastic sections*, vol. 13, Supp 2, pp. 1338-1339. Microscopy and Microanalysis, Bethlehem, PA.

Kowalski K and M Valiev. 2006. "Multiscale Dynamical Framework for High-Level Calculations of Finite Temperature Ground and Excited State Properties." Abstract submitted to SciDAC (Scientific Discovery through Advanced Computing Program), Denver, CO. PNNL-SA-50026. Published in *Multiscale Dynamical Framework for High-Level Calculations of Finite Temperature Ground and Excited State Properties*, vol. 46, pp. 244-248. Journal of Physics: Conference Series, Richland.

Li XS, GE Fryxell, MH Engelhard, and CM Wang. 2007. "The Synthesis of Cadmium or Ag Doped Mesoporous TiO_2." Abstract submitted to American Chemical Society 234th National Meeting, Boston, MA. PNNL-SA-54719. Published in *Inorganic Chemistry Communications 10*, vol. 6, pp. 639-641. Elsevier Science BV, Amsterdam, Netherlands.

Pierce EM, DM Strachan, EA Rodriguez, and JC Marra. 2007. "Effect of SiO_2 (aq) activity on Lanthanide Borosilicate Glass Dissolution under Acidic Conditions." Abstract submitted to American Chemical Society Conference 233rd National Meeting, Chicago, IL. PNNL-SA-52869. Published in *Book of Abstracts of the 233rd American Chemical Society National Meeting.* American Chemical Society, Washington, DC.

Richards EL, AM Davis, and EM Pierce. 2007. "Evaluation of Solution Composition on Aluminoborosilicate Waste Glass Dissolution at 40°C." Abstract submitted to American Chemical Society Conference 233rd National Meeting, Chicago, IL. PNNL-SA-52763. Published in *Book of Abstracts of the 233rd American Chemical Society National Meeting.* American Chemical Society, Washington, DC.

Taylor RC, CS Oehmen, and R Aurora. 2007. "Correlations in Whole-Genome Time Course Data Using Network Inference." Abstract submitted to EMSL Membrane Biology Grand Challenge Meeting, St. Louis, MO. PNNL-SA-54730. Published in *Correlations in Whole-Genome Time Course Data Using Network Inference.* 9th Cyanobacterial Workshop, Wisconsin, WI.

Book Chapter

Chen G and Y Lin. 2006. "Microfabricated Devices for Sample Extraction, Concentrations, and Related Sample Processing Technologies." Chapter 8 in *Bio-MEMS: Technologies and Applications*, ed. W Wang and SA Soper, pp. 213-236. CRC Press, Boca Raton, FL.

Jiang M and Y Lin. 2006. "Carbon Nanotube Based Sensors." In *Encyclopedia of Sensors*, vol. 2, ed. C. A. Grimes, E. C. Dickey, and M. V. Pishko, pp. 25-51. American Scientific Publishers, Stevenson Ranch, CA.

Laskin J. 2006. "Energy and Entropy Effects in the Gas-Phase Dissociation of Peptides and Proteins." In *Principles of Mass Spectrometry Applied to Biomolecules: Wiley-Interscience Series on Mass Spectrometry*, ed. J. Laskin and C. Lifshitz, pp. 619-666. John Wiley & Sons, Hoboken, NJ.

Mattigod SV, DT Hobbs, KE Parker, DE McCready, and LQ Wang. 2006. "Effects of Sodium Hydroxide and Sodium Aluminate on the Precipitation of Aluminum Containing Species in Tank Wastes." Chapter 18 in *Nuclear Waste Management: Accomplishments of the Environmental Management Science Program, ACS Symposium Series*, vol. 943, ed. Paul W. Wang, Tiffany Zachry, pp. 319 - 335. American Chemical Society, Washington DC.

Wang J, G Liu, and Y Lin. 2007. "Nanotubes, Nanowires, and Nanocantilevers in Biosensor Development." Chapter 3 in *Nanomaterials for Biosensors, Nanotechnologies for Life Sciences*, vol. 8, ed. Challa S.S.R. Kumar, pp. 56-100. Wiley-VCH, Weinheim, Germany.

Yang X, XB Wang, Y FU, and LS Wang. 2006. "Probing The Electronic Structure of Fe-S Clusters: Ubiquitous Electron Transfer Centers in Metalloproteins Using Anion Photoelectron Spectroscopy in the Gas Phase." Chapter 2 in *Principles of Mass Spectrometry Applied to Biomolecules: Wiley-Interscience Series on Mass Spectrometry*, ed. J. Laskin and C. Lifshitz, pp. 63-118. John Wiley & Sons Inc., New York, NY.

Yantasee W, Y Lin, and GE Fryxell. 2007. "Electrochemical sensors based on nanomaterials for environmental monitoring ." Chapter 15 in *Environmental Applications of Nanomaterials*, pp. 401-438. World Scientific Publishing Co., Hackensack, NJ.

Zachara JM, JK Fredrickson, RK Kukkadapu, and YA Gorby. 2007. "Anaerobic Microbial-Mineral Processes with Fe(III) Oxides: Experimental Considerations and Approaches." Chapter 4 in *Methods for Investigating Microbial-Mineral Interactions*, vol. 14, pp. 117-165. The Clay Minerals Society, West Lafayette, IN.

Zheng F, RS Addleman, CL Aardahl, GE Fryxell, DR Brown, and TS Zemanian. 2007. "Amine Functionalized Nanoporous Materials for Carbon Dioxide Capture." In *Environmental Applications of Nanomaterials: Synthesis, Sorbents and Sensors*. Imperial College Press, London, UK.

Book/Conference Proceedings

Weber WJ, LR Corrales, R Devanathan, F Gao, and HL Heinisch. 2007. *Computer Simulation of Radiation Effects in Solids, Proceedings of the Eighth International Conference on Computer Simulations of Radiation Effects in Solids (COSIRES 2006) - Nuclear Instruments and Methods in Physics Research, Section B* Vol. 255, Issue 1 (2007) . Elsevier, Amsterdam, Netherlands.

Conference Papers

Antony J, J Nutting, DR Baer, and Y Qiang. 2006. "Nanoporous and Nanostructured Materials Made out of Clusters for Environmental Applications." In *Nanoporous and Nanostructured Materials for Catalysis, Sensor, and Gas Separation Applications. 2005 Spring Meeting Proceedings of the Materials Research Symposium*, vol. 876E, pp. R10.4.1-4.6. Materials Research Society, Warrendale, PA.

Bacon DH, MD White, N Gupta, JR Sminchak, and ME Kelley. 2006. "Assessment of CO_2 Injection Potential and Monitoring Well Location at the Mountaineer Power Plant Site." In *8th International Conference on Greenhouse Gas Control Technologies: GHGT-8, 19-22 June, 2006, Trondheim, Norway*, p. 6 pages. Elsevier Amsterdam, Amsterdam, Netherlands.

Boily J, J Szanyi, and AR Felmy. 2007. "Temperature-Programmed Desorption of Oxalate from the Goethite Surface." In *Geochimica et Cosmochimica Acta Abstracts of the 17th Annual V. M. Goldschmidt Conference*, vol. 71, no. 15, p. A105. Elsevier, Leads, United Kingdom.

Calligan LJ and EM Pierce. 2007. "Experimental Study of the Dissolution Rates of a Simulated Borosilicate Waste Glass as a Function of Ph and Temperature." In *Preprints of Extended Abstracts presented at the 234th ACS National Meeting, American Chemical Society, Division of Environmental Chemistry*, vol. 48, no. 1, ed. G. Coimbatore, pp. 18-27. American Chemical Society, Division of Environmental Chemistry, Washington, DC.

Dixon DA, Z Dohnalek, J Hu, Q Huo, E Iglesia, BD Kay, J Kwak, J Liu, CHF Peden, L Wang, Y Wang, JM White, and HJ Zhai. 2007. "Early Transition Metal Oxides as Catalysts: Crossing Scales from Clusters to Single Crystals to Functioning Materials." In *Proceedings of the 2007 DOE-BES Catalysis Program Meeting*. Department of Energy.

Farnan I, HM Cho, and WJ Weber. 2006. "Identifying and Quantifying Actinide Radiation Damage in $ZrSiO_4$ Minerals and Ceramics with Nuclear Magnetic Resonance." In *Proceedings of the Eighth Actinides Conference, Actinides 2005, 4-8 July 2005, University of Manchester, UK. Published in Recent Advances in Actinide Science*, ed. I May, R Alvarez, N Bryan, pp. 305-310. Royal Society of Chemistry, Cambridge, United Kingdom.

Heald SM, JM Zachara, B Jeon, JP McKinley, RK Kukkadapu, and DA Moore. 2007. "XAFS Study of the Chemical and Structural States of Technetium in Fe(III) Oxide Co-precipitates." In *X-RAY Absorption Fine Structure - XAFS13: 13th*

International Conference. AIP Conference Proceedings, vol. 882, pp. 173-175. American Institute of Physics, Melville, NY. doi:10.1063/1.2644465

Hu J, DN Rommereim, RA Wind, KR Minard, and JA Sears. 2006. "A Simple Approach for Obtaining High Resolution, High Sensitivity ^{1}H NMR Metabolite Spectra of Biofluids with Limited Mass Supply." In *Proceedings of the 2006 International Conference on Bioinformatics and Computational Biology (BIOCOMP '06)*, ed. HR Arabnia and H. Valafar, pp. 360-366. CSREA Press, Las Vegas, NV.

Kispert LD, A Focsan, TA Konovalova, J Lawrence, MK Bowman, DA Dixon, P Molnar, and J Deli. 2007. "Magnetic Resonance Studies of Proton Loss from Carotenoid Radical Cations." In *29th DOE Solar Photochemistry Research Conference, Airlie Conference Center, Airlie, Virginia.* Dept of Energy, Airlie.

Krstic P, SJ Stuart, and CO Reinhold. 2006. "Chemical Sputtering of Fusion Plasma-Facing Carbon Surfaces." In *23rd Summer School and International Symposium on the Physics of Ionized Gases*, vol. 876, pp. 201-208. American Institute of Physics, Melville, NY.

McCready DE, Y Liang, V Shutthanandan, CM Wang, and S Thevuthasan. 2006. "Thermal Lattice Expansion in Epitaxial $SrTiO_3$(100) on Si(100)." In *Advances in X-ray Analysis, Proceedings of the 55th Annual Denver X-ray Conference, August 7-11, Denver Marriott Tech Center Hotel, Denver, Colorado, U.S.A.*, vol. 49, pp. 175-179. JCPDS-International Centre for Diffraction Data, Newton Square, PA.

Meakin P, AM Tartakovsky, TD Scheibe, DM Tartakovsky, G Redden, PE Long, SC Brooks, and Z Xu. 2007. "Particle Methods for Simulation of Subsurface Multiphase Fluid Flow and Biogeological Processes." In *Journal of Physics: Conference Series*, vol. 78, p. paper no. 012047 (11 pages). IOP Publishing, Bristol, United Kingdom. doi:10.1088/1742-6596/78/1/012047

Morgan WF, and MB Sowa. 2007. "Towards Resolving Conflicting Reports of Radiation-Induced Genomic Instability in Populations Exposed to Ionizing Radiation: Implications for the Hibakusha." In *Radiation Risk Perspectives: Proceedings of the Second Nagasaki Symposium of International Consortium for Medical Care of Hibakusha and Radiation Life Science, Nagasaki, Japan, 26–27 July 2006. Published in International Congress Series*, vol. 1299, pp. 128-134. Elsevier B.V., Amsterdam, Netherlands. doi:doi:10.1016/j.ics.2006.10.003

Richards EL, AM Davis, and EM Pierce. 2007. "Evaluation of Solution Composition Aluminoborosilicate Waste Glass Dissolution at 40°C." In *Preprints of Extended Abstracts presented at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry, 2007*, vol. 47, no. 1, pp. 125-134. American Chemical Society, Division of Environmental Chemistry, Washington, DC.

Scheibe TD, AM Tartakovsky, DM Tartakovsky, GD Redden, and P Meakin. 2007. "Hybrid Numerical Methods for Multiscale Simulations of Subsurface Biogeochemical Processes." In *SciDAC 2007. Published in Journal of Physics: Conference Series*, vol. 78, p. 012063 (5 pages). Institute of Physics, Washington, DC. doi:10.1088/1742-6596/78/1/012063

Sharp JL, KK Anderson, DS Daly, DL Auberry, JJ Borkowski, and WR Cannon. 2007. "Inferring Protein Associations Using Protein Pulldown Assays." In *2006 Joint Statistical Meetings: Statistics for an Uncertain World: Meeting Global Challenges, August 6-10, Seattle, WA*, p. 5 pages. American Statistical Association, Alexandria, VA.

Sharpe SW, TJ Johnson, DM Sheen, and DA Atkinson. 2006. "Relative Infrared (IR) and Terahertz (THz) Signatures of Common Explosives." In *SPIE Proceedings*, vol. 6378, p. 63780A. SPIE Publishing, Bellingham, WA.

Trease LL, HE Trease, and J Fowler. 2007. "Quantitative 3-D Imaging, Segmentation and Feature Extraction of the Respiratory System in Small Mammals for Computational Biophysics Simulations." In *Eighth IASTED International Conference on Signal and Image Processing, SIP, Aug 14-16, 2006, Honolulu, HI, USA*, pp. 335-340. Acta Press, Anaheim, CA.

Journal Articles

Alexandrova AN, AI Boldyrev, H Zhai, and LS Wang. 2006. "All-Boron Aromatic Clusters as Potential New Inorganic Ligands and Building Blocks in Chemistry." *Coordination Chemistry Reviews* 250(21-22):2811-2866.

