2016 Symposium of the Pacific Northwest Chapter of the AVS

September 14-16 2016
Environmental Molecular Sciences Laboratory
Pacific Northwest National Laboratory
Richland WA, 99352

Chair and Vice-Chair:
Scott Smith, Pacific Northwest National Laboratory
Liney Arnadottir, Oregon State University

Local Organizing Program Committee:
Mark Engelhard, Pacific Northwest National Laboratory
Tiffany Kaspar, Pacific Northwest National Laboratory
Shuttha Shutthanandan, Pacific Northwest National Laboratory

Registration and Badging
Douglas L. Jones, Omega Analytical Services
PJ Jones

Vendor Exhibits Coordinator:
Mr. Joe Gray, Palmborg Associates, Inc.

Local Arrangements:
Diane Stephens, Pacific Northwest National Laboratory
Welcome to the 2016 PNWAVS Symposium

On behalf of the Pacific Northwest Chapter of the AVS Science and Technology Society (PNWAVS), we warmly welcome you to the 27th Annual Symposium of PNWAVS. We hope that colleagues and friends, together with new arrivals in the field, will find the sessions stimulating and that they will create, renew and deepen acquaintance and collaboration throughout the conference.

About PNWAVS

The Pacific Northwest Chapter of AVS was founded in 1962, just ten years after the founding of the national AVS organization. PNWAVS was the first regional chapter of AVS, and includes Alaska, British Columbia, Washington, Idaho, and Oregon. As an interdisciplinary, professional Society, AVS supports professionals involved in a variety of disciplines - chemistry, physics, biology, mathematics, and all engineering disciplines, through common interests related to basic science, technology development, and commercialization of materials, interfaces, and processing. The PNWAVS symposium has a long tradition of providing a stimulating interdisciplinary program in a relaxed, informal atmosphere. The meeting attracts a broad representation of government, corporate, and university researchers from throughout the Pacific Northwest, Western Canada and Alaska.

2016 PNWAVS Board

Scott Smith, Chair
Liney Árnadóttir, Vice-Chair
Tiffany Kaspar, Secretary
Doug Jones, Treasurer
Joe Gray, Vendor Exhibit Coordinator
Shuttha Shutthanandan, Web Activities and Tutorials
Alex Chang, Eastern Oregon Representative
Mark Engelhard, Central Washington Representative
Fumio Ohuchi, University of Washington Representative

We are always looking for new members! If you are interested in getting involved, for example as a PNWAVS representative from your school or region, please let one of the Board members know, and join us for our annual Board meeting after the Symposium on Friday.
We greatly appreciate the generous contributions from Vendors!

<table>
<thead>
<tr>
<th>Company</th>
<th>Representative</th>
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<tbody>
<tr>
<td>AARD Technology</td>
<td>Allan Biegaj Debbie Hsieh</td>
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<tr>
<td>Agilent Vacuum Products</td>
<td>Ron Neikirk</td>
</tr>
<tr>
<td>Applied Vacuum Tech</td>
<td>Ben Bowers Perry Henderson</td>
</tr>
<tr>
<td>Busch Vacuum</td>
<td>Jerry Balducci Ming Lee</td>
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<td>Edwards Vacuum</td>
<td>Joe Gray</td>
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<td>Electron Microscopy Sciences</td>
<td>Chad Tabbatt</td>
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<td>GNB Corporation</td>
<td>Ken Harrison</td>
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<tr>
<td>Kratos Analytical</td>
<td>Chris Moffitt</td>
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<td>Kurt J Lesker Company</td>
<td>Velibor Mandic</td>
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<td>MANTIS Deposition, Inc.</td>
<td>Anthony Graziano</td>
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<td>McAllister Technical Services, Inc.</td>
<td>Jeff Beebout Tyler Alvarado</td>
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<td>MDC Vacuum Product</td>
<td>Tom Bogdan Joe Gray</td>
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<td>Nor-Cal Products, Inc.</td>
<td>Steve Greul</td>
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<td>Oerlikon Leybold Vacuum</td>
<td>Gene Ligman</td>
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<td>Palmborg Assoc, Inc</td>
<td>Joe Gray Rod Palmborg</td>
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<td>Physical Electronics, Inc</td>
<td>John Calligan</td>
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<td>SAES Group</td>
<td>Russell Graybehl</td>
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<td>SemiTorr</td>
<td>Mike Mueller Tom Leeland</td>
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<td>Synergy Systems Corporation</td>
<td>Gary Schritter Frank Jankowsky</td>
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<tr>
<td>Thermionics Northwest, Inc</td>
<td>Rick Killam</td>
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Have You Considered Attending the AVS International Symposium & Exhibition?

