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SCIENCE OF INTERFACIAL PHENOMENA: CATALYSIS

William R. Wiley
EMSL NEWS
Environmental Molecular Sciences Laboratory

Taming the Rough Surface

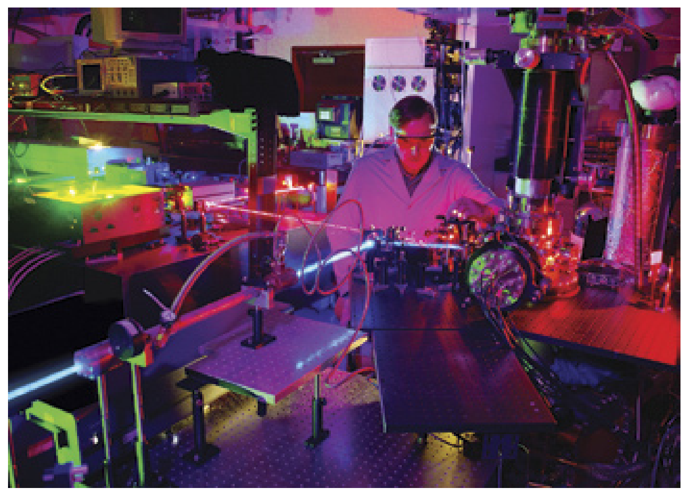
London research team combines lasers and theory to study solid surfaces at atomic scale

A team of Environmental Molecular Sciences Laboratory (EMSL) users from University College London are combining high-level theoretical calculations and laser-based experiments toward customizing surface structures on an atomic scale. Such structures have valuable applications to forefront research in catalysis and microelectronics.

Professor Alex Shluger and his colleague, Dr. Peter Sushko, are focusing their research at EMSL on laser desorption studies to manipulate solid surfaces on an atomic scale. For example, the team reported in *Surface Science* the novel result that laser excitation at a particular frequency, 4.6 eV, causes oxygen atoms to be desorbed from magnesium oxide thin-film surface corners. These kinds of discoveries are a step toward tailoring surfaces atom by atom.

In general, surfaces and interfaces between surfaces of even the most carefully designed devices are rough on an atomic scale. This is not necessarily detrimental as these imperfections can lead to interesting chemical properties such as highly efficient catalysts or other materials with unique physical properties. In other cases, surface roughness can degrade operating characteristics of devices such as microelectronic circuits. Surface roughness becomes a very serious problem as device dimensions are decreased. Therefore, developing methods to control surface roughness is a key technical challenge for the electronics industry and the burgeoning nanotechnology field.

An EMSL user for several years, Shluger's original studies involved understanding radiation processes of alkali halides—a group of materials used for radiation damage studies. The work with alkali halides led to theories of control of laser desorption from ionic crystal surfaces. Current work is unraveling laser desorption processes in alkaline earth oxides such as magnesium and calcium oxides, which show much more complex behavior than the simpler alkali halide systems.



EMSL laser resources are among the experimental capabilities the user facility is providing University College London researchers to study solid surfaces at the atomic scale.

"We were interested in seeing whether the initial theories we developed could be extended to more complex and technologically relevant materials, and oxide materials were the natural choice because of their use in electronics and as catalysts," said Shluger. "We have already found interesting differences between even such similar materials such as magnesium and calcium oxides."

To verify their theoretical models, the London team is working with EMSL researcher Kenneth Beck, as well as Alan Joly and Wayne Hess of Pacific Northwest National