Alexeev Y, MW Schmidt, TL Windus, and MS Gordon. 2007. "A Parallel Distributed Data CPHF Algorithm for Analytic Hessians." *Journal of Computational Chemistry* 28(10):1685-1694. doi:10.1002/jcc.20633

Allen PJ, BR Johnson, RT Baran, NC Anheier, JR, SK Sundaram, MH Engelhard, and BT Broocks. 2006. "Surface Degradation of As_2S_3 Thin Films." *Physics and Chemistry of Glasses* 47(6):681-687.

Anderson GA, N Tolic, JE Bruce, and X Tang. 2007. "Informatics Strategies for Large-Scale Novel Cross-Linking Analysis." *Journal of Proteome Research* 6(9):3412-3421. doi:10.1021/pr070035z

Antony J, S Pendyala, DE McCready, MH Engelhard, D Meyer, A Sharma, and Y Qiang. 2006. "Ferromagnetism in Ti-Doped ZnO Nanoclusters above Room Temperature." *IEEE Transactions on Magnetics* 42(10):2697-2699. doi:10.1109/TMAG.2006.879723

Antony J, Y Qiang, F Muhammad, D Meyer, DE McCready, and MH Engelhard. 2007. "Ferromagnetic Semiconductor Nanoclusters: Co-doped Cu_2O." *Applied Physics Letters* 90(1):art. no. 013106 (3 pages). doi:10.1063/1.2429018

Archer PI, SA Santangelo, and DR Gamelin. 2007. "Direct Observation of sp-d Exchange Interactions in Colloidal Mn^{2+}- and Co^{2+}-Doped CdSe Quantum Dots." *Nano Letters* 7(4):1037-1043. doi:10.1021/nl0702362

Averkiev BB, AI Boldyrev, X Li, and LS Wang. 2007. "Probing the Structure and Bonding in Al_6N^- and Al_6N by Photoelectron Spectroscopy and Ab Initio Calculations." *Journal of Physical Chemistry A* 111(1):34-41. doi:10.1021/jp066747e

Baas T, CR Baskin, DL Diamond, A Garcia-Sastre, H Bielefeldt-Ohmann, TM Tumpey, MJ Thomas, VS Carter, TH Teal, N Van Hoven, S Proll, JM Jacobs, Z Caldwell, MA Gritsenko, R Hukkanen, DG Camp, II, RD Smith, and MG Katze. 2006. "Integrated Molecular Signature of Disease: Analysis of Influenza Virus-Infected Macaques through Functional Genomics and Proteomics." *Journal of Virology* 80(21):10813 (16 pages). doi:10.1128/JVI.00851-06

Bae I, Y Zhang, WJ Weber, M Higuchi, and L Giannuzzi. 2007. "Electron-Beam Induced Recrystallization in Amorphous Apatite." *Applied Physics Letters* 90(2):021912, 1-3. doi:10.1063/1.2430779

Baer DR. 2007. "Improving Surface Analysis Methods for Characterization of Advanced Materials by Development of Standards, Reference Data, and Interlaboratory Comparisons." *Surface and Interface Analysis* 39(4):283-293. doi:10.1002/sia.2508

Barlow SE. 2007. "The Mass Multiplet in Penning Trap Ion Cyclotron Resonance Mass Spectroscopy." *Journal of Applied Physics* 101(2):Art. No. 024919.

Barnard AS and LA Curtiss. 2007. "Modeling the Preferred Shape, Orientation and Aspect Ratio of Gold Nanorods." *Journal of Materials Chemistry* 17:3315-3323. doi:10.1039/b704798c

Bell RC, K Wu, MJ Iedema, and JP Cowin. 2007. "Hydronium Ion Motion in Nanometer 3-Methyl-pentane Films." *Journal of Chemical Physics* 127(2):Art. 024704. doi:10.1063/1.2748756

Belov ME, MA Buschbach, DC Prior, K Tang, and RD Smith. 2007. "Multiplexed Ion Mobility Spectrometry - Orthogonal Time-Of-Flight Mass Spectrometry ." *Analytical Chemistry* 79(6):2451-2462. doi:10.1021/ac0617316

Berryman OB, V Bryantsev, DP Stay, DW Johnson, and BP Hay. 2007. "Structural Criteria for the Design of Anion Receptors: The Interaction of Halides with Electron-Deficient Arenes." *Journal of the American Chemical Society* 129(1):48-58.

Bertino MF, Z Sun, R Zhang, and LS Wang. 2006. "Facile Syntheses of Monodisperse Ultra-Small Au Clusters." *Journal of Physical Chemistry B* 110(43):21416-21418. doi:10.1021/jp065227g

Biju VP, D Pan, YA Gorby, JK Fredrickson, JS Mclean, D Saffarini, and HP Lu. 2007. "Combined Spectroscopic and Topographic Characterization of Nanoscale Domains and Their Distributions of a Redox Protein on Bacterial Cell Surfaces." *Langmuir* 23(3):1333-1338. doi:10.1021/la061343z

Boggavarapu K, X Li, H Zhai, and LS Wang. 2006. "Gold as Hydrogen: Structural and Electronic Properties and Chemical Bonding in $Si_3Au3^{+/0/-}$ ·and Comparisons to $Si_3H3^{+/0/-}$·" *Journal of Chemical Physics* 125(13):133204.

Boily J. 2007. "Charge Localization in Cation-Sulfate Complexes: Implications for Thermodynamic Surface Complexation Models of the Mineral/Water Interface." *Journal of Physical Chemistry C* 111(3):1299-1306. doi:10.1021/jp0647784

Bondarchuk O, Y Kim, JM White, J Kim, BD Kay, and Z Dohnalek. 2007. "Surface Chemistry of 2-Propanol on TiO_2(110): Low and High Temperature Dehydration, Isotope Effects, and Influence of Local Surface Structure." *Journal of Physical Chemistry C* 111(29):1105-11067. doi:doi:10.1021/jp072298m

Borch T, Y Masue, RK Kukkadapu, and S Fendorf. 2007. "Phosphate Imposed Limitations on Biological Reduction and Alteration of Ferrihydrite Mineralization." *Environmental Science & Technology* 41(1):166-172.

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

Boynton PE, RM Bonicalzi, AM Kalet, AM Kleczewski, JK Lingwood, KJ Mckenney, MW Moore, JH Steffen, EC Berg, WD Cross, RD Newman, and RE Gephart. 2007. "Gravitation Physics at BGPL." *New Astronomy Reviews* 51(3-4):334-340. doi:10.1016/j.newar.2006.11.035

Brooks KP, J Hu, H Zhu, and R Kee. 2007. "Methanation of carbon dioxide by hydrogen reduction using the Sabatier process in microchannel reactors." *Chemical Engineering Science* 62(4):1161-1170. doi:10.1016/j.ces.2006.11.020

Buchko GW, H Robinson, S Ni, HB Pakrasi, and MA Kennedy. 2006. "Cloning, Expression, Crystallization and Preliminary Crystallographic Analysis of a Pentapeptide-Repeat Protein (Rfr23) from Bacterium *Cyanothece 511421*." *Acta Crystallographica. Section F* 62(12):1251-1254. doi:10.1107/S174430910604663X

Buchko GW, S Ni, H Robinson, EA Welsh, HB Pakrasi, and MA Kennedy. 2006. "Characterization of Two Potentially Universal Turn Motifs that Shape the Repeated Five-Residues Fold - Crystal Structure of a Lumenal Pentapeptide Repeat Protein from *Cyanothece 51142*." *Protein Science* 15(11):2579-2595.

Buchko GW, S Ni, NM Lourette, RC Reeves, and MA Kennedy. 2007. "NMR Resonance Assignments of the Human High Mobility Group Protein HMGA1." *Journal of Biomolecular NMR* 38(2):185. doi:10.1007/s10858-006-9116-8

Bulusu S, S Yoo, E Apra, SS Xantheas, and X Zeng. 2006. "Lowest-Energy Structures of Water Clusters $(H_2O)_{11}$ and $(H_2O)_{13}$." *Journal of Physical Chemistry A* 110(42):11781-11784.

Bulusu S, X Li, LS Wang, and X Zeng. 2007. "Structural Transitions from Pyramidal to Fused Planar to Tubular to Core/Shell Compact in Gold Clusters: Au_n^- (n=21-25)." *Journal of Physical Chemistry C* 111(11):4190-4198. doi:10.1021/jp068897v

Burt JB, N Ross, GV Gibbs, GR Rossman, and KM Rosso. 2007. "Potential Protonation Sites in the Al_2SiO_5 Polymorphs Based on Polarized FTIR Spectroscopy and Properties of the Electron Density Distribution." *Physics and Chemistry of Minerals* 34(5):295-306.

Bylaska EJ, M Valiev, JR Rustad, and JH Weare. 2007. "Structure and Dynamics of the Hydration Shells of the Al^{3+} Ion." *Journal of Chemical Physics* 126(10):Art.no.104505. doi:10.1063/1.2566868

Cader T, LJ Westra, HJ Mcallister, A Marquez, and KM Regimbal. 2007. "Performance of a Rack of Liquid-Cooled Servers." *ASHRAE Transactions* 113:101-114.

Cai M, SC Langford, JT Dickinson, G Xiong, TC Droubay, AG Joly, KM Beck, and WP Hess. 2007. "An In Situ Study of the Martensitic Transformation in Shape Memory Alloys Using Photoemission Electron Microscopy." *Journal of Nuclear Materials* 361(2-3):306-312. doi:10.1016/j.jnucmat.2006.12.008

Cai M, SC Langford, MJ Wu, WM Huang, G Xiong, TC Droubay, AG Joly, K Beck, WP Hess, and JT Dickinson. 2007. "Study of Martensitic Phase transformation in a NiTiCu Thin Film Shape Memory Alloy Using Photoelectron Emission Microscopy." *Advanced Functional Materials* 17(1):161-167. doi:10.1002/adfm.200600611

Cai Y, AN Zelenyuk, and DG Imre. 2006. "A High Resolution Study of the Effect of Morphology on the Mass Spectra of Single PSL Particles with Na-Containing Layers and Nodules." *Aerosol Science and Technology* 40(12):1111-1122. doi:10.1080/02786820601001677

Cannon WR, DJ Taasevigen, DJ Baxter, and J Laskin. 2007. "Evaluation of the Influence of Amino Acid Composition on the Propensity for Collision-Induced Dissociation of Model Peptides Using Molecular Dynamics Simulations." *Journal of the American Society for Mass Spectrometry* 18(9):1625-1637. doi:10.1016/j.jasms.2007.06.005

Cao C, DR Palo, and Y Wang. 2007. "Catalyst Screening and Kinetic Studies Using Microchannel Reactors." *Catalysis Today* 125:29-33.

Cao H, Y Xiong, T Wang, B Chen, TC Squier, and MU Mayer. 2007. "A Red Cy3-Based Biarsenical Fluorescent Probe Targeted to a Complementary Binding Peptide." *Journal of the American Chemical Society* 129:8672-73. doi:10.1021/ja070003c

Cavanaugh L, X Chen, B Richardson, D Ungar, I Pelczer, J Rizo, and FM Hughson. 2007. "Structural Analysis of Conserved Oligomeric Golgi Complex Subunit 2." *Journal of Biological Chemistry* 282(32):23418-23426. doi:10.1074/jbc.M703716200

Chambers SA, DA Schwartz, WK Liu, KR Kittilstved, and DR Gamelin. 2007. "Growth, Electronic and Magnetic Properties of Doped ZnO Epitaxial and Nanocrystalline Films." *Applied Physics A, Materials Science and Processing* 88(1):1-5. doi:10.1007/s00339-007-3948-2

Chambers SA, TC Droubay, CM Wang, KM Rosso, SM Heald, SA Schwartz, KR Kittilstved, and DR Gamelin. 2006. "Ferromagnetism in Oxide Semiconductors." *Materials Today* 9(11):28-35.

Chan EY, W Qian, DL Diamond, T Liu, MA Gritsenko, ME Monroe, DG Camp, II, RD Smith, and MG Katze. 2007. "Quantitative Analysis of Human Immunodeficiency Virus Type 1-Infected CD4(+) Cell Proteome: Dysregulated Cell Cycle Progression and Nuclear Transport Coincide with Robust Virus Production." *Journal of Virology* 81(14):7571-7583.

Chang C, V Shutthanandan, SC Singhal, and S Ramanathan. 2007. "In-Situ Ion Scattering and X-Ray Photoelectron Spectroscopy Studies of Stability and Nanoscale Oxidation of Single Crystal (100) Inas." *Applied Physics Letters* 90(20):203109-203112. doi:10.1063/1.2740200

Chang JH, ME Park, Y Shin, GJ Exarhos, KJ Kim, S Lee, and K Oh. 2007. "Functional Scaffolds of Bicontinuous, Thermoresponsive L3-phase Silica/Hydroxyapatite Nanocomposites." *Journal of Materials Chemistry* 17(3):238-242. doi:10.1039/b609409k

Chaparadza A, SB Rananavare, and V Shutthanandan. 2007. "Synthesis and Characterization of Lithium-Doped Tin Dioxide Nanocrystalline Powders." *Materials Chemistry and Physics* 102(2-3):176-180. doi:10.1016/j.matchemphys.2006.11.022

Chen C, BW Beck, K Krause, TE Weksberg, and B Pettitt. 2006. "Effects of Dimerization of Serratia Marcescens Endonuclease on Water Dynamics." *Biopolymers* 85(3):241-252. doi:10.1002/bip

Chen G, X Xu, Y Lin, and J Wang. 2007. "A Sol-Gel-Modified Poly(methyl methacrylate) Electrophoresis Microchip with a Hydrophilic Channel Wall." *Chemistry - a European Journal* 13(22):6461-6467. doi:10.1002/chem.200700242

Chen J, Y Lin, and G Chen. 2007. "Fabrication of Poly(Methyl Methacrylate) Microfluidic Chips by Redox-Initiated Polymerization." *Electrophoresis* 28(16):2897-2903.