Each fall, the weeklong AVS International Symposium and Exhibition brings together more than 2,500 attendees from around the globe to:

Engage and Connect - AVS Brings Together a Diverse Community of Scientists and Engineers
Empower Your Career - AVS Provides Professional Growth Activities, Workshops, and Tutorials
Expand Your Knowledge - AVS Delivers the Latest Advances in Materials, Processing and Interfaces

KEY BENEFITS

- **Technical Sessions** — provides the latest advances in the science of materials, surfaces, interfaces, and processing with:
  - 1250+ technical presentations in 15+ parallel oral sessions
  - 2 poster sessions
  - 100+ post-meeting online technical Presentations on Demand

- **Short Courses, Tutorials, and Workshops** — delivers practical training in vacuum and equipment technology; materials and interface characterization; and materials processing

- **Exhibits** — showcases 250+ vendors tools, equipment, services, and publications—plus technology spotlight presentations from exhibitors

- **Networking** — engages professionals from industry, academia, and national labs as well as students at sessions, exhibits, and during social functions like the Welcome Mixer, Awards Ceremony and Reception, and 5k Run

- **Professional Development** — offers insights on fundraising, professional skills, work/life balance—plus opportunities to attend the business meetings and become involved in leadership of AVS chapters, divisions and groups

- **Career Services** — connects job seekers and potential employers at the Career Center—benefit from workshops and other activities including Job Information Forum

- **Awards** — recognizes outstanding scientific research, technological innovation, and leadership at the AVS Awards Ceremony and Reception
PNNL Map and EMSL Location

EMSL Bldg
EMSL Lobby

George Washington Way
Central Richland
EMSL Map and Key Meeting Locations

- **BBQ Location**
- **Bistro Patio**
- **Dr. Bill’s Bistro**
- **EMSL Auditorium Oral Presentations**
- **Restrooms**
- **Posters will be here**
- **Registration**
- **Vendor Exhibit**

EMSL Lobby
<table>
<thead>
<tr>
<th>Event</th>
<th>Time</th>
<th>Description</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wednesday, September 14th</strong></td>
<td></td>
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<tr>
<td>XPS, SIMS, and He Ion Microscopy Tutorials</td>
<td>1:00 - 5:00 pm</td>
<td></td>
<td>EMSL Auditorium</td>
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<tr>
<td>Registration</td>
<td>3:00 - 6:00 pm</td>
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<td>EMSL Lobby</td>
</tr>
<tr>
<td><strong>Thursday, September 15th</strong></td>
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<tr>
<td>Coffee and Light Refreshment</td>
<td>7:30 - 8:00 am</td>
<td></td>
<td>EMSL 1075 / 1077</td>
</tr>
<tr>
<td>Welcome</td>
<td>8:00 - 8:20 am</td>
<td></td>
<td>EMSL Auditorium</td>
</tr>
<tr>
<td>Session I: Surface Physics and Analysis</td>
<td>8:20 - 10:00 am</td>
<td></td>
<td>EMSL Auditorium</td>
</tr>
<tr>
<td>Coffee and Vendor Exhibit</td>
<td>10:00 - 10:30 am</td>
<td></td>
<td>EMSL 1075 / 1077</td>
</tr>
<tr>
<td>Session II: Theory of Surface Interactions and Reactions</td>
<td>10:30 - 11:50 am</td>
<td></td>
<td>EMSL Auditorium</td>
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<tr>
<td>Lunch</td>
<td>11:50 - 1:00 pm</td>
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<td>Patio outside of EMSL Bistro</td>
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<tr>
<td>Session III: Imaging and Characterization of Surfaces and Interfaces</td>
<td>1:00 to 2:20 pm</td>
<td></td>
<td>EMSL Auditorium</td>
</tr>
<tr>
<td>Coffee Break and Vendor Exhibit</td>
<td>2:20 - 2:50 pm</td>
<td></td>
<td>EMSL 1075 / 1077</td>
</tr>
<tr>
<td>Session IV: Catalytic Materials</td>
<td>2:50 - 4:10 pm</td>
<td></td>
<td>EMSL Auditorium</td>
</tr>
<tr>
<td>Poster Session / Vendor Exhibit</td>
<td>4:10 - 6:00 pm</td>
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<td>EMSL lobby and EMSL 1075 / 1077</td>
</tr>
<tr>
<td>BBQ Dinner</td>
<td>6:00 to 7:30 pm</td>
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<td>Patio outside of EMSL Lobby Entrance</td>
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<tr>
<td>Guest Speaker: Vern Sandberg from the Laser Interferometer Gravitational-Wave Observatory (LIGO)</td>
<td>7:30 to 8:30 pm</td>
<td></td>
<td>EMSL Auditorium</td>
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<tr>
<td><strong>Friday, September 16th</strong></td>
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<tr>
<td>Coffee and Light Refreshment</td>
<td>7:30 - 8:20 am</td>
<td></td>
<td>EMSL 1075 / 1077</td>
</tr>
<tr>
<td>Session V: Imaging and functionalization of Surfaces</td>
<td>8:20 - 10:00 am</td>
<td></td>
<td>EMSL Auditorium</td>
</tr>
<tr>
<td>Coffee Break and Awards</td>
<td>10:00 - 10:30 am</td>
<td></td>
<td>EMSL 1075 / 1077</td>
</tr>
<tr>
<td>Session VI: Catalytic Reactions and Interface induced processes</td>
<td>10:30 - 11:50 am</td>
<td></td>
<td>EMSL Auditorium</td>
</tr>
<tr>
<td>PNW-AVS Board Meeting</td>
<td>12:30 - 1:30 pm</td>
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<td>TBD</td>
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</table>