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EMSL DIRECTOR'S MESSAGE

Catalysis

Allison Campbell
EMSL Director

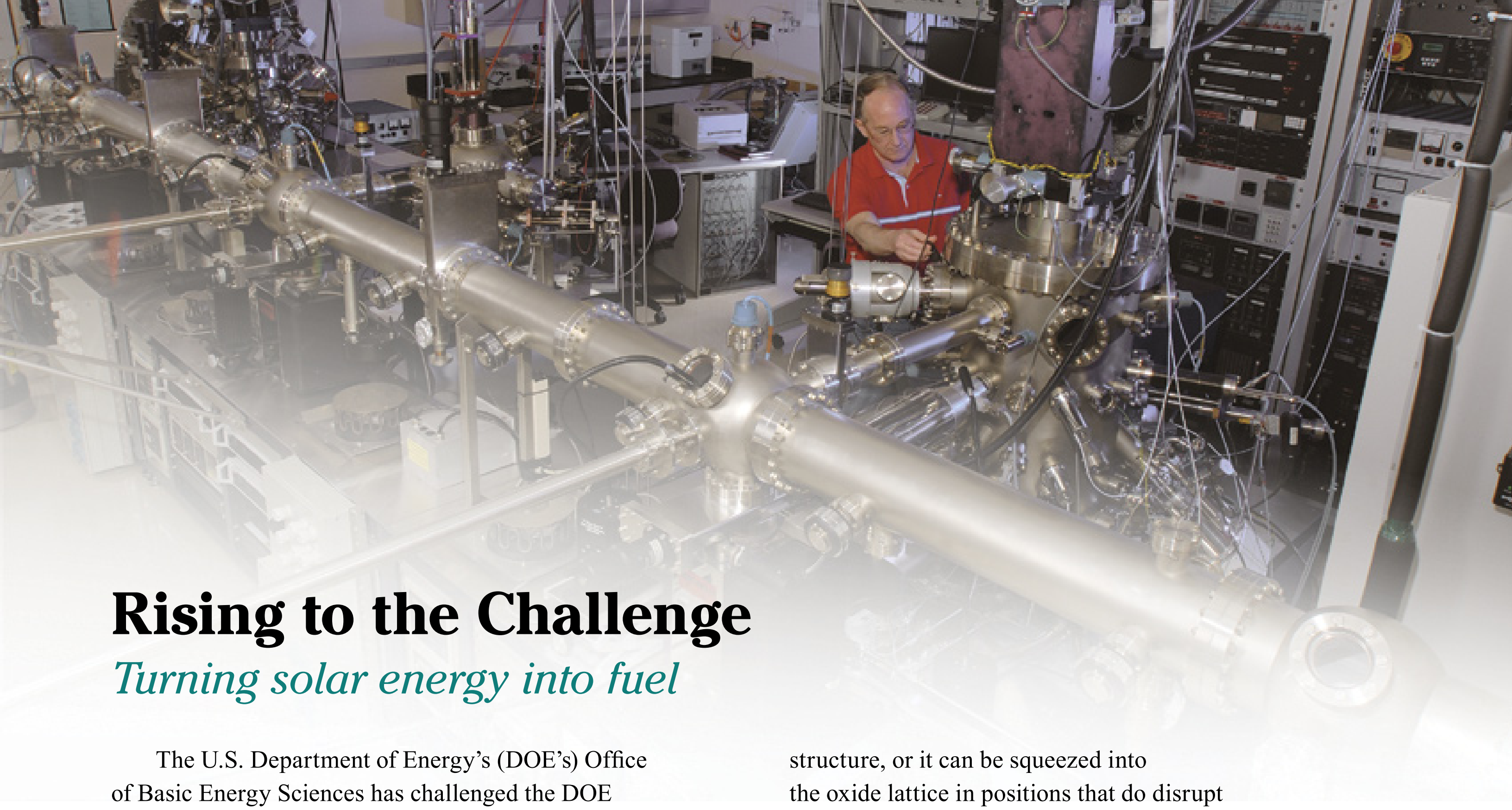
In 2006, the Environmental Molecular Sciences Laboratory (EMSL) began focusing on four emerging areas of research where visiting researchers could deploy the user facility's capabilities to make a scientific impact on challenges important to our sponsor, the Department of Energy, and the nation. These four Science Themes, as they are called, encompass atmospheric aerosol chemistry, biological interactions and dynamics, geochemistry/biogeochemistry and subsurface science, and science of interfacial phenomena.

This issue of EMSL News focuses on the Science of Interfacial Phenomena Science Theme—specifically catalysis. Catalysis involves designing and tailoring interfaces that are important to both fundamental and applied sciences—they can be created to study a particular scientific issue or engineered for a specific end use. Our users are using EMSL's state-of-the-art resources to conduct a variety of catalysis research with applications to alternative fuels, biomedicine, microelectronics, nanotechnologies, and more. This issue of EMSL News provides a small sampling of this research and the capabilities available to our users. We will introduce you to research undertaken by colleagues at the University College London and the Pacific Northwest National Laboratory, and we will introduce you to our newest instrument, the focused ion beam/scanning electron microscope.

If you have not joined the growing ranks of EMSL users, I welcome you to investigate the capabilities and expertise we have to offer you—just go to http://www.emsl.pnl.gov.