Cheng C, JC Lehmann, JE Thies, SD Burton, and MH Engelhard. 2006. "Oxidation of Black Carbon by Biotic and Abiotic Processes." *Organic Geochemistry* 37(11):1477-1488. doi:10.1016/j.orggeochem.2006.06.022

Cheung I, P Nachimuthu, AG Joly, MH Engelhard, MK Bowman, and SA Chambers. 2007. "N Incorporation and Electronic Structure in N-doped TiO_2(110) Rutile." *Surface Science* 601(7):1754-1762. doi:10.1016/j.susc.2007.01.051

Choudhury N and B Pettitt. 2007. "The Dewetting Transition and The Hydrophobic Effect." *Journal of the American Chemical Society* 129(15):4847-4852. doi:10.1021/ja069242a

Cliff JB, PJ Bottomley, DJ Gaspar, and DD Myrold. 2006. "Nitrogen Mineralization and Assimilation at Millimeter Scales." *Soil Biology and Biochemistry* 39(3):823–826. doi:10.1016/j.soilbio.2006.10.005

Conrad BR, WG Cullen, DB Dougherty, IV Lyubinetsky, and ED Williams. 2007. "Spatial First-passage Statistics of Al/Si(111)-(sqrt[3] x sqrt[3]) Step Fluctuations." *Physical Review. E, Statistical Physics, Plasmas, Fluids, and Related Interdisciplinary Topics* 75(2 PT 1):443-448. doi:10.1103/PhysRevE.75.021603

Crocombette J, G Dumazer, NQ Hoang, F Gao, and WJ Weber. 2007. "Molecular Dynamics Modeling of the Thermal Conductivity of Irradiated SiC as a Function of Cascade Overlap." *Journal of Applied Physics* 101(2):023527. doi:10.1063/1.2431397

Cui L, L Wang, and LS Wang. 2007. "Evolution of the Electronic Properties of Sn-n Clusters (n=4-45) and the Semiconductor-to-Metal Transition." *Journal of Chemical Physics* 126(6):064505. doi:10.1063/1.2435347

Cui L, X Huang, L Wang, J Li, and LS Wang. 2007. "Endohedral Stannaspherenes M@Sn12-: A Rich Class of Stable Molecular Cage Clusters." *Angewandte Chemie International Edition* 46(5):742-745. doi:10.1002/anie.200603226

Cui L, Y Lin, D Sundholm, and LS Wang. 2007. "A Photoelectron Spectroscopic and Computational Study of Sodium Auride Clusters, NanAun-(n=1-3)." *Journal of Physical Chemistry A* 111(31):7555-7561.

Dagle RA, Y Wang, GG Xia, JJ Strohm, JD Holladay, and DR Palo. 2007. "Selective CO Methanation Catalysts for Fuel Processing Applications." *Applied Catalysis. A, General* 326(2):213-218.

Dantas G, AL Watters, B Lunde, Z Eletr, NG Isern, T Roseman, J Lipfert, S Doniach, M Tompa, B Kuhlman, BL Stoddard, G Varani, and D Baker. 2006. "Mis-translation of a Computationally Designed Protein Yields an Exceptionally Stable Homodimer: Implications for Protein Engineering and Evolution." *Journal of Molecular Biology* 362(5):1004-1024. doi:10.1016/j.jmb.2006.07.092

Dantas G, C Corrent, SL Reichow, JJ Havranek, Z Eletr, NG Isern, B Kuhlman, G Varani, E Merritt, and D Baker. 2007. "High-resolution Structural and Thermodynamic Analysis of Extreme Stabilization of Human Procarboxypeptidase by Computational Protein Design." *Journal of Molecular Biology* 366(4):1209-1221. doi:10.1016/j.jmb.2006.11.080

Del Negro AS, CJ Seliskar, WR Heineman, SE Hightower, SA Bryan, and BP Sullivan. 2006. "Highly Oxidizing Excited States of Re and Tc Complexes." *Journal of the American Chemical Society* 128(51):16494-16495. doi:10.1021/ja067114g

Deng Y, M Flury, JB Harsh, AR Felmy, and O Qafoku. 2006. "Cancrinite and Sodalite Formation in the Presence of Cesium, Potassium, Magnesium, Calcium and Strontium in Hanford Tank Waste Simulants." *Applied Geochemistry* 21(12):2049-2063.

Deskins NA, and M Dupuis. 2007. "Electron Transport via Polaron Hopping in Bulk TiO_2: a Density Functional Theory Characterization." *Physical Review. B, Condensed Matter and Materials Physics* 75(19):Art. No. 195212. doi:10.1103/PhysRevB.75.195212

Deskins NA, SN Kerisit, KM Rosso, and M Dupuis. 2007. "Molecular Dynamics Characterization of Rutile-Anatase Interfaces." *Journal of Physical Chemistry C* 111(26):9290-9298. doi:10.1021/jp0713211

Devanathan R, A Venkatnathan, and M Dupuis. 2007. "Atomistic Simulation of Nafion Membrane: I. Effect of Hydration on Membrane Nanostructure." *Journal of Physical Chemistry B* 111(28):8069-8079. doi:10.1021/jp0726992

Devanathan R and WJ Weber. 2007. "Radiation Effects in a Model Ceramic for Nuclear Waste Disposal." *JOM. The Journal of the Minerals, Metals and Materials Society* 59(4):32-35.

Devanathan R, F Gao, and WJ Weber. 2007. "Atomistic Modeling of Amorphous Silicon Carbide Using a Bond-Order Potential." *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 255(1):130-135. doi:10.1016/j.nimb.2006.11.045

Devanathan R, LR Corrales, WJ Weber, A Chartier, and C Meis. 2006. "Molecular Dynamics Simulation of Energetic Uranium Recoil Damage in Zircon." *Molecular Simulation* 32(12-13):1069-1077.

Devanathan R, P Durham, J Du, LR Corrales, and EM Bringa. 2007. "Molecular Dynamics Simulation of Amorphization in Forsterite by Cosmic Rays." *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 255(1):172-176. doi:10.1016/j.nimb.2006.11.021

Ding J, CM Sorensen, Q Zhang, H Jiang, N Jaitly, EA Livesay, Y Shen, RD Smith, and T Metz. 2007. "Capillary LC Coupled with High-Mass Measurement Accuracy Mass Spectrometry for Metabolic Profiling." *Analytical Chemistry* 79(16):6081-6093. doi:10.1021/ac070064t

Ding S, W Qian, and RD Smith. 2007. "Quantitative Proteomic Approaches for Studying Phosphotyrosine Signaling." *Expert Review of Proteomics* 4(1):13-23. doi:doi:10.1586/14789450.4.1.13

Droubay TC, KM Rosso, SM Heald, DE Mccready, CM Wang, and SA Chambers. 2007. "Structure, Magetism, and Conductivity in Eitaxial Ti-doped α-Fe_2O_3 Hematite: Experiment and Density Functional Theory Calculations." *Physical Review. B, Condensed Matter and Materials Physics* 75(10):, doi:10.1103/PhysRevB.75.104412

Du J, LR Corrales, K Tsemekhman, and EJ Bylaska. 2007. "Electron, Hole and Exciton Self-Trapping in Germanium Doped Silica Glass from DFT Calculations with Self-Interactions Correction." *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 255(1 (SP ISS)):188-194.

Du J, R Devanathan, LR Corrales, WJ Weber, and AN Cormack. 2006. "Short- and Medium-Range Structure of Amorphous Zircon from Molecular Dynamics Simulations." *Physical Review. B, Condensed Matter* 74(21):art. no.:214204, (14 pages). doi:10.1103/PhysRevB.74.214204

Elias DA, F Yang, HM Mottaz, AS Beliaev, and MS Lipton. 2007. "Enrichment of Functional Redox Reactive Proteins and Identification by Mass Spectrometry Results in Several Terminal Fe(III)-Reducing Candidate Proteins in *Shewanella oneidensis* MR-1." *Journal of Microbiological Methods* 68(2):367-375.

Exarhos GJ, CF Windisch, Jr, KF Ferris, and RR Owings. 2007. "Cation Defects and Conductivity in Transparent Oxides." *Applied Physics A, Materials Science and Processing* 89(1):9-18. doi:10.1007/s00339-007-4040-7

Fang J, Z Gu, D Gang, C Liu, ES Ilton, and B Deng. 2007. "Cr(VI) Removal from Aqueous Solution by Activated Carbon Coated with Quaternized Poly(4-vinylpyridine)." *Environmental Science and Technology* 41(13):4748-4753. doi:10.1021/es061969b

Fanourgakis GS, GK Schenter, and SS Xantheas. 2006. "A Quantitative Account of Quantum Effects in Liquid Water." *Journal of Chemical Physics* 125(14):Art. No. 141102.

Farber R. 2007. " Balancing Computation and Experiment." *Innovation: America's Journal of Technology Commercializatio* 5(2):24,25, 37.

Farber R. 2007. " The HPC Brick Wall." *Scientific Computing* 24(6):16.

Farber R. 2007. "Data Management, the Victorian Era Child of the 21st Century." *Scientific Computing* 24(4):12.

Farber R. 2007. "HPC Balance and Common Sense." *Scientific Computing* 24(3):12.

Farber R. 2007. "Keeping "Performance" in HPC." *Scientific Computing* 24(8):15.

Farber R. 2007. "The Cure for HPC Neurosis: Multiple, Virtual Personalities!" *Scientific Computing* 24(7):16.

Farber R. 2007. "Will Your Next Supercomputer Come from Costco?" *Scientific Computing* 24(5):13.

Farnan I, HM Cho, and WJ Weber. 2007. "Quantification of Actinide Alpha-Radiation Damage in Minerals and Ceramics." *Nature* 445:190-193. doi:10.1038/nature05425

Feaver AM, S Sepehri, PJ Shamberger, AC Stowe, T Autrey, and G Cao. 2007. "Coherent Carbon Cryogel-Ammonia Borane Nanocomposites for Improved Hydrogen Storage." *Journal of Physical Chemistry B* 111(26):7469-7472. doi:10.1021/jp072448t

Feindel KW, KJ Ooms, and RE Wasylishen. 2007. "A Solid-State 55Mn NMR Spectroscopy and DFT Investigation of Manganese Pentacarbonyl Compounds." *Physical Chemistry Chemical Physics. PCCP* 9:1226-1238. doi:10.1039/b616821c

Flaherty DW, Z Dohnalek, A Dohnalkova, BW Arey, DE McCready, N Ponnusany, C Mullins, and BD Kay. 2007. "Reactive Ballistic Deposition of Porous TiO_2 Films: Growth and Characterization." *Journal of Physical Chemistry C* 111(12):4765-4773. doi:10.1021/jp067641m

Forquer IP, R Covian, MK Bowman, B Trumpower, and DM Kramer. 2006. "Similar Transition States Mediate the Q-cycle and Superoxide Production by the Cytochrome bc1 Complex." *Journal of Biological Chemistry* 281(50):38459-38465. doi:10.1074/jbc.M605119200

Fryxell GE, SV Mattigod, Y Lin, H Wu, SK Fiskum, KE Parker, F Zheng, W Yantasee, TS Zemanian, RS Addleman, J Liu, J Xu, KM Kemner, S Kelly, and X Feng. 2007. "Design and Synthesis of Self-Assembled Monolayers on Mesoporous Supports (SAMMS): The Importance of Ligand Posture in Functional Nanomaterials." *Journal of Materials Chemistry* 17:2863-2874. doi:10.1039/b702422c

Fryxell GE. 2006. "The Synthesis of Functional Mesoporous Materials." *Inorganic Chemistry Communications* 9(11):1141-1150.

Fu Y, J Laskin, and LS Wang. 2007. "Electronic Structure and Fragmentation Properties of $[Fe_4S_4(SEt)_{4-X}(SSEt)_x]^{2-}$." *International Journal of Mass Spectrometry* 263(2-3):260-266.

Gao F, J Du, EJ Bylaska, M Posselt, and WJ Weber. 2007. "Ab Initio Atomic Simulations of Antisite Pair Recovery in Cubic Silicon Carbide." *Applied Physics Letters* 90(22):Art. No. 221915. doi:10.1063/1.2743751

Gao F, LW Campbell, R Devanathan, Y Xie, Y Zhang, AJ Peurrung, and WJ Weber. 2007. "Gamma-Ray Interaction in Ge: A Monte Carlo Simulation." *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 255(1):286-290. doi:10.1016/j.nimb.2006.11.031

Gao F, Y Zhang, R Devanathan, M Posselt, and WJ Weber. 2007. "Atomistic Simulations of Epitaxial Recrystallization in 4H-SiC along the [0001] Direction." *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 255(1):136-140. doi:10.1016/j.nimb.2006.11.016

Gibbs GV, D Jayatilaka, MA Spackman, DF Cox, and KM Rosso. 2006. "Si-O Bonded Interactions in Silicate Crystals and Molecules: A Comparison." *Journal of Physical Chemistry A* 110(46):12678 (6 pages).