**Program Overview**
<table>
<thead>
<tr>
<th>Time</th>
<th>Invited speakers</th>
</tr>
</thead>
</table>
| Thursday Morning 8:20 am    | Richard Osgood, Jr  
Department of Applied Physics and Applied Mathematics  
Columbia University |
| Thursday Morning 10:30 am   | Jean-Sabin McEwen  
School of Chemical Engineering and Bioengineering  
Washington State University |
| Thursday Afternoon 1:00 pm  | Lara Gamble  
Department of Bioengineering  
University of Washington |
| Thursday Afternoon 2:50 pm  | Haiyan Zhao  
Department of Chemical & Materials Engineering  
University of Idaho |
| Friday Morning 8:20 am      | Dan Killelea  
Department of Chemistry and Biochemistry  
Loyola University Chicago |
| Friday Morning 10:30 am     | Zhenrong Zhang  
Department of Physics  
Baylor University |
# Technical Program

**Thursday Morning, September 15<sup>th</sup>, EMSL Auditorium**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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<tbody>
<tr>
<td>8:00a</td>
<td>Welcome</td>
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### Session I. Surface Physics and Analysis  
**Moderator: Scott Smith, PNNL**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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</thead>
<tbody>
<tr>
<td>8:20a</td>
<td>Rick Osgood Columbia</td>
<td><strong>Invited:</strong> Understanding the Science of Energetic Beam Interactions with Solid-Gas Interfaces</td>
</tr>
<tr>
<td>9:00a</td>
<td>Steven R. Spurgeon PNNL</td>
<td>Correlative Aberration-Corrected STEM-HAADF and STEM-EELS Analysis of Interface-Induced Polarization in LaCrO$_3$-SrTiO$_3$ Superlattices</td>
</tr>
<tr>
<td>9:20a</td>
<td>Chris E. Moffitt Kratos, Analytical, Inc</td>
<td>Enhanced surface chemical information using gas cluster ion source technology: cleaning just the adventitious hydrocarbon from samples</td>
</tr>
<tr>
<td>9:40a</td>
<td>Yuntao Xu PNNL</td>
<td>Exploring “no man’s land” of Supercooled Liquid Water in Ultrahigh Vacuum with Nanosecond Pulsed Laser Heating</td>
</tr>
</tbody>
</table>

| Time   | Coffee Break and Vendor Exhibit |                                                                      |