In Memoriam

J.M. (Mike) White, Director of Pacific Northwest National Laboratory's (PNNL's) Institute for Interfacial Catalysis and professor of chemistry at the University of Texas at Austin, unexpectedly passed away on August 31, 2007, in Oklahoma. Mike pioneered research in many areas of surface chemistry, catalysis, the dynamics of surface reactions, and photoassisted surface reactions. He will long be remembered for his insightful leadership and mentorship, his kindness to staff and colleagues, and his enjoyment and enthusiasm at seeing his colleagues shine in their careers. Mike will be truly missed by his colleagues around the world, including those of us at EMSL and PNNL.



Rising to the Challenge

Turning solar energy into fuel

The U.S. Department of Energy's (DOE's) Office of Basic Energy Sciences has challenged the DOE science community and national laboratories to perform fundamental research to develop truly new solar energy sources—not just improvements on existing technologies. Environmental Molecular Sciences Laboratory (EMSL) users are rising to this challenge by researching solar energy technologies that would produce chemical fuels directly from sunlight in a robust, cost-efficient fashion.

Even before DOE's solar energy challenge, EMSL user Michael Henderson, a Pacific Northwest National Laboratory (PNNL) Fellow and internationally recognized leader in oxide surface science, and his team were investigating titanium dioxide (TiO_2) as a photocatalyst for producing hydrogen and other fuels. By combining light, water, and a photocatalyst, such as TiO_2, the energy from the light can drive a water-splitting reaction, such that water is converted into oxygen and hydrogen. Finding a photocatalyst that is active in visible light, such that sunlight can be used to split water, may be the key to turning solar energy into fuel.

Titanium dioxide is a natural photocatalyst under ultraviolet light, and Henderson's team is studying how to modify TiO_2 to make it active under visible light emitted by the sun by doping it with certain negative ions (anions) such as carbon, nitrogen, or sulfur. Henderson's interest is to develop a fundamental, molecular-level understanding of how this anion-doping effect works and how sunlight drives the photocatalytic water-splitting reaction.

EMSL user Scott Chambers, a member of Henderson's team and also a PNNL Fellow, recently reported in *Surface Science* that an anion like nitrogen can be incorporated in TiO_2 in several ways. For example, it can be substituted for an oxygen atom, which does not disrupt the oxide's crystal structure, or it can be squeezed into the oxide lattice in positions that do disrupt the crystal structure. Chamber's work allows scientists to determine which form of nitrogen is responsible for making TiO_2 active in visible light, and it will guide researchers in their efforts to develop the most efficient means of producing TiO_2 that is active in visible sunlight.

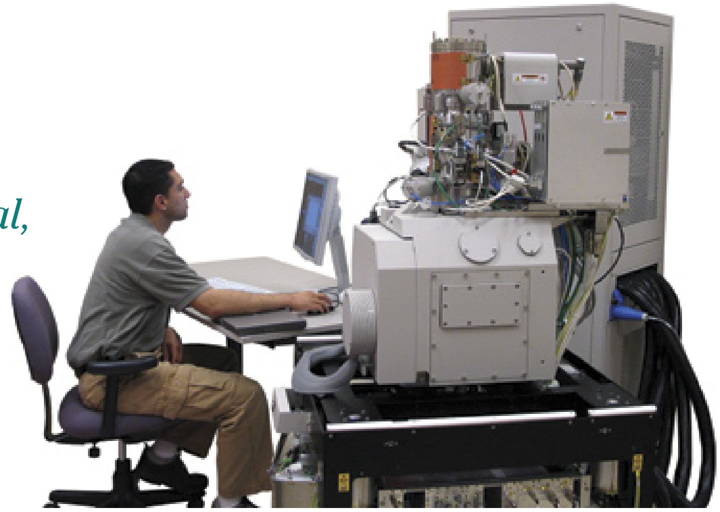
Creating the proper photocatalyst to split water, however, is only part of the energy battle. Another problem in water splitting is that it is energetically favorable for water that is split to rejoin, rather than for the hydrogen atoms to combine on the surface to make an H_2 molecule. Zdenek Dohnalek, a member of Henderson's team, reported in a recent issue of the *Journal of Physical Chemistry* that part of this problem may be that hydrogen atoms prefer not to be near each other on the TiO_2 surface. Furthermore, when heat is applied to the system, the hydrogen atoms find it easier to remove an oxygen atom from the oxide surface and make water than to combine and make H_2. The team is now researching ways to modify the TiO_2 surface so that hydrogen atoms prefer to combine instead of remaking water.