Gibbs GV, DF Cox, KM Rosso, NL Ross, RT Downs, and MA Spackman. 2007. "Theoretical Electron Density Distributions for Fe- and Cu-Sulfide Earth Materials: A Connection between Bond Length, Bond Critical Point Properties, Local Energy Densities, and Bonded Interactions." *Journal of Physical Chemistry B* 111(8):1923-1931. doi:10.1021/jp065086i

Gibbs GV, MA Spackman, D Jayatilaka, KM Rosso, and DF Cox. 2006. "Bond Length and Local Energy Density Property Connections for Non-transition- Metal-Oxide-Bonded Interactions." *Journal of Physical Chemistry A* 110(44):12259-12266. doi:10.1021/jp062992m

Goering J, E Kadossov, U Burghaus, Z Yu, S Thevuthasan, and LV Saraf. 2007. "Adsorption of iso-/n-butane on an Anatase Thin Film: A Molecular Beam Scattering and TDS Study." *Catalysis Letters* 116(1-2):9-14. doi:10.1007/s10562-007-9121-x

Gorokhovsky V, C Bowman, PE Gannon, D VanVorous, AA Voevodin, A Rutkowski, C Muratore, RJ Smith, AN Kayani, DS Gelles, V Shutthanandan, and BG Trusov. 2006. "Tribological Performance of Hybrid Filtered Arc-Magnetron Coatings - Part I: Coating Deposition Process and Basic Coating Properties Characterization." *Surface & Coatings Technology* 201(6):3732-3747. doi:10.1016/j.surfcoat.2006.09.007

Greeley JP, and M Mavrikakis. 2007. "On the Role of Subsurface Oxygen and Ethylenedioxy in Ethylene Epoxidation on Silver." *Journal of Physical Chemistry C* 111(22):7992-7999. doi:10.1021/jp070490i

Groenewold GS, AK Gianotto, KC Cossel, MJ Van Stipdonk, J Oomens, N Polfer, D Moore, WA De Jong, and ME McIIwain. 2007. "Mid-Infrared Vibrational Spectra of Discrete Acetone-Ligated Cerium Hydroxide Cations." *Physical Chemistry Chemical Physics. PCCP* 9(5):596-606.

Gu W, T Frigato, T Straatsma, and VH Helms. 2007. "Dynamic Protonation Equilibrium of Solvated Acetic Acid." *Angewandte Chemie International Edition* 46(16):2939-2943.

Gu X, S Bulusu, X Li, X Zeng, J Li, XG Gong, and LS Wang. 2007. "Au_{34}^{-}: A Fluxional Core-Shell Cluster." *Journal of Physical Chemistry C* 111(23):8228-8232. doi:10.1021/jp071960b

Gupta N, S Tanner, N Jaitly, JN Adkins, MS Lipton, R Edwards, MF Romine, A Osterman, V Bafna, RD Smith, and PA Pevzner. 2007. "Whole proteome analysis of post-translational modifications: applications of mass-spectrometry for proteogenomic annotation." *Genome Research* 17(9):1362-1377. doi:0.1101/gr.6427907

Hadjar O, P Wang, JH Futrell, Y Dessiaterik, Z Zhu, JP Cowin, MJ Iedema, and J Laskin. 2007. "Design and Performance of a Novel Instrument for Soft-Landing of Biomolecular Ions on Surfaces." *Analytical Chemistry* 79(17):6566-6574. doi:10.1021/ac070600h

Hammond JR, M Valiev, WA De Jong, and K Kowalski. 2007. "Calculations of Molecular Properties in Hybrid Coupled-Cluster and Molecular Mechanics Approach." *Journal of Physical Chemistry A* 111(25):5492-5498. doi:10.1021/jp070553x

Haranczyk M, and MS Gutowski. 2007. "Differences in Electrostatic Potential Around DNA Fragments Containing Guanine and 8-oxo-Guanine." *Theoretical Chemistry Accounts* 117(2):291-296. doi:10.1007/s00214-006-0133-1
Haranczyk M, and MS Gutowski. 2007. "Quantum Mechanical Energy-based Screening of Combinatorially Generated Library of Tautomers. TauTGen: A Tautomer Generator Program." *Journal of Chemical Information and Modeling* 47(2):686-694. doi:10.1021/ci6002703

Haranczyk M, JH Miller, and MS Gutowski. 2007. "Differences in Electrostatic Potential Around DNA Fragments Containing Adenine and 8-oxo-Adenine. An Analysis Based on Regular Cylindrical Projection." *Journal of Molecular Graphics and Modelling* 26(1):282-289.

Hays J, KM Reddy, NY Graces, MH Engelhard, V Shutthanandan, M Luo, C Xu, NC Giles, CM Wang, S Thevuthasan, and A Punnoose. 2007. "Effect of Co Doping on the Structural, Optical and Magnetic Properties of ZnO Nanoparticles." *Journal of Physics. Condensed Matter* 19(26):Art. No. 266203. doi:10.1088/0953-8984/19/26/266203

Hegg DA, DS Covert, KK Crahan, H Jonsson, and Y Liu. 2006. "Measurements of Aerosol Size-Resolved Hygroscopicity at Sub and Supermicron Sizes." *Geophysical Research Letters* 33(21):L21808. doi:10.1029/2006GL026747

Herrera JE, J Kwak, J Hu, Y Wang, and CHF Peden. 2006. "Synthesis of Nanodispersed Oxides of Vanadium, Titanium, Molybdenum, and Tungsten on Mesoporous Silica using Atomic Layer Deposition." *Topics in Catalysis* 39(3-4):245-255. doi:10.1007/s11244-006-0063-0

Hixson KK, JN Adkins, SE Baker, RJ Moore, RD Smith, SL McCutchen-Maloney, and MS Lipton. 2006. "Biomarker Candidate Identification in Yersinia pestis Using Organism-Wide Semiquantitative Proteomics ." *Journal of Proteome Research* 5(11):3008-3017.

Holladay JD, KP Brooks, RS Wegeng, J Hu, J Sanders, and S Baird. 2007. "Microreactor Development for Martian In-Situ Propellant Production." *Catalysis Today* 120(1):35-44. doi:doi:10.1016/j.cattod.2006.07.019

Hopkins RJ, KM Lewis, Y Dessiaterik, Z Wang, A Tivanski, WP Arnott, A Laskin, and MK Gilles. 2007. "Correlations Between Optical, Chemical and Physical Properties of Biomass Burn Aerosols." *Geophysical Research Letters* 34(L18806):1-5.

Hu J, Y Wang, C Cao, DC Elliott, DJ Stevens, and JF White. 2007. "Conversion of Biomass-Derived Syngas to Alcohols and C2 Oxygenates Using Supported Rh Catalysts in a Microchannel Reactor." *Catalysis Today* 120(1):90-95. doi:10.1016/j.cattod.2006.07.006

Ibrahim YM, ME Belov, AV Tolmachev, DC Prior, and RD Smith. 2007. "Ion Funnel Trap Interface for Orthogonal Time-of-Flight Mass Spectrometry." *Analytical Chemistry* 79(20):7845-7852. doi:10.1021/ac071091m S0003-2700(07)01091-8

Istok JD, MM Park, AD Peacock, M Oostrom, and TW Wietsma. 2007. "An experimental investigation of nitrogen gas produced during denitrification." *Ground Water* 45(4):461-467.

Jaisi DP, H Dong, and C Liu. 2007. "Influence of Biogenic Fe(II) on the Extent of Microbial Reduction of Fe(III) in Clay Minerals Nontronite, Illite, and Chlorite." *Geochimica et Cosmochimica Acta* 71(5):1145-1158. doi:10.1016/j.gca.2006.11.027

Jaisi DP, H Dong, and C Liu. 2007. "Kinetic Analysis of Microbial Reduction of Fe(III) in Nontronite." *Environmental Science and Technology* 41(7):2437-2444. doi:10.1021/es0619399

Jaitly N, ME Monroe, VA Petyuk, TRW Clauss, JN Adkins, and RD Smith. 2006. "Robust Algorithm for Alignment of Liquid Chromatography-Mass Spectrometry Analyses in an Accurate Mass and Time Tag Data Analysis Pipeline." *Analytical Chemistry* 78(21):7397-7409.

Jastrow JD, JE Amonette, and VL Bailey. 2007. "Mechanisms controlling soil carbon turnover and their potential application for enhancing carbon sequestration ." *Climatic Change* 80(1-2):5-23.

Jiang W, I Bae, and WJ Weber. 2007. "Disordering and Dopant Behaviour in Au+ Ion-Irradiated AlN." *Journal of Physics. Condensed matter* 19(35):356207, 1-10. doi:10.1088/0953-8984/19/35/356207

Jiang W, P Nachimuthu, WJ Weber, and L Ginzbursky. 2007. "Variation in Lattice Parameters of 6H-SiC Irradiated to Extremely Low Doses." *Applied Physics Letters* 91(9):091918, 1-3. doi:10.1063/1.2778630

Jiang W, Y Zhang, MH Engelhard, WJ Weber, GJ Exarhos, J Lian, and RC Ewing. 2007. "Behavior of Si and C Atoms in Ion Amorphized SiC." *Journal of Applied Physics* 101(2):Art. No. 023524. doi:10.1063/1.2431941

Jiang W, Y Zhang, V Shutthanandan, S Thevuthasan, and WJ Weber. 2006. "Temperature response of 13C Atoms in Amorphized 6H-SiC." *Applied Physics Letters* 89(26):art. no.:261902, (3 pages). doi:10.1063/1.2422892

Johnson BR, NL Canfield, DN Tran, RA Dagle, XS Li, JD Holladay, and Y Wang. 2007. "Engineered SMR catalysts based on hydrothermally stable, porous, ceramic supports for microchannel reactors." *Catalysis Today* 120(1):54-62.

Johnson KS, B de Foy, BM Zuberi, L Molina, MJ Molina, Y Xie, A Laskin, and V Shutthanandan. 2006. "Aerosol Composition and Source Apportionment in the Mexico City Metropolitan Area with PIXE/PESA/STIM and Multivariate Analysis." *Atmospheric Chemistry and Physics* 6(12):4591-4600.

Joly AG, G Xiong, CM Wang, DE McCready, KM Beck, and WP Hess. 2007. "Synthesis and Photoexcited Charge Carrier Dynamics of beta-FeOOH Nanorods." *Applied Physics Letters* 90(10):Art. No. 103503.

Kang H, L Pasa-Tolic, and RD Smith. 2007. "Targeted Tandem Mass Spectrometry for High-Throughput Comparative Proteomics Employing NanoLC-FTICR MS with External Ion Dissociation." *Journal of the American Society for Mass Spectrometry* 18(7):1332-1343. doi:doi:10.1016/j.jasms.2007.04.011

Kariev AM, VS Znamenskiy, and ME Green. 2007. "Quantum Mechanical Calculations of Charge Effects on Gating the KcsA Channel." *Biochimica et Biophysica Acta--General Subjects* 1218-1229.

Kayani AN, RJ Smith, S Teintze, M Kopczyk, PE Gannon, M Deibert, V Gorokhovsky, and V Shutthanandan. 2006. "Oxidation studies of CrAlON nanolayered coatings on steel plates." *Surface & Coatings Technology* 201(3-4):1685-1694. doi:10.1016/j.surfcoat.2006.02.053

Kelly RT, JS Page, Q Luo, RJ Moore, DJ Orton, K Tang, and RD Smith. 2006. "Chemically Etched Open Tubular and Monolithic Emitters for Nanoelectrospray Ionization Mass Spectrometry." *Analytical Chemistry* 78(22):7796-7801.

Kerisit SN, KM Rosso, M Dupuis, and M Valiev. 2007. "Molecular Computational Investigation of Electron Transfer Kinetics across Cytochrome-Iron Oxide Interfaces." *Journal of Physical Chemistry C* 111(30):11363-11375.

Kim D, J Kwak, J Szanyi, SD Burton, and CHF Peden. 2007. "Water-induced Bulk Ba(NO3)2 Formation From NO2 Exposed Thermally Aged BaO/Al2O3." *Applied Catalysis. B, Environmental* 72(3-4):233-239.

Kim D, Y Chin, GG Muntean, A Yezerets, N Currier, WS Epling, H Chen, H. Hess, and CHF Peden. 2007. "Design of a Reaction Protocol for Decoupling Sulfur Removal and Thermal Aging Effects during Desulfation of Pt-BaO/Al_2O_3 Lean NOx Trap Catalysts." *Industrial and Engineering Chemistry Research* 46(9):2735-2740. doi:10.1021/ie061542d

Kim J, O Bondarchuk, BD Kay, JM White, and Z Dohnalek. 2007. "Preparation and Characterization of Monodispersed WO3 Nanoclusters on TiO2(110)." *Catalysis Today* 120(2):186-195. doi:10.1016/j.cattod.2006.07.050

Kim M, J Kim, J Lee, H Jia, H Na, J Youn, J Kwak, A Dohnalkova, JW Grate, P Wang, T Hyeon, H Park, and H Chang. 2007. "Crosslinked Enzyme Aggregates in Hierarchically-Ordered Mesoporous Silica: A Simple and Effective Method for Enzyme Stabilization." *Biotechnology and Bioenegineering* 96(2):210-218. doi:10.1002/bit.21107

Kimmel GA, NG Petrik, Z Dohnalek, and BD Kay. 2007. "Crystalline Ice Growth on Pt(111) and Pd(111): Nonwetting Growth on a Hydrophobic Water Monolayer." *Journal of Chemical Physics* 126(11):Art. No. 114702.

Knudsen J, AU Nilekar, RT Vang, J Schnadt, EL Kunkes, JA Dumesic, M Mavrikakis, and F Besenbacher. 2007. "A Cu/Pt Near-Surface Alloy for Water-Gas Shift Catalysis." *Journal of the American Chemical Society* 129(20):6485-6490. doi:10.1021/ja0700855

Kokubo H, and B Pettitt. 2007. "Preferential Solvation in Urea Solutions at Different Concentrations: Properties from Simulation Studies." *Journal of the American Chemical Society* 111(19):5233-5242. doi:10.1021/jp067659x

Komlos J, Jr., RK Kukkadapu, JM Zachara, and PR Jaffe. 2007. "Biostimulation of Iron Reduction and Subsequent Oxidation of Sediment Containing Fe-silicates and Fe-oxides: Effect of Redox Cycling on Fe(III) Bioreduction." *Water Research* 41(13):2996-3004. doi:10.1016/j.watres.2007.03.019

Koropatkin N, DW Koppenaal, HB Pakrasi, and TJ Smith. 2007. "The Structure of a Cyanobacterial Bicarbonate Transport Protein, CmpA." *Journal of Biological Chemistry* 282(4):2606-2614. doi:10.1074/jbc.M610222200

Kowalski K and M Valiev. 2006. "Asymptotic Extrapolation Scheme for Large-Scale Calculations with Hybrid Coupled Cluster and Molecular Dynamic Simulations." *Journal of Physical Chemistry A* 110(48):13106-13111.