### Session II. Theory of Surface Interactions and Reactions  
**Moderator: Líney Árnadóttir, Oregon State University**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
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</thead>
<tbody>
<tr>
<td>10:30a</td>
<td>Jean-Sabin McEwen Washington State University</td>
<td><strong>Invited:</strong> More Accurate Adsorption Energies from First Principles: An Adaptive Sum of Energies from RPBE and vdW Density Functionals</td>
</tr>
<tr>
<td>11:10a</td>
<td>Renqin Zhang Washington State University</td>
<td>Multiple H$_2$O and NH$_3$ Adsorbed on Cu-SSZ-13: XANES and XES Study from First Principles</td>
</tr>
<tr>
<td>11:30a</td>
<td>Breanna Wong Washington State University</td>
<td>Developing Multi-Scale Models of Bimetallic Catalysts for the Hydrodeoxygenation of Bio-oil Compounds</td>
</tr>
</tbody>
</table>

| Time   | Lunch                           |                                                                      |

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### Thursday Afternoon September 15th

**Session III. Imaging and Characterization of Surfaces and Interfaces**  
**Moderator: Mark Engelhard, PNNL**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Institution/Group</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:00p</td>
<td>Lara Gamble</td>
<td>University of Washington</td>
<td><strong>Invited:</strong> Imaging mass spectrometry of biology in 2D and 3D</td>
</tr>
<tr>
<td>1:40p</td>
<td>Yanyan Zhang</td>
<td>Beijing National Laboratory</td>
<td>In situ Mass Spectrometric Monitoring of Dynamic Electrochemical Process at the Electrode-Electrolyte Interface, a SIMS Approach</td>
</tr>
<tr>
<td>2:00p</td>
<td>Jiandong Zhang</td>
<td>Lanzhou University</td>
<td>Nanoscale Imaging of Alteration Layers of Corroded International Standard Glass Particles using ToF-SIMS</td>
</tr>
<tr>
<td>2:20p</td>
<td></td>
<td></td>
<td>Coffee Break</td>
</tr>
</tbody>
</table>

**Session IV. Catalytic Materials**  
**Moderator: Janos Szanyi, PNNL**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Institution/Group</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:50p</td>
<td>Haiyan Zhao</td>
<td>University of Idaho</td>
<td><strong>Invited:</strong> Investigation on Noble Catalytic Material Synthesis and Chemisorption</td>
</tr>
<tr>
<td>3:30p</td>
<td>Grant Johnson</td>
<td>PNNL</td>
<td>Synthesis and Stability of Ligated Gold Clusters</td>
</tr>
<tr>
<td>3:50p</td>
<td>Alyssa Hensley</td>
<td>Washington State University</td>
<td>Elucidating the Catalytic Nature of Pt Single Sites Supported on the “29” CuxO/Cu(111) Surface via CO Oxidation</td>
</tr>
</tbody>
</table>
|       |                          |                                                        | 4:10p - 6:00p  
Poster Session and Vendor Exhibit |
<p>| 6:00p |                          |                                                        | BBQ Dinner (Patio outside of EMSL Lobby Entrance)                     |
| 7:30p | <strong>Guest Speaker:</strong> Vern Sandberg | LIGO Hanford                                      | <strong>The Detection of Gravitational Waves and Observation of Black Holes in the Vacuum of Deep Space</strong> |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>University</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:20a</td>
<td>Dan Killelea</td>
<td>Loyola University Chicago</td>
<td>Invited: High Oxygen Coverages on Ag(111) and Rh(111) and the Formation of Subsurface Oxygen</td>
</tr>
<tr>
<td>9:00a</td>
<td>Zbynek Novotny</td>
<td>PNNL</td>
<td>Functionalization of Graphene on Ru(0001) with Atomic Oxygen</td>
</tr>
<tr>
<td>9:20a</td>
<td>David Lee</td>
<td>Washington State University</td>
<td>Direct Surface and Electronic Structural Modification of a Porphyrin Monolayer using Atomic Radicals</td>
</tr>
<tr>
<td>9:40a</td>
<td>Austin Lee</td>
<td>Simon Fraser University</td>
<td>Functionalization of Silica Nanoparticles with Alcohol Containing Compounds</td>
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<tr>
<td>10:00a</td>
<td></td>
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<td>Coffee Break and Awards</td>
</tr>
</tbody>
</table>

Session VI. Catalytic Reactions and Interface induced processes
Moderator: Tiffany Kaspar, PNNL