This research was funded by DOE's Office of Basic Energy Sciences. Instruments applied to this research include custom tools unique to EMSL, including oxygen plasma-assisted molecular beam epitaxy as well as photochemistry and molecular dynamics laboratory systems. In addition, the team used ion implantation for controlled doping of the TiO_2, density functional theory methods for theoretical modeling, and ultrahigh vacuum-based surface science methods.

EMSL systems, such as molecular beam epitaxy (shown above with EMSL user Scott Chambers), are helping scientists with their quest to research solar energy technologies that would produce fuels from sunlight.

A Good Type of FIB

It's no fib at all—EMSL's newest instrument being prepared for biological, materials science research



EMSL's new FIB/SEM (above) will be available to users in October. The system will support biological and materials science research.

The Environmental Molecular Sciences Laboratory (EMSL) received one of its newest "heavy hitters" this summer—a Helios Nanolab™ DualBeam™ focused ion beam/scanning electron microscope (FIB/SEM) purchased as part of EMSL's effort to refresh its instrumentation. The new instrument will be available to EMSL users in October 2007.

The FIB/SEM provides rapid and selected-region preparation of samples for transmission electron microscopy (TEM) and other spectroscopies, three-dimensional analyses of nanoscale materials and other small objects, and the capability for nanoscale lithography.

Benefiting Users' Research

The FIB/SEM will significantly benefit EMSL users whose studies are part of the Science of Interfacial Phenomena Science Theme, and it will play important roles in the Geochemistry/Biogeochemistry and Subsurface as well as Biological Interactions and Dynamics Science Themes, enabling scientific advancements across many disciplines. Most notably, the FIB/SEM will foster discoveries in biological and material science research, such as studies pertaining to environmental contaminants, solid oxide fuel cells, molecular sensors, biomedical tools, semiconductors, and light emitting diodes.

Users are encouraged to apply to use this new capability for studies not previously possible with EMSL resources. Such studies include:

- site-specific sample preparation, patterning, manipulation, and compositional analysis not possible with traditional methods
- investigations of the chemical and structural properties at interfaces in cross-sections and TEM specimens
- studies of the grain boundary and other specific features in materials
- nano-scale lithography and/or maskless writing at the nanoscale with the help of a new integrated 16-bit digital pattern generator for electron and ion beams.

Even though the FIB/SEM is still being prepared for use, EMSL users are already showing an interest in the instrument. During its first-ever Capabilities-Based Call for

Quick Specs	
Capabilities	FIB, SEM, EBSD, EDXS, STEM, cryostage, 16-bit digital pattern generation for electron and ion beams, automated TEM lift out, platinum and carbon deposition
Operating Vacuum Conditions	$\leq 2x10^{-6}$ Torr
Spot Size	Focused spot 7 nm or smaller
Field-Emission Electron Gun	Energy range 0.2-30 keV • 0.8 nm resolution at 15 keV • 1.5 nm resolution at 1keV
Ion Species	2-30 keV Ga+
Specimen Exchange	Sample introduction system
Data Acquisition/Analysis	Windows-based computer workstation interface Two- and three-dimensional nano-characterization

Proposals sent out this spring, EMSL received seven proposals for use of the instrument.

Instrument Detail

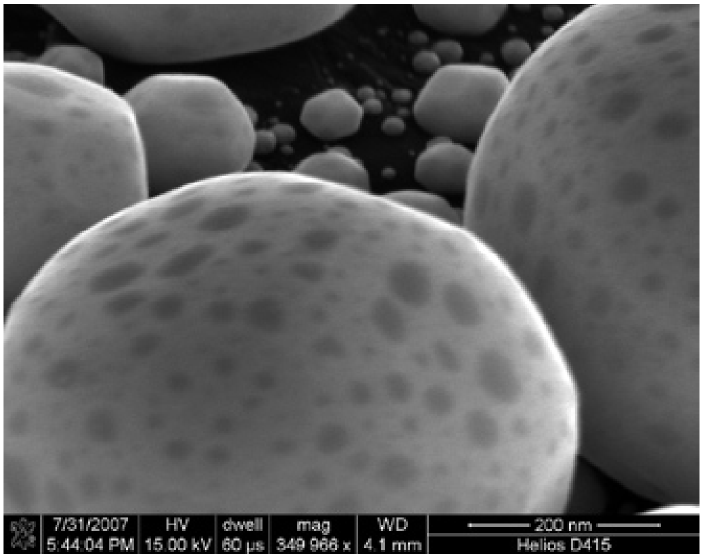
The FIB/SEM includes computer-controlled ion-beam micromachining using a gallium (Ga) liquid-metal ion source and high-resolution SEM imaging using a thermal field-emission electron gun source. Full functionality incorporates automated sample sectioning with access to electron beam, ion beam, stage positioning (allowing patterning or lithography), and gas injector (allowing *in situ* etching or material deposition) control. The FIB/SEM is configured to perform these operations either simultaneously or independently, as well as attended or unattended by the operator.