Krstic P, CO Reinhold, and SJ Stuart. 2007. "Chemical Sputtering from Amorphous Carbon under Bombardment by Deuterium Atoms and Molecules." *New Journal of Physics* 9(209):1-25. doi:10.1088/1367-2630/9/7/209

Krstic P, CO Reinhold, and SJ Stuart. 2007. "Chemical Sputtering by Impact of Excited Molecules." *Europhysics Letters* 77:33002-p1-p6. doi:10.1209/0295-5075/77/3300

Kuchibhatla SN, AS Karakoti, and S Seal. 2007. "Hierarchical Assembly of Inorganic Nanostructure Building Blocks to Octahedral Superstructures – A True Template-Free Self-Assembly." *Nanotechnology* 18(7):075303. doi:10.1088/0957-4484/18/7/075303

Kuchibhatla SN, AS Karakoti, and S Seal. 2007. "Hierarchical Assembly of Inorganic Nanostructure Building Blocks to Octahedral Superstructures – A True Template-Free Self-Assembly." *Nanotechnology* 18(7):075303. doi:10.1088/0957-4484/18/7/075303

Kundu SN, S Johnston , and LC Olsen. 2006. "Traps identification in Copper-Indium-Gallium-Sulfur-Selenide Solar Cells Completed with Various Buffer Layers by Deep Level Transient Spectroscopy ." *Thin Solid Films* 515(4):2625-2631. doi:10.1016/j.tsf.2006.03.046

Kwak J, D Kim, T Szailer, CHF Peden, and J Szanyi. 2006. "NOx Uptake Mechanism on Pt/BaO/Al_2O_3 Catalysts." *Catalysis Letters* 111(3-4):119-126.

Laskin J, JH Futrell, and IK Chu. 2007. "Is Dissociation of Peptide Radical Cations an Ergodic Process?" *Journal of the American Chemical Society* 129(31):9598-9599.

Laskin J, P Wang, O Hadjar, JH Futrell, J Alvarez, and RG Cooks. 2007. "Charge Retention by Peptide Ions Soft-Landed onto Self-Assembled Monolayer Surfaces." *International Journal of Mass Spectrometry* 265(1):237-243.

Laskin J, Z Yang, C Lam, and IK Chu. 2007. "Charge-Remote Fragmentation of Odd-Electron Peptide Ions." *Analytical Chemistry* 79(17):6607-6614. doi:10.1021/ac070777b

Ledbetter RN, SA Connon, AL Neal, A Dohnalkova, and TS Magnuson. 2007. "Biogenic Mineral Production by a Novel Arsenic-Metabolizing Thermophilic Bacterium from The Alvord Basin, OR." *Applied and Environmental Microbiology* 73(18):5928-5936.

Lei C, Y Shin, JK Magnuson, GE Fryxell, LL Lasure, DC Elliott, J Liu, and EJ Ackerman. 2006. "Characterization of Functionalized Nanoporous Supports for Protein Confinement." *Nanotechnology* 17(22):5531-5538. doi:10.1088/0957-4484/17/22/001

Li GH, F Su, WJ Wang, K Ding, W Chen, Y Liu, and AG Joly. 2007. "Pressure Behaviour of the UV and Green Emission Bands in ZnO Micro-rods." *Physica Status Solidi B, Basic Research* 244(1):87-92. doi:10.1002/pssb.200672545

Li J, SM Kathmann, GK Schenter, and MS Gutowski. 2007. "Isomers and Conformers of $H(NH_2BH_2)_nH$ Oligomers: Understanding the Geometries and Electronic Structure of Boron-Nitrogen-Hydrogen Compounds as Potential Hydrogen Storage Materials." *Journal of Physical Chemistry C* 111(8):3294-3299. doi:10.1021/jp066360b

Li XS, GE Fryxell, CM Wang, and JA Young. 2007. "Templating Mesoporous Hierarchies in Silica Thin Films Using the Thermal Degradation of Cellulose Nitrate." *Microporous and Mesoporous Materials* 99(3):308-318.

Li XS, GE Fryxell, MH Engelhard, and CM Wang. 2007. "The Synthesis of Cadmium Doped Mesoporous TiO_2." *Inorganic Chemistry Communications* 10(6):639-641. doi:10.1016/j.inoche.2007.02.018

Lilach Y, MJ Iedema, and JP Cowin. 2007. "Dissociation of water buried under ice on Pt(111) ." *Physical Review Letters* 98(1):Art. No. 016105 .

Lin Y, G Liu, CM Wai, and Y Lin. 2007. "Magnetic Beads-based Bioelectrochemical Immunoassay of Polycyclic Aromatic Hydrocarbons." *Electrochemistry Communications* 9(7):1547-1552. doi:10.1016/j.elecom.2007.02.007

Lipton AS, and PD Ellis. 2007. "Modeling the Metal Center of Cys4 Zinc Proteins." *Journal of the American Chemical Society* 129(29):9192-9200. doi:10.1021/ja071430t

Liu C, B Jeon, JM Zachara, and Z Wang. 2007. "Influence of Calcium on Microbial Reduction of Solid Phase Uranium (VI)." *Biotechnology and Bioengineering* 97(6):1415-1422. doi:10.1002/bit.21357

Liu C, B Jeon, JM Zachara, Z Wang, A Dohnalkova, and JK Fredrickson. 2006. "Kinetics of Microbial Reduction of Solid Phase U(VI)." *Environmental Science and Technology* 40(20):6290-6296.

Liu C, JM Zachara, W Yantasee, PD Majors, and JP McKinley. 2006. "Microscopic Reactive Diffusion of Uranium in the Contaminated Sediments at Hanford, United States." *Water Resources Research* 42(W12420):1-15. doi:10.1029/2006WR005031

Liu C. 2007. "An Ion Diffusion Model in Semi-Permeable Clay Materials." *Environmental Science and Technology* 41(15):5403-5409. doi:10.1021/es0624117

Liu G, and Y Lin. 2007. "Electrochemical Quantification of Single Nucleotide Polymorphisms Using Nanoparticle Probes." *Journal of the American Chemical Society* 129(34):10394-10401. doi:10.1021/ja070429r

Liu G, H Wu, A Dohnalkova, and Y Lin. 2007. "Apoferritin-Templated Synthesis of Encoded Metallic Phosphate Nanoparticle Tags." *Analytical Chemistry* 79(15):5614-5619. doi:10.1021/ac070086f

Liu G, J Wang, H Wu, and Y Lin. 2006. "Versatile Apoferritin Nanoparticle Labels for Assay of Protein ." *Analytical Chemistry* 78(21):7417-7423. doi:10.1021/ac060653j

Liu G, J Wang, H Wu, Y Lin, and Y Lin. 2007. "Nanovehicles based Bioassay Labels." *Electroanalysis* 19(7-8):777-785. doi:10.1002/elan.200603787

Liu L, MH Engelhard, and M Yan. 2006. "Surface and Interface Control on Photochemically Initiated Immobilization." *Journal of the American Chemical Society* 128(43):14067 (6 pages).

Liu T, ME Belov, N Jaitly, W Qian, and RD Smith. 2007. "Accurate Mass Measurements in Proteomics." *Chemical Reviews* 107(8):3621-3653. doi:10.1021/cr068288j

Liu T, W Qian, HM Mottaz, MA Gritsenko, AD Norbeck, RJ Moore, SO Purvine, DG Camp, II, and RD Smith. 2006. "Evaluation of Multi-Protein Immunoaffinity Subtraction for Plasma Proteomics and Candidate Biomarker Discovery Using Mass Spectrometry ." *Molecular & Cellular Proteomics. MCP* 5(11):2167-2174.

Liu Y, DA MacDonald, X Yu, SV Hering, JL Collett, Jr, and CS Henry. 2006. "Analysis of Anions in Ambient Aerosols by Microchip Capillary Electrophoresis." *The Analyst* 131(11):1226-1231. doi:10.1039/b608945c

Lopez JG, G Vayner, U Lourderaj, SV Addepalli, S Kato, WA De Jong, TL Windus, and WL Hase. 2007. "Direct Dynamics Trajectory Study of F− + CH3OOH Reactive Collisions Reveals a Major Non-IRC Reaction Path." *Journal of the American Chemical Society* 129(32):9976-9985.

Lower BH, L Shi, R Yongsunthon, TC Droubay, DE Mccready, and SK Lower. 2007. "Specific Bonds between an Iron Oxide Surface and Outer Membrane Cytochromes MtrC and OmcA from Shewanella oneidensis MR-1." *Journal of Bacteriology* 189(13):4944-4952. doi:10.1128/JB.01518-06

Lyubinetsky IV, Z Yu, and MA Henderson. 2007. "Direct Observation of Adsorption Evolution and Bonding Configuration of TMAA on TiO2(110)." *Journal of Physical Chemistry C* 111(11):4342-4346. doi:10.1021/jp067264d

Manes NP, JK Gustin, J Rue, HM Mottaz, SO Purvine, AD Norbeck, ME Monroe, JS Zimmer, T Metz, JN Adkins, RD Smith, and F Heffron. 2007. "Targeted Protein Degradation by Salmonella under Phagosome-Mimicking Culture Conditions Investigated Using Comparative Peptidomics." *Molecular & Cellular Proteomics. MCP* 6(4):717-727. doi:10.1074/mcp.M600282-MCP200

Marshall MJ, AE Plymale, DW Kennedy, L Shi, Z Wang, S Reed, A Dohnalkova, CJ Simonson, C Liu, D Saffarini, MF Romine, JM Zachara, AS Beliaev, and JK Fredrickson. 2007. "Hydrogenase- and Outer Membrane c-Type Cytochrome-Facilitated Reduction of Technetium(VII) by *Shewanella oneidensis* MR-1." *Environmental Microbiology.*

Maryasov AG, MK Bowman, and YD Tsvetkov. 2007. "Dipole-Dipole Interactions of High-spin Paramagnetic Centers in Disordered Systems." *Applied Magnetic Resonance* 30(3-4):683-702.

Masiello T, AG Maki, and TA Blake. 2007. "The Analysis of Combination and Overtone States of 11BF3 from 1650 to 4600 cm-1." *Journal of Molecular Spectroscopy* 243(1):16-31. doi:10.1016/j.jms.2007.02.019

Matus MH, K Anderson, DM Camaioni, T Autrey, and DA Dixon. 2007. "Reliable Predictions of the Thermochemistry of Boron-Nitrogen Hydrogen Storage Compounds: BxNxHy, x=2,3 ." *Journal of Physical Chemistry A* 111(20):4411-4421. doi:10.1021/jp070931y

Mazurkiewicz K, M Haranczyk, MS Gutowski, and J Rak. 2007. "Can an excess electron localise on a purine moiety in the adenine-thymine Watson-Crick base pair? A computational study." *International Journal of Quantum Chemistry* 107(12):2224-2232. doi:10.1002/qua.21359

Mazurkiewicz K, M Haranczyk, MS Gutowski, J Rak, D Radisic, S Eustis, D Wang, and KH Bowen. 2007. "Valence anions in complexes of adenine and 9-methyladenine with formic acid - stabilization by intermolecular proton transfer." *Journal of the American Chemical Society* 129(5):1216-1224. doi:10.1021/ja066229h

Mazurkiewicz K, R Bachorz, MS Gutowski, and J Rak. 2006. "On the unusual stability of valence anions of thymine based on very rare tautomers. A computational study." *Journal of Physical Chemistry B* 110(48):24696-24707. doi:10.1021/jp065666f

McFarlane SA, JH Mather, and TP Ackerman. 2007. "Analysis of tropical radiative heating profiles: A comparison of models and observations ." *Journal of Geophysical Research. D. (Atmospheres)* 112:D14218. doi:10.1029/2006JD008290

Mei D, NA Deskins, M Dupuis, and Q Ge. 2007. "Methanol adsorption on the clean CeO2(111) surface: A density functional theory study." *Journal of Physical Chemistry C* 111(28):10514-10522.

Metz T, Q Zhang, JS Page, Y Shen, SJ Callister, JM Jacobs, and RD Smith. 2007. "The future of liquid chromatography-mass spectrometry in metabolic profiling and metabolomic studies for biomarker discovery." *Biomarkers in Medicine* 1(1):159-185. doi:doi: 10.2217/17520363.1.1.159

Metz TO, JM Jacobs, MA Gritsenko, G Fontes, W Qian, DG Camp, II, VJ Poitout, and RD Smith. 2006. "Characterization of the Human Pancreatic Islet Proteome by Two-Dimensional LC/MS/MS." *Journal of Proteome Research* 5(12):3345-3354. doi: 10.1021/pr060322n

Meyer FW, P Krstic, LI Vergara, HF Krause, CO Reinhold, and SJ Stuart. 2007. "Low Energy Chemical Sputtering of ATJ Graphite by Atomic and Molecular Deuterium Ions." *Physica Scripta* T128:50-54. doi:10.1088/0031-8949/2007/T128/010

Minard KR, VV Vishwanathan, PD Majors, LQ Wang, and PC Rieke. 2006. "Magnetic Resonance Imaging (MRI) of PEM Dehydration and Gas Manifold Flooding During Continuous Fuel Cell Operation." *Journal of Power Sources* 161(2):856-863.