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>University</th>
<th>Title</th>
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</thead>
<tbody>
<tr>
<td>10:30a</td>
<td>Zhenrong Zhang</td>
<td>Baylor University</td>
<td>Invited: Catalytic Reactions on TiO₂ and Tip-Enhanced Raman Spectroscopy of MoS₂</td>
</tr>
<tr>
<td>11:10a</td>
<td>Long Chen</td>
<td>PNNL</td>
<td>Toluene and Benzyl Radical Formation during Deoxygenation of Phenylmethanol on Rutile TiO₂(110)</td>
</tr>
<tr>
<td>11:30a</td>
<td>Chunqing Yuan</td>
<td>PNNL</td>
<td>Surface and Bulk Crystallization Kinetics of Amorphous Solid Water Nanoscale Films</td>
</tr>
<tr>
<td>11:50a</td>
<td>Xiaofei Yu</td>
<td>PNNL</td>
<td>In-Situ Molecular Characterization of the Solid-Electrolyte Interface on Lithium Metal Anode</td>
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<tr>
<td>G1</td>
<td>Fanglin Che, Washington State University</td>
<td>Field-Dependent Methane Reforming over Ni-Based Catalysts</td>
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<tr>
<td>G3</td>
<td>Somayeh Ramezanian, Washington State University</td>
<td>Multiscale approach to fundamental understanding of biofilm-mineral interactions</td>
<td></td>
</tr>
<tr>
<td>G4</td>
<td>Lynza H. Sprowl, Oregon State University</td>
<td>Hindered Translator and Hindered Rotor Models for Calculating the Entropy of Adsorbed Species</td>
<td></td>
</tr>
<tr>
<td>G5</td>
<td>Kofi Oware Sarfo, Oregon State University</td>
<td>Ab Initio Calculations of the Interface Between $\alpha$-$\text{Al}_2\text{O}_3$ and Pt (111)</td>
<td></td>
</tr>
<tr>
<td>G6</td>
<td>Ryan T. Frederick, Oregon State University</td>
<td>Growth and Stability of Titanium Oxide Nanoclusters on Graphene/Ru(0001)</td>
<td></td>
</tr>
<tr>
<td>G7</td>
<td>Qin Pang, Oregon State University</td>
<td>Density functional theory study on the effect of OH and Cl adsorption on the surface structure of $\alpha$-$\text{Fe}_2\text{O}_3$</td>
<td></td>
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<tr>
<td>G8</td>
<td>Michael A. Newton, University of Washington</td>
<td>Surface Analysis and Functional Assay Characterization to Engineer DNA-AuNP Devices</td>
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<tr>
<td>G9</td>
<td>Blake Bluestein, University of Washington</td>
<td>Imaging ToF-SIMS of Human Breast Cancer Tissues: Results from a Clinical Trial</td>
<td></td>
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<tr>
<td>G10</td>
<td>Yujuan He, Oregon State University</td>
<td>Inkjet Printed Hollow Silica Nanoparticles for Anti-reflective Coating</td>
<td></td>
</tr>
<tr>
<td>G11</td>
<td>Elisa Harrison, University of Washington</td>
<td>A Multi-technique Approach for Studying the Effect of Protein G B1 Orientation on Antibody Binding</td>
<td></td>
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<tr>
<td>G12</td>
<td>Yujing Zhang, Oregon State University</td>
<td>Localized Surface Plasmon Resonance Enhanced Infrared CO$_2$ Sensing Using Room-Temperature, Solution-Processed Copper Sulfide Nanostructured Thin Films</td>
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<td>#</td>
<td>Presenter</td>
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<tr>
<td>G13</td>
<td>Zhongwei Gao</td>
<td>Scalable fabrication of patterned nanostructures by using microreactor-assisted nanoparticle deposition process and microfluidic channels</td>
<td></td>
</tr>
<tr>
<td>G14</td>
<td>Austin W.H. Lee</td>
<td>Microwave Assisted Covalent Surface Modification of Silicon Oxide Surfaces with Alcohol Compounds</td>
<td></td>
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<tr>
<td>G15</td>
<td>Changqing Pan</td>
<td>Microreactor-Assisted Continuous ZnS Thin Film Deposition and Characterization</td>
<td></td>
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<tr>
<td>G16</td>
<td>Han Mei</td>
<td>Microreactor-Assisted Fabrication of ZnO-Ag Hybrid Structure</td>
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<tr>
<td>G17</td>
<td>Xuewei Fu</td>
<td>A Protein Solid Electrolyte with Decoupled Ion Transportation</td>
<td></td>
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<tr>
<td>G18</td>
<td>Rachel Komorek</td>
<td>Molecular Analysis of Bacterial Collagen-Like Proteins by Time-of-Flight Secondary Ion Mass Spectrometry</td>
<td></td>
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<tr>
<td>G19</td>
<td>Wenchao Wei</td>
<td>Characterization of microbial aggregates using ToF-SIMS</td>
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<tr>
<td>G20</td>
<td>Fei Zhang</td>
<td>Probing Glyoxal Aqueous Surface Chemistry by In Situ Molecular Imaging</td>
<td></td>
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<tr>
<td>G21</td>
<td>Lei Zhu</td>
<td>Development of Microwave-assisted Catalytically Green Route from Low Density Polyethylene (LDPE) to Hydrocarbon Fuels</td>
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# Under Graduate Student Poster Competition