Energy dispersive X-ray spectroscopy (EDXS) and electron backscattering diffraction (EBSD) systems, including all necessary hardware and software for quantitative and qualitative analyses, are incorporated to allow phase identifications based on crystallographic data obtained from EBSD and compositional data based on EDXS.

In addition, the instrument allows specimens prepared by FIB micromachining to be manipulated for scanning TEM imaging or fabrication purposes such as welding to a TEM sample grid without breaking the vacuum within the instrument. It is also equipped with a cryostage and features 16-bit digital pattern generation for electron and ion beams as well as platinum and carbon deposition.

Generating Complementary Data

Complementary information about samples can be generated using additional resources available at EMSL. Samples prepared using the FIB/SEM can be analyzed by several surface- and bulk-sensitive electron, ion, and X-ray-based capabilities including Auger electron spectroscopy, X-ray photoelectron spectroscopy, secondary ion mass spectrometry, and TEM.



Images taken during preparation of the system for operation show gold on carbon using two detectors to obtain the three-dimensional view.

Capabilities to Support Science of Interfacial Phenomena Research

A next-generation transmission electron microscope (TEM) with aberration correction capability and an environmental cell is planned for purchase in Fiscal Year 2008. The new system will focus on real-time and *in situ*—sometimes called *operando*—measurements. This TEM will help our users unravel the mechanisms of interfacial reactions of importance in environmental remediation and catalysis.

Other new capabilities that will be available at EMSL for research under the Science of Interfacial Phenomena Science Theme include:

- An X-ray photon spectroscopy system with C-60 sputter capability, which was delivered to EMSL in September 2007.
- A time-of-flight, secondary ion mass spectrometry system with advanced temperature control and ion cluster sputter capability, which will be installed in November 2007.

To view information about other capabilities available to users for research at EMSL, see http://www.emsl.pnl.gov/capabs/instruments/.

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For more information about the FIB/SEM, contact:

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Become an EMSL User

To submit a proposal to use EMSL's new FIB/SEM, visit the EMSL website at http://www.emsl.pnl.gov.

Taming the Rough Surface *(continued from page 1)*

Laboratory, to measure oxygen atom emissions induced by laser excitation. The experiments use ultrasensitive laser ionization detection capabilities at EMSL to measure the relative yield and speed of the desorbed oxygen atoms to determine the fundamental mechanism of the emission process. Other experiments involve using femtoseocond laser pulses to measure emission ultrafast dynamics in real time. In these experiments, the emission mechanism can be probed in the first 100 femtoseconds following laser excitation. By learning about the initial motions of surface atoms, it may become possible to control surface structure and morphology in technically important materials such as complex metal oxides.

A future direction this research may take is to study the properties of desorbed atoms such as oxygen, magnesium, and calcium. Stimulated by the laser pulses, they leave surfaces at very high velocities, and their initial direction of motion can be controlled. Therefore, in addition to controlling the surface structure, the same experimental apparatus can be used as a source of high-purity atomic beams in ultrahigh vacuum.

This research was funded in part by the U.S. Department of Energy's Office of Basic Energy Sciences. Instruments used for this research include custom tools unique to EMSL, such as an ultrahigh vacuum laser desorption apparatus, facilities for reactive ballistic deposition of thin films, a variety of nanosecond pulsed lasers, and a high-power ultrafast femtosecond laser system. In addition, the team used density functional theory methods for theoretical modeling and other ultrahigh vacuum-based surface science methods.

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The William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) is a Department of Energy (DOE) national scientific user facility located at Pacific Northwest National Laboratory (PNNL) in Richland, Washington. The EMSL is operated by PNNL for the DOE Office of Biological and Environmental Research.

For additional details about the capabilities and research being performed at EMSL, please visit our web site at http://www.emsl.pnl.gov or call us at 509-376-1343.

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