Mitsui T, E Fomin, DF Ogletree, M Salmeron, AU Nilekar, and M Mavrikakis. 2007. "Manipulation and Patterning of the Surface Hydrogen Concentration on Pd(111) by Electric Fields." *Angewandte Chemie International Edition* 46(30):5757-5761. doi:10.1002/anie.200604498

Monroe ME, N Tolic, JL Shaw, N Jaitly, JN Adkins, and RD Smith. 2007. "VIPER: an advanced software package to support high-throughput LC-MS peptide identification." *Bioinformatics* 23(15- August 2007):2021-2023. doi:doi:10.1093/bioinformatics/btm281

Morgan WF, and MB Sowa. 2007. "Non-Targeted Bystander Effects Induced by Ionizing Radiation." *Mutation Research* 616(1-2):159-164.

Nie L, G Wu, and W Zhang. 2006. "Correlation of mRNA expression and protein abundance affected by multiple sequence features related to translational efficiency in *Desulfovibrio vulgaris*: A quantitative analysis." *Genetics* 174(4):2229-2243. doi:10.1534/genetics.106.065862

Norbeck AD, SJ Callister, ME Monroe, N Jaitly, DA Elias, MS Lipton, and RD Smith. 2006. "Proteomic approaches to bacterial differentiation." *Journal of Microbiological Methods* 67(3):473-486.

Oda T, Y Oya, S Tanaka, and WJ Weber. 2007. "Validation of Potential Models for Li2O in Classical Molecular Dynamics Simulation." *Journal of Nuclear Materials* 367-370:263-268. doi:10.1016/j.jnucmat.2007.03.139

Oostrom M, C Hofstee, and TW Wietsma. 2006. "Behavior of a Viscous LNAPL under Variable Water Table Conditions." *Soil & Sediment Contamination* 15(6):543-564. doi:10.1080/15320380600958976

Oostrom M, JH Dane, and TW Wietsma. 2007. "A Review of Multidimensional, Multifluid Intermediate-scale Experiments: Flow Behavior, Saturation Imaging, and Tracer Detection and Quantification ." *Vadose Zone Journal* 6(3):610-637. doi:10.2136/vzj2006.0178

Oostrom M, MJ Truex, PD Thorne, and TW Wietsma. 2007. "Three-Dimensional Multifluid Flow and Transport at the Brooklawn Site near Baton Rouge, LA: A Case Study." *Soil & Sediment Contamination* 16(2):109-141.

Oostrom M, TW Wietsma, MA Covert, and VR Vermeul. 2007. "Zero-Valent Iron Emplacement in Permeable Porous Media Using Polymer Additions." *Ground Water Monitoring and Remediation* 27(1):122-130.

Ozensoy E, CHF Peden, and J Szanyi. 2006. "Model NOx storage systems: Storage capacity and thermal aging of BaO/theta- Al2O3/NiAl(100)." *Journal of Catalysis* 243(1):149-157. doi:10.1016/j.jcat.2006.06.028

Paci I, I Szleifer, and MA Ratner. 2007. "Chiral Separation: Mechanism Modeling in Two-Dimensional Systems." *Journal of the American Chemical Society* 129(12):3545-3555. doi:10.1021/ja066422b

Paci JT, T Belytschko, and GC Schatz. 2006. "Mechanical Properties of Ultrananocrystalline Diamond Prepared in a Nitrogen-Rich Plasma: A Theoretical Study." *Physical Review. B, Condensed Matter* 74:184112/1-9. doi:10.1103/PhysRevB.74.184112

Palmer BJ, SM Kathmann, M Krishnan, V Tipparaju, and J Nieplocha. 2007. "The Use of Processor Groups in Molecular Dynamics Simulations to Sample Free-Energy States." *Journal of Chemical Theory and Computation* 3(2):583-592. doi:10.1021/ct600260u

Palumbo AV, JR Tarver, LA Fagan, MS McNeilly, R Ruther, LS Fisher, and JE Amonette. 2007. "Comparing metal leaching and toxicity from high pH, low pH, and high ammonia fly ash." *Fuel* 86(10-11):1623-1630. doi:10.1016/j.fuel.2006.11.018

Pan D, D Hu, R Liu, X Zeng, S Kaplan, and HP Lu. 2007. "Fluctuating Two-State Light Harvesting in a Photosynthetic Membrane." *Journal of Physical Chemistry C* 111(25):8948-8956. doi:10.1021/jp071493y

Parks G, M Pease, AW Burns, KA Layman, ME Bussell, X Wang, J Hanson, and J Rodriguez. 2007. "Characterization and Hydrodesulfurization Properties of Catalysts Derived from Amorphous Metal-boron Materials." *Journal of Catalysis* 246(2):277-292. doi:10.1016/j.jcat.2006.12.009

Perrine KA, BL Lamarche, DF Hopkins, SE Budge, L Opresko, HS Wiley, and MB Sowa. 2007. "High Speed Method for in Situ Multispectral Image Registration." *Microscopy Research and Technique* 70(4):382-389. doi:10.1002/jemt.20423

Petyuk VA, W Qian, MH Chin, HH Wang, EA Livesay, ME Monroe, JN Adkins, N Jaitly, DJ Anderson, DG Camp, II, DJ Smith, and RD Smith. 2007. "Spatial Mapping of Protein Abundances in the Mouse Brain by Voxelation Integrated with High-Throughput Liquid Chromatography ─ Mass Spectrometry." *Genome Research* 17(3):328-336. doi:doi:10.1101/gr.5799207

Pierce EM, BP McGrail, P Martin, JC Marra, BW Arey, and KN Geiszler. 2007. "Accelerated Weathering of High-Level and Plutonium-bearing Lanthanide Borosilicate Waste Glasses under Hydraulically Unsaturated Conditions." *Applied Geochemistry* 22(9):1841-1859. doi:10.1016/j.apgeochem.2007.03.056

Punnoose A, KM Reddy, A Thurber, J Hays, and MH Engelhard. 2007. "Novel Magnetic Hydrogen Sensing: A Case Study Using Antiferromagnetic Hematite Nanoparticles." *Nanotechnology* 18(16):Art. No. 165502. doi:10.1088/0957-4484/18/16/165502

Qafoku O, and AR Felmy. 2007. "Development of Accurate Chemical Equilibrium Models for Oxalate Species to High Ionic Strength in the System: Na-Ba-Ca-Mn-Sr-Cl-NO3-PO4-SO4-H2O at 25°C." *Journal of Solution Chemistry* 36(1):81-95.

Ramana CV, VV Atuchin, VG Kesler, VA Kochubey, LD Pokrovsky, V Shutthanandan, U Becker, and RC Ewing. 2007. "Growth and surface characterization of sputter-deposited molybdenum oxide thin films." *Applied Surface Science* 253(12):5368-5374. doi:10.1016/j.apsusc.2006.12.012

Ramelot TA, A Yee, JR Cort, A Semesi, CH Arrowsmith, and MA Kennedy. 2007. "NMR structure and binding studies confirm that PA4608 from Pseudomonas aeruginosa is a PilZ domain and a c-di-GMP binding protein." *Proteins. Structure, Function, and Bioinformatics* 66(2):266-271. doi:10.1002/prot.21199

Reddy KM, J Hays, A Thurber, MH Engelhard, V Shutthanandan, R Hansen, WB Knowlton, and A Punnoose. 2007. "On the room-temperature ferromagnetism of Zn1-xCrxO thin films deposited by reactive co-sputtering." *Solar Energy Materials and Solar Cells* 91(15-16):1496-1502.

Reddy KM, J Holmes, J Hays, BI Kim, A Punnoose, S Kundu, K Dua, PK Biswas, V Shutthanandan, MH Engelhard, and CM Wang. 2007. "Effect of Mn doping on the structural, morphological, optical and magnetic properties of indium tin oxide films." *Journal of Materials Science. Materials in Electronics* 18(12):1197-1201. doi:10.1007/s10854-007-9277-6

Resch W, KK Hixson, RJ Moore, MS Lipton, and B Moss. 2007. "Protein Composition of the Vaccinia Virus Mature Virion." *Virology* 358(1):233-247.
Rezayat T, and AK Shukla. 2007. "Dissociative Scattering of Hyperthermal Energy CF3+ Ions from Modified Surfaces." *Journal of Chemical Physics* 126(8):Art. No. 084701. doi:10.1063/1.2484290

Riley BJ, BR Johnson, SK Sundaram, MH Engelhard, RE Williford, and JD Olmstead. 2006. "Pressure-temperature dependence of nanowire formation in the arsenic-sulfur system ." *Physics and Chemistry of Glasses* 47(6):675-680.

Saraf LV, MH Engelhard, CM Wang, AS Lea, DE McCready, V Shutthanandan, DR Baer, and SA Chambers. 2007. "Metalorganic chemical vapor deposition of carbon-free ZnO using the bis(2,2,6,6 tetramethyl-3,5-heptanedionato)zinc precursor." *Journal of Materials Research* 22(5):1230-1234. doi:10.1557/JMR.2007.0146

Saraf LV, MH Engelhard, P Nachimuthu, V Shutthanandan, CM Wang, SM Heald, DE McCready, AS Lea, DR Baer, and SA Chambers. 2007. "Nucleation and Growth of MOCVD Grown (Cr, Zn)O Films – Uniform Doping vs. Secondary Phase Formation." *Journal of the Electrochemical Society* 154(3):D134-D138. doi:10.1149/1.2424422

Schlag EW, S Sheu, D Yang, HL Selzle, and S Lin. 2007. "Distal Charge Transport in Peptides." *Angewandte Chemie International Edition* 46:2-17. doi:10.1002/anie.200601623

Schuchardt KL, BT Didier, TO Elsethagen, L Sun, V Gurumoorthi, JM Chase, J Li, and TL Windus. 2007. " Basis Set Exchange: A Community Database for Computational Sciences ." *Journal of Chemical Information and Modeling* 47(3):1045-1052. doi:10.1021/ci600510j

Shankaran H, H Resat, and HS Wiley. 2007. "Cell surface receptors for signal transduction and ligand transport - a design principles study." *PLoS Computational Biology* 3(6):e101. doi:10.1371/journal.pcbi.0030101

Shao R, CM Wang, DE McCready, TC Droubay, and SA Chambers. 2007. "Growth and structure of MBE grown TiO2 anatase films with rutile nano-crystallites ." *Surface Science* 601(6):1582-1589. doi:10.1016/j.susc.2007.01.039

Sharma S, DC Simpson, N Tolic, N Jaitly, AM Mayampurath, RD Smith, and L Pasa-Tolic. 2007. "Proteomic profiling of intact proteins using WAX-RPLC 2-D separations and FTICR mass spectrometry." *Journal of Proteome Research* 6(2):602-610. doi:10.1021/pr060354a

Sharp JL, KK Anderson, GB Hurst, DS Daly, DA Pelletier, WR Cannon, DL Auberry, DD Schmoyer, W McDonald, AM White, BS Hooker, KD Victry, MV Buchanan, V Kery, and HS Wiley. 2007. "Statistically inferring protein-protein associations with affinity isolation LC-MS/MS assays." *Journal of Proteome Research* 6(9):3788-3795.

Shin Y, and GJ Exarhos. 2007. "Template synthesis of porous titania using cellulose nanocrystals." *Materials Letters* 61(11-12):2594-2597. doi:10.1016/j.matlet.2006.10.005

Shin Y, BW Arey, CM Wang, XS Li, MH Engelhard, and GE Fryxell. 2007. "Synthesis and Characterization of Phosphate-coated Mesoporous Titania and Cd-doping of Same via Ion-Exchange." *Inorganic Chemistry Communications* 10(6):642-645. doi:10.1016/j.inoche.2007.02.016

Shin Y, CM Wang, WD Samuels, and GJ Exarhos. 2007. "Synthesis of SiC nanorods from bleached wood pulp." *Materials Letters* 61(13):2814-2817. doi:10.1016/j.matlet.2006.10.035

Shin Y, I Bae, BW Arey, and GJ Exarhos. 2007. "Simple preparation and stabilization of nickel nanocrystals on cellulose nanocrystal." *Materials Letters* 64(14-15):3215-3217.

Shin Y, JM Blackwood, I Bae, BW Arey, and GJ Exarhos. 2007. "Synthesis and stabilization of selenium nanoparticles on cellulose nanocrystal ." *Materials Letters* 61(21):4297-4300. doi:10.1016/j.matlet.2007.01.091

Shvartsburg AA, and RD Smith. 2007. "Scaling of the Resolving Power and Sensitivity for Planar FAIMS and Mobility-Based Discrimination in Flow- and Field-Driven Analyzers." *Journal of the American Society for Mass Spectrometry* 18(9):1672–1681. doi:10.1016/j.jasms.2007.06.013

Shvartsburg AA, F Li, K Tang, and RD Smith. 2007. "Distortion of Ion Structures by Field Asymmetric Waveform Ion Mobility Spectrometry." *Analytical Chemistry* 79(4):1523-1528. doi:10.1021/ac061306c

Smallwood HS, NM Lourette, CB Boschek, DJ Bigelow, RD Smith, L Pasa-Tolic, and TC Squier. 2007. "Identification of a Denitrase Activity Against Calmodulin in Activated Macrophages Using High-Field Liquid Chromatography - FTICR Mass Spectrometry." *Proceedings of the National Academy of Sciences of the United States of America* 43(37):10498-10505.

Smirnov S, NG Isern, ZG Jiang, DW Hoyt, and CJ Mcknight. 2007. "The Isolated Sixth Gelsolin Repeat and Headpiece Domain of Villin Bundle F-Actin in the Presence of Calcium and Are Linked by a 40-Residue Unstructured Sequence." *Biochemistry* 46(25):7488-7496. doi:10.1021/bi700110v

Sowa MB, W Goetz, JE Baulch, and WF Morgan. 2006. "Low-LET Bystander Responses in Gap Junction Null Human Colon Carcinoma Cells (RK036)." *Radiation Research* 166(4):688-689.