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<tr>
<th>#</th>
<th>Presenter</th>
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<tbody>
<tr>
<td>U22</td>
<td>Yousif Almulla</td>
<td>A Density Functional Theory Study of Adsorbate-Adsorbate Interactions as a Function of Coverage and Hubbard U on RuO₂</td>
</tr>
<tr>
<td>U23</td>
<td>Jonathon Lopez</td>
<td>Synthesis of Cu₃SbS₄ Nanoparticles for Solution Processed Thin Film Solar Cells</td>
</tr>
<tr>
<td>U24</td>
<td>Ashleigh Schwarz</td>
<td>Characterizing the Solid Electrolyte Interface of Lithium-Sulfur Batteries using in situ XPS</td>
</tr>
<tr>
<td>U25</td>
<td>Alvin Chang</td>
<td>Effect of Water on DME and Platinum Interactions</td>
</tr>
<tr>
<td>U26</td>
<td>Kyle Groden</td>
<td>Exploration of the Site-Pairing Preference of Framework Aluminum in ZSM-5 from its Reaction with Ga(CH₃)₃</td>
</tr>
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## Contributed Posters

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<tr>
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<td>Infrared Nanospectroscopy for Visualization of Heterogeneity in Soft Matter and Biological Systems</td>
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<td>Jiandong Zhang</td>
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<td>Colin Harthcock,</td>
<td>Investigation of the broadening of the bandgap of monolayer graphene supported on Cu(111)</td>
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## Program Overview

### Wednesday, September 14\(^{th}\)

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<tr>
<th>Time</th>
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<tr>
<td>1:00 - 5:00 pm</td>
<td>XPS, SIMS, and He Ion Microscopy Tutorials</td>
<td>EMSL Auditorium</td>
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<tr>
<td>3:00 - 6:00 pm</td>
<td>Registration</td>
<td>EMSL Lobby</td>
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### Thursday, September 15\(^{th}\)

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<tbody>
<tr>
<td>7:30 - 8:00 am</td>
<td>Coffee and Light Refreshment</td>
<td>EMSL 1075 / 1077</td>
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<tr>
<td>8:00 - 8:20 am</td>
<td>Welcome</td>
<td>EMSL Auditorium</td>
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<tr>
<td>8:20 - 10:00 am</td>
<td>Session I: Surface Physics and Analysis</td>
<td>EMSL Auditorium</td>
</tr>
<tr>
<td>10:00 - 10:30 am</td>
<td>Coffee Break and Vendor Exhibit</td>
<td>EMSL 1075 / 1077</td>
</tr>
<tr>
<td>10:30 - 11:50 am</td>
<td>Session II: Theory of Surface Interactions and Reactions</td>
<td>EMSL Auditorium</td>
</tr>
<tr>
<td>11:50 - 1:00 pm</td>
<td>Lunch</td>
<td>Patio outside of EMSL Bistro</td>
</tr>
<tr>
<td>1:00 to 2:20 pm</td>
<td>Session III. Imaging and Characterization of Surfaces and Interfaces</td>
<td>EMSL Auditorium</td>
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<tr>
<td>2:20 - 2:50 pm</td>
<td>Coffee Break and Vendor Exhibit</td>
<td>EMSL 1075 / 1077</td>
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<tr>
<td>2:50 - 4:10 pm</td>
<td>Session IV. Catalytic Materials</td>
<td>EMSL Auditorium</td>
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<tr>
<td>4:10 - 6:00 pm</td>
<td>Poster Session / Vendor Exhibit</td>
<td>EMSL lobby and EMSL 1075 / 1077</td>
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<tr>
<td>6:00 to 7:30 pm</td>
<td>BBQ Dinner</td>
<td>Patio outside of EMSL Lobby Entrance</td>
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<tr>
<td>7:30 to 8:30 pm</td>
<td>Guest Speaker: Vern Sandberg from the Laser Interferometer Gravitational-Wave Observatory (LIGO)</td>
<td>EMSL Auditorium</td>
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### Friday, September 16\(^{th}\)