Stephens FH, R Baker, MH Matus, DJ Grant, and DA Dixon. 2006. "Acid Initiation of Ammonia-Borane Dehydrogenation for Hydrogen Storage." *Angewandte Chemie International Edition* 46(5):746-749. doi:10.1002/anie.200603285

Stowe AC, WJ Shaw, JC Linehan, B Schmid, and T Autrey. 2007. "In situ solid state B-11 MAS-NMR studies of the thermal decomposition of ammonia borane: mechanistic studies of the hydrogen release pathways from a solid state hydrogen storage material." *Physical Chemistry Chemical Physics. PCCP* 9(15):1831-1836. doi:10.1039/b617781f

Straub T, K Honer Zu Bentrup, P Orosz Coghlan, A Dohnalkova, BK Mayer, RA Bartholomew, CO Valdez, CJ Bruckner-Lea, CP Gerba, MA Abbaszadegan, and CA Nickerson. 2007. "Cell culture assay for human noroviruses [authors response]." *Emerging Infectious Diseases* 13(7):1117-1118.

Straub T, K Honer Zu Bentrup, PA Orosz Coghlan, A Dohnalkova, BK Mayer, RA Bartholomew, CO Valdez, CJ Bruckner-Lea, CP Gerba, M Abbaszadegan, and CA Nickerson. 2007. "In Vitro Cell Culture Infectivity Assay for Human Noroviruses." *Emerging Infectious Diseases* 13(3):396-403.

Stuart SJ, P Krstic, TA Embry, and CO Reinhold. 2007. "Methane Production by Deuterium Impact at Carbon Surfaces." *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 255(1):202-207.

Su F, W Wang, K Ding, G Li, Y Liu, AG Joly, and W Chen. 2006. "Pressure Dependence of the Near-Band-Edge Photoluminescence from ZnO Microds at Low Temperature." *The Journal of Physics and Chemistry of Solids* 67(11):2376-2381.

Szanyi J, J Kwak, D Kim, X Wang, J Hanson, RJ Chimentao, and CHF Peden. 2007. "Water-induced morphology changes in BaO/γ-Al2O3 NOx storage materials." *Chemical Communications* 2007(9):984-986. doi:10.1039/b613674e

Szanyi J, J Kwak, D Kim, X Wang, RJ Chimentao, J Hanson, WS Epling, and CHF Peden. 2007. "Water-induced morphology changes in BaO/γ-Al2O3 NOx storage materials: an FTIR, TPD, and time-resolved synchrotron XRD study." *Journal of Physical Chemistry C* 111(12):4678-4687. doi:10.1021/jp067932v

Szanyi J, J Kwak, RJ Chimentao, and CHF Peden. 2007. "The effect of H2O on the adsorption of NO2 on γ-Al2O3: an in situ FTIR/MS study." *Journal of Physical Chemistry C* 111(6):2661-2669. doi:10.1021/jp066326x

Tait SL, Jr., Z Dohnalek, CT Campbell, and BD Kay. 2006. "n-alkanes on Pt(111) and on C(0001)/Pt(111): Chain Length Dependence of Kinetic Desorption Parameters." *Journal of Chemical Physics* 125(23):Art. No. 234308. doi:10.1063/1.2400235

Tarasevich BJ, CJ Howard, JL Larson, ML Snead, J Simmer, ML Paine, and WJ Shaw. 2007. "The Nucleation and growth of Calcium Phosphate by Amelogenin." *Journal of Crystal Growth* 304(2):407-415.

Thornton EC, L Zhong, and M Oostrom. 2006. "Development of a Field Design for In Situ Gaseous Treatment of Sediment Based on Laboratory Column Test Data." *Journal of Environmental Engineering (ASCE)* 132(12):1626-1632.

Thurber A, J Hays, KM Reddy, V Shutthanandan, and A Punnoose. 2007. "Fluorine doping in dilute magnetic semiconductor Sn1–xFexO2." *Journal of Materials Science* 18(11):1151-1155. doi:10.1007/s10854-007-9145-4

Timchalk C, JA Campbell, G Liu, Y Lin, and AA Kousba. 2007. "Development of a Non-Invasive Biomonitoring Approach to Determine Exposure to the Organophosphorus Insecticide Chlorpyrifos in Rat Saliva." *Toxicology and Applied Pharmacology* 219(2-3):217-225. doi:10.1016/j.taap.2006.10.002

Tobin JG, S Morton, SW Yu, GD Waddill, IK Schuller, and SA Chambers. 2007. "Spin resolved photoelectron spectroscopy of Fe3O4: the case against half-metallicity." *Journal of Physics. Condensed matter* 19(31):paper #315218.

Tolmachev AV, ME Monroe, N Jaitly, VA Petyuk, JN Adkins, and RD Smith. 2006. "Mass Measurement Accuracy In Analyses Of Highly Complex Mixtures Based Upon Multidimensional Recalibration." *Analytical Chemistry* 78(24):8374-8385. doi:10.1021/ac0606251

Umar AN, TN Luider, JA Foekens, and L Pasa-Tolic. 2007. "NanoLC-FT-ICR MS improves proteome coverage attainable for ~3000 laser microdissected breast carcinoma cells." *Proteomics* 7(2):323-329. doi:10.1002/pmic.200600293

Valentine SJ, MD Plasencia, X Liu, M Krishnan, S Naylor, HR Udseth, RD Smith, and DE Clemmer. 2006. "Toward Plasma Proteome Profiling with Ion Mobility-Mass Spectrometry." *Journal of Proteome Research* 5(11):2977-2984. doi:10.1021/pr060232i

Valiev M, and K Kowalski. 2006. "Hybrid Coupled Cluster and Molecular Dynamics Approach: Application to the Excitation Spectrum of Cytosine in the Native DNA Environment." *Journal of Chemical Physics* 125(21):Art. No. 211101. doi:10.1063/1.2403847

Valiev M, BC Garrett, MK Tsai, K Kowalski, SM Kathmann, GK Schenter, and M Dupuis. 2007. "Hybrid Approach for Free Energy Calculations with High-Level Methods: Application to the S(N)2 Reaction of CHCl3 and OH- in Water." *Journal of Chemical Physics* 127(5):51102 (1-4).

Vander Wal RL, A Yezerets, N Currier, D Kim, and CM Wang. 2007. "HRTEM Study of Diesel Soot Collected from Diesel Particulate Filters ." *Carbon* 45(1):70-77. doi:10.1016/j.carbon.2006.08.005

Velasco E, BK Lamb, H Westberg, EJ Allwine, G Sosa, JL Arriaga-Colina, BT Jobson, M Alexander, P Prazeller, WB Knighton, T Rogers, M Grutter, S Herndon, CE Kolb, MA Zavala, B de Foy, RM Volkamer, L Molina, and MJ Molina. 2007. "Distribution, Magnitudes, Reactivities, Ratios and Diurnal Patterns of Volatile Organic Compounds in the Valley of Mexico During the MCMA 2002 & 2003 Field Campaigns." *Atmospheric Chemistry and Physics* 7(2):329-353.

Venkatnathan A, R Devanathan, and M Dupuis. 2007. "Atomistic Simulations of Hydrated Nafion and Temperature Effects on Hydronium Ion Mobility." *Journal of Physical Chemistry B* 111(25):7234-7244. doi:10.1021/jp0700276

Verma S, Y Xiong, MU Mayer, and TC Squier. 2007. " Remodeling of Bacterial RNA Polymerase Supramolecular Complex in Response to Environmental Conditions." *Biochemistry* 46(11):3023-3035. doi:10.1021/bi0621157

Wall ST, JC Walker, KE Healy, MB Ratcliffe, and JM Guccione. 2006. "Theoretical Impact of the Injection of Material into the Myocardium: A Finite Element Model

Simulation." *Circulation* 114:2627-586. doi:10.1161/CIRCULATIONAHA.106.657270

Wander MC, KM Rosso, and MA Schoonen. 2007. "Structure and Charge Hopping Dynamics in Green Rust ." *Journal of Physical Chemistry C* 111(30):11414-11423. doi:10.1021/jp072762n

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):Art. No. 255603. doi:10.1088/0957-4484/18/25/255603

Wang D, J Liu, Q Huo, Z Nie, W Lu, RE Williford, and Y Jiang. 2006. "Surface-Mediated Growth of Transparent, Oriented, and Well-Defined Nanocrystalline Anatase Titania Films ." *Journal of the American Chemical Society* 128(42):13670-13671. doi:10.1021/ja0655993

Wang J, G Liu, MH Engelhard, and Y Lin. 2006. "Sensitive Immunoassay of a Biomarker Tumor Necrosis Factor-[alpha] Based on Poly(guanine)-Functionalized Silica Nanoparticle Label." *Analytical Chemistry* 78(19):6974-6979. doi:10.1021/ac060809f

Wang L, S Bulusu, H Zhai, X Zeng, and LS Wang. 2007. "Doping Golden Buckyballs: Cu@Au16- and Cu@Au17- Cluster Anions." *Angewandte Chemie International Edition* 46(16):2915-2918. doi:10.1002/anie.200700060

Wang L, W Huang, BB Averkiev, AI Boldyrev, and LS Wang. 2007. "CB7-: Experimental and Theoretical Evidence Against Hypercoordinated Planar Carbon." *Angewandte Chemie International Edition* 46(24):4550-4553.

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* 129:8682-8683.

Wang XB, H Woo, B Jagoda-Cwiklik, P Jungwirth, and LS Wang. 2006. "First Steps Towards Dissolution of NaSO4- by Water." *Physical Chemistry Chemical Physics. PCCP* 8(37):4294-4296. doi:10.1039/b609941f

Wang XB, Y Wang, H Woo, J Li, G Wu, and LS Wang. 2006. "Free Tetra-and hexa-coordinated Platinum-Cyanide Dianions, PT(CN)4 2- and PT(CN)6 2-: A Combined Photodetachment Photoelectron Spectroscopic and Theoretical Study." *Chemical Physics* 329(1-3):230-238.

Wang Y, and DL King. 2007. "Preface." *Catalysis Today* 120(1):1.
Wang Y, S Ding, W Wang, JM Jacobs, W Qian, RJ Moore, F Yang, DG Camp, II, RD Smith, and RL Klemke. 2007. "Profiling Signaling Polarity in Chemotactic Cells." *Proceedings of the National Academy of Sciences of the United States of America* 104(20):8328-8333. doi:10.1073/pnas.0701103104

Wang Z, F Gao, J Crocombette, X Zu, L Yang, and WJ Weber. 2007. "Thermal Conductivity of GaN Nanotubes Simulated by Nonequilibrium Molecular Dynamics." *Physical Review. B, Condensed Matter* 75(12):Art. No. 153303. doi:10.1103/PhysRevB.75.153303

Wang Z, X Zu, F Gao, and WJ Weber. 2006. "Atomistic Simulation of Brittle to Ductile Transition in GaN Nanotubes." *Applied Physics Letters* 89(24):243123, 1-3. doi:10.1063/1.2405879

Wang Z, X Zu, F Gao, and WJ Weber. 2007. "Atomistic Study of the Melting Behavior of Single Crystalline Wurtzite Gallium Nitride Nanowires." *Journal of Materials Research* 22(3):742-747. doi:10.1557/JMR.2007.0095

Wang Z, X Zu, F Gao, and WJ Weber. 2007. "Size Dependence of Melting of Gan Nanowires with Triangular Cross Sections." *Journal of Applied Physics* 101(4):043511. doi:10.1063/1.2512140

Wang Z, X Zu, F Gao, WJ Weber, and J Crocombette. 2007. "Atomistic Simulation of the Size and Orientation Dependences of Thermal Conductivity in GaN Nanowires." *Applied Physics Letters* 90(16):Art. No. 161923. doi:10.1063/1.2730747

Wang Z, X Zu, L Yang, F Gao, and WJ Weber. 2007. "Atomistic Simulations of the Size, Orientation and Temperature Dependence of Tensile Behavior in GaN Nanowires." *Physical Review. B, Condensed Matter and Materials Physics* 76(4):Art. No. 045310. doi:10.1103/PhysRevB.76.045310

Waters T, XB Wang, and LS Wang. 2007. "Electroscopy Ionization Photoelectron Spectroscopy: Probing the Electronic Structure of Inorganic Metal Complexes in the Gas Phase." *Coordination Chemistry Reviews* 251(3-4):474-491.

Wei W, SL Parker, Y Sun, JM White, G Xiong, AG Joly, KM Beck, and WP Hess. 2007. "Study of Copper Diffusion Through Ruthenium Thin Film by Photoemission Electron Microscopy." *Applied Physics Letters* 90:111906. doi:10.1063/1.2712832

Weksberg TE, GC Lynch, K Krause, and B Pettitt. 2007. "Molecular Dynamics Simulations of Trichomonas vaginalis Ferredoxin Show a Loop-Cap Transition." *Biophysical Journal* 92:3337-3345. doi:10.1529/biophysj.106.088096

Wellman DM, SV Mattigod, BW Arey, MI Wood, and SW Forrester. 2007. "Experimental Limitations Regarding the Formation and Characterization of Uranium-Mineral Phases in Concrete Waste Forms." *Cement and Concrete Research* 37(2):151-160.

Whiteaker JR, H Zhang, JK Eng, R Fang, BD Piening, L Feng, TD lorentzen, RM Schoenherr, JF Keane, T Holzman, M Fitzgibbon, C Lin, H Zhang, K Cooke, T Liu, DG Camp, II, LN Anderson, J Watts, RD Smith, M McIntosh, and AG Paulovich. 2007. "Head-to-Head Comparison of Serum Fractionation Techniques." *Journal of Proteome Research* 6(2):828-836. doi:10.1021/pr0604920

Wigginton NS, KM Rosso, BH Lower, L Shi, and MF Hochella. 2007. "Electron tunneling properties of outer-membrane decaheme cytochromes from Shewanella oneidensis." *Geochimica et Cosmochimica Acta* 71(3):543-555.

Williams SD, TJ Johnson, T Gibbons, and CL Kitchens. 2007. "Relative Raman Intensities in C6H6, C6D6, and C6F6: A Comparison of Different Computational Methods." *Theoretical Chemistry Accounts* 117(2):283-290. doi:10.1007/s00214-006-1350-z

Wind RA, and J Hu. 2006. "In vivo and ex vivo high-resolution ^{1}H NMR in biological systems using low-speed magic angle spinning." *Progress in Nuclear Magnetic Resonance Spectroscopy* 49(3-4):207-259.

Windisch CF, Jr, DR Baer, RH Jones, and MH Engelhard. 2007. "Electrochemical Effects of S Accumulation on Ion-implanted Alloy 22 in 1 M NaCl Solutions." *Corrosion Science* 49(6):2497-2511. doi:10.1016/j.corsci.2006.12.003

Witek HA, S Irle, G Zheng, WA De Jong, and K Morokuma. 2006. "Modeling Carbon Nanostructures with the Self-Consistent Charge Density-Functional Tight-Binding Method: Vibrational Spectra and Electronic Structure of C_{28}, C_{60}, and C_{70}." *Journal of Chemical Physics* 125(21):Art. No. 214706.

Woo H, K Lau, XB Wang, and LS Wang. 2006. "Observation of Cysteine Thiolate and -S...H-O Intermolecular Hydrogen Bond." *Journal of Physical Chemistry A* 110(46):12603-12606.

Wu H, G Liu, J Wang, and Y Lin. 2007. "Quantum-Dots Based Electrochemical Immunoassay of Interleukin-1α." *Electrochemistry Communications* 9(7):1573-1577. doi:10.1016/j.elecom.2007.02.024

Xiong G, AG Joly, KM Beck, and WP Hess. 2006. "Laser-Induced Oxygen Vacancy Formation and Diffusion on TiO2(110) Surfaces Probed by Photoemission Electron Microscopy." *Physica Status Solidi. C* 3(10):3598-3602.

Xiong G, R Shao, TC Droubay, AG Joly, KM Beck, SA Chambers, and WP Hess. 2007. "Photoemission Electron Microscopy of TiO2 Anatase Films Embedded with Rutile Nanocrystals." *Advanced Functional Materials* 17(13):2133-2138.

Xiong Y, L Shi, B Chen, MU Mayer, BH Lower, Y londer, S Bose, MF Hochella, JM Zachara, JK Fredrickson, and TC Squier. 2006. "High-Affinity Binding and Direct Electron Transfer to Solid Metals by the S*hewanella oneidensis* MR-1 Outer Membrane c-type Cytochrome OmcA." *Journal of the American Chemical Society* 128(43):13978-13979. doi:10.1021/ja063526d

Xu L, CT Campbell, H Jonsson, and GA Henkelman. 2007. "Kinetic Monte Carlo Simulations of Pd Deposition and Island Growth on MgO(100)." *Surface Science* 601(14):3133-3142. doi:10.1016/j.susc.2007.05.027

Yabusaki SB, Y Fang, PE Long, CT Resch, AD Peacock, J Komlos, Jr., PR Jaffe, SJ Morrison, R Dayvault, DC White, and RT Anderson. 2007. "Uranium Removal from Groundwater via In Situ Biostimulation: Field-Scale Modeling of Transport and Biological Processes." *Journal of Contaminant Hydrology* 93(2007):216-235. doi:10.1016/j.jconhyd.2007.02.005

Yakovkin IN, and MS Gutowski. 2007. "Driving Force for the WO3(001) Surface Relaxation." *Surface Science* 601(6):1481-1488. doi:doi:10.1016/j.susc.2007.01.013

Yang Z, O Hadjar, and J Laskin. 2007. "Effect of the Surface Morphology on the Energy Transfer in Ion-Surface Collisions." *International Journal of Mass Spectrometry* 265(1):124-129. doi:10.1016/j.ijms.2007.01.018

Yantasee W, C Timchalk, and Y Lin. 2007. "Microanalyzer for Biomonitoring of Lead (Pb) in Blood and Urine ." *Analytical and Bioanalytical Chemistry* 387(1):335-341. doi:10.1007/s00216-006-0940-1

Yantasee W, CL Warner, T Sangvanich, RS Addleman, TG Carter, RJ Wiacek, GE Fryxell, C Timchalk, and MG Warner. 2007. "Removal of Heavy Metals from Aqueous Systems with Thiol Functionalized Superparamagnetic Nanoparticles." *Environmental Science & Technology* 41(14):p.5114-5119. doi:10.1021/es0705238

Yantasee W, GE Fryxell, and Y Lin. 2006. "Voltammetric Analysis of Europium at Screen-Printed Electrodes Modified with Salicylamide Self-Assembled on Mesoporous Silica." *Analyst* 131(12):1342-1346. doi:10.1039/b609211j

Yongsunthon R, V Fowler, Jr., BH Lower, FP Vellano, E Alexander, L Reller, G Corey, and SK Lower. 2007. "Correlation between fundamental binding forces and clinical prognosis of Staphylococcus aureus infections of medical implants." *Langmuir* 23(5):2289-2292.

Yu Z, CM Wang, MH Engelhard, P Nachimuthu, DE McCready, IV Lyubinetsky, and S Thevuthasan. 2007. "Epitaxial Growth and Microstructure of Cu2O Nanoparticle/thin Films on SrTiO3(100)." *Nanotechnology* 18:Art. No. 115601. doi:10.1088/0957-4484/18/11/115601

Yu Z, Y Zhang, CM Wang, V Shutthanandan, IV Lyubinetsky, MH Engelhard, LV Saraf, DE McCready, CH Henager, P Nachimuthu, and S Thevuthasan. 2007. "Synthesis and Characterization of Compositionally Graded Si1-xGex Layers on Si substrate." *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 261(1-2):723-726.

Zachara JM, SM Heald, B Jeon, RK Kukkadapu, C Liu, JP McKinley, A Dohnalkova, and DA Moore. 2007. "Reduction of Pertechnetate [Tc(VII)] by Aqueous Fe(II) and the Nature of Solid Phase Redox Products." *Geochimica et Cosmochimica Acta* 71(9):2137-2157. doi:doi:10.1016/j.gca.2006.10.025

Zelenyuk AN, and DG Imre. 2007. "On the Effect of Particle Alignment in the DMA." *Aerosol Science and Technology* 41(2):112-124.

Zelenyuk AN, DG Imre, and LA Cuadra-Rodriguez. 2006. "Evaporation of Water from Particles in the Aerodynamic Lens Inlet: An Experimental Study." *Analytical Chemistry* 78(19):6942-6947.

Zelenyuk AN, DG Imre, Y Cai, K Mueller, Y Han, and P Imrich. 2006. "SpectraMiner, an Interactive Data Mining and Visualization Software for Single Particle Mass Spectroscopy: A Laboratory Test Case." *International Journal of Mass Spectrometry* 258(1-3):58-73.

Zhai H, and LS Wang. 2006. "Probing The Electronic Properties of Dichromium Oxide Clusters Cr2On-(n=1-7) Using Photoelectron Spectroscopy." *Journal of Chemical Physics* 125(16):164315.

Zhai H, and LS Wang. 2007. "Probing the Electronic Structure and Band Gap Evolution of Titanium Oxide Clusters (TiO2)n- (n=1-10) Using Photoelectron Spectroscopy." *Journal of the American Chemical Society* 129(10):3022-3026. doi:10.1021/ja068601z

Zhai H, L Wang, S Li, and LS Wang. 2007. "Vibrationally Resolved Photoelectron Spectroscopy of BO- and BO2-: A Joint Experimental and Theoretical Study." *Journal of Physical Chemistry A* 111(6):1030-1035. doi:10.1021/jp0666939

Zhang H, JR Rustad, and JF Banfield. 2007. "Interaction between Water Molecules and Zinc Sulfide Nanoparticles Studied by Temperature-Programmed Desorption and Molecular Dynamics Simulations." *Journal of Physical Chemistry A* 111(23):5008-5014. doi:10.1021/jp0688916

Zhang Q, A Frolov, N Tang, R Hoffman, T van der Goor, T Metz, and RD Smith. 2007. "Application of Electron Transfer Dissociation Mass Spectrometry in Analyses of Non-enzymatically Glycated Peptides." *Rapid Communications in Mass Spectrometry* 21(5):661-666. doi:10.1002/rcm.2884

Zhang Q, LV Saraf, and F Hua. 2007. "Transparent thin-film transistor with self-assembled nanocrystals." *Nanotechnology* 18(19):Art. No. 195204. doi:10.1088/0957-4484/18/19/195204

Zhang Q, N Tang, JW Brock, HM Mottaz, JM Ames, J Baynes, RD Smith, and T Metz. 2007. "Enrichment and Analysis of Nonenzymatically Glycated Peptides: Boronate Affinity Chromatography Coupled with Electron-Transfer Dissociation Mass Spectrometry." *Journal of Proteome Research* 6(6):2323-2330. doi:doi:10.1021/pr070112q

Zhang Q, W Qian, TV Knyushko, TRW Clauss, SO Purvine, RJ Moore, CA Sacksteder, MH Chin, DJ Smith, DG Camp, II, DJ Bigelow, and RD Smith. 2007. "A Method for Selective Enrichment and Analysis of Nitrotyrosine-Containing Peptides in Complex Proteome Samples." *Journal of Proteome Research* 6(6):2257-2268. doi:10.1021/pr0606934

Zhang W, DE Culley, MA Gritsenko, RJ Moore, L Nie, JC Scholten, K Petritis, EF Strittmatter, DG Camp, II, RD Smith, and FJ Brockman. 2006. "LC-MS/MS based proteomic analysis and functional inference of hypothetical proteins in Desulfovibrio vulgaris." *Biochemical and Biophysical Research Communications* 349(4):1412-1419. doi:10.1016/j.bbrc.2006.09.019

Zhang W, Y Wang, J Li, J Xue, H Ji, Q Ouyang, J Xu, and Y Zhang. 2007. "Controllable shrinking and shaping of silicon nitride nanopores under electron irradiation." *Applied Physics Letters* 90(16):Art. No. 163102. doi:10.1063/1.2723680

Zhang Y, BD Milbrath, WJ Weber, M Elfman, and HJ Whitlow. 2007. "Radiation detector resolution over a continuous energy range." *Applied Physics Letters* 91(09):094105, 1-3. doi:10.1063/1.2776978

Zhang Y, CM Wang, MH Engelhard, and WJ Weber. 2006. "Irradiation behavior of SrTiO3 at temperatures close to the critical temperature for amorphization." *Journal of Applied Physics* 100(11):113533 (8 pages). doi:10.1063/1.2399932

Zhang Y, F Gao, R Devanathan, and WJ Weber. 2007. "A Fast Screening Technique to Evaluate Detector Response." *Nuclear Instruments and Methods in Physics Research. Section A, Accelerators, Spectrometers, Detectors and Associated Equipment* 579(1):108-112. doi:10.1016/j.nima.2007.04.019

Zhang Y, J Jensen, G Possnert, DA Grove, I Bae, and WJ Weber. 2007. "Stopping power measurements of He ions in Si and SiC by time-of-flight spectrometry." *Nuclear Instruments and Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 261(1-2):1180-1183. doi:10.1016/j.nimb.2007.04.276

Zhang Z, O Bondarchuk, BD Kay, JM White, and Z Dohnalek. 2006. "Imaging Water Dissociation on TiO2(110): Evidence for Inequivalent Geminate OH Groups." *Journal of Physical Chemistry B* 110(43):21840-21845. doi:10.1021/jp063619h

Zhang Z, O Bondarchuk, BD Kay, JM White, and Z Dohnalek. 2007. "Direct Visualization of 2-Butanol Adsorption and Dissociation on TiO2(110)." *Journal of Physical Chemistry C* 111(7):3021-3027. doi:10.1021/jp067461c

Zhao H, J Kwak, C Zhang, HM Brown, BW Arey, and JE Holladay. 2007. "Studying cellulose fiber structure by SEM, XRD, NMR and acid hydrolysis." *Carbohydrate Polymers* 68(2):235-241. doi:10.1016/j.carbpol.2006.12.013

Zhao H, J Kwak, Y Wang, JA Franz, JM White, and JE Holladay. 2007. "Interactions between cellulose and N-Methylmorpholine-N-oxide." *Carbohydrate Polymers* 67(1):97-103. doi:10.1016/j.carbpol.2006.04.019

Zhao H, JE Holladay, HM Brown, and C Zhang. 2007. "Metal Chlorides in Ionic Liquid Solvents Convert Sugars to 5-Hydroxymethylfurfural." *Science* 316(5831):1597-1600. doi:10.1126/science.1141199

Zhao H, JE Holladay, J Kwak, and C Zhang. 2007. "Inverse Temperature-Dependent Pathway of Cellulose Decrystallization in Trifluoroacetic Acid." *Journal of Physical Chemistry B* 111(19):5295-5300. doi:10.1021/jp070253f

Zheng G, Z Wang, S Irle, and K Morokuma. 2006. "Origin of the Linear Relationship between CH2/NH/O-SWNT Reaction Energies and Sidewall Curvature: Armchair Nanotubes." *Journal of the American Chemical Society* 128(47):15117-15126. doi:10.1021/ja061306u

Znamenskiy VS, and ME Green. 2006. "Quantum Calculations on Hydrogen Bonds in Certain Water Clusters Show Cooperative Effects." *Journal of Chemical Theory and Computation* 3(1):103-114. doi:10.1021/ct600139d

Zubarev DY, AI Boldyrev, J Li, H Zhai, and LS Wang. 2007. "On The Chemical Bonding of Gold In Auro-Boron Oxide Clusters AunBO-(n=1-3)." *Journal of Physical Chemistry A* 111(9):1648-1658. doi:10.1021/jp0657437