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<tr>
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<tbody>
<tr>
<td>7:30 - 8:20 am</td>
<td>Coffee and Light Refreshment</td>
<td>EMSL 1075 / 1077</td>
</tr>
<tr>
<td>8:20 - 10:00 am</td>
<td>Session V. Imaging and functionalization of Surfaces</td>
<td>EMSL Auditorium</td>
</tr>
<tr>
<td>10:00 - 10:30 am</td>
<td>Coffee Break and Awards</td>
<td>EMSL 1075 / 1077</td>
</tr>
<tr>
<td>10:30 - 11:50 am</td>
<td>Session VI. Catalytic Reactions and Interface induced processes</td>
<td>EMSL Auditorium</td>
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<tr>
<td>12:30 - 1:30 p</td>
<td>PNW-AVS Board Meeting</td>
<td>TBD</td>
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**Financial support for this meeting has been provided by:**

![EMSL](image1.png) and ![Pacific Northwest National Laboratory](image2.png)
Thursday Morning, September 15th, 8:20 to 10:00a
Session I. Surface Physics and Analysis

Understanding the Science of Energetic Beam Interactions with Solid-Gas Interfaces

Richard Osgood, Jr
Columbia University

The key to building new atomic or near-atomic scale structures is often control in the fabrication of their interface – particularly the interface of the thin film and its support. New fabrication tools and methods have been developed, which permit ultra-high-resolution lithography and pattern transfer for both electronic and optical nanoscale devices. The materials structures for these devices must be fabricated in a way that their atomic structure, reactions, and mechanical state are precisely known and understood. This talk will focus examining the limits of the properties of these materials as we approach nanometer-scale size.
Emergent phenomena at complex oxide interfaces continue to attract attention as the basis for a variety of next-generation devices, including photovoltaics and spintronics. Tremendous progress has been made toward understanding the role of interfacial defects, cation intermixing, and film stoichiometry in single heterojunction systems; however, the techniques commonly used to study these interfaces, such as X-ray photoelectron and absorption spectroscopies, are either sensitive only to near-surface regions or do not offer depth resolution to probe individual interfaces. Here we explore the induced polarization in superlattices of LaCrO$_3$ (LCO) and SrTiO$_3$ (STO) using a combination of aberration-corrected scanning transmission electron microscopy (STEM) and monochromated electron energy loss spectroscopy (STEM-EELS). We show that a correlative approach, utilizing an array of local and non-local probes, is necessary to fully understand the defect-mediated origin of the induced polarization in this system.

We have conducted detailed high-angle annular dark field imaging (STEM-HAADF) to directly measure the induced ferroelectric polarization in the STO layers. We first acquire a relatively high-speed time series of multiple fast frames (0.4 $\mu$s px$^{-1}$), which are then aligned using both rigid and non-rigid registration to remove both sample drift and scan distortion. Using this procedure we directly measure the induced ferroelectric polarization with picometer precision, as we have demonstrated elsewhere. Our results reveal that the built-in asymmetric potential across the LCO / STO interfaces is sufficient to induce a sizable polarization, on the order of 40-70 $\mu$C cm$^{-2}$, in good agreement with $ab$ $initio$ calculations.

We next perform detailed characterization of chemical intermixing and local electronic fine structure changes to explore how defects affect the induced polarization. An improved energy resolution of better than 0.120 eV allows us to observe significant Ti intermixing through the superlattice, as well as subtle fine structure changes in the vicinity of the LCO layers not apparent in earlier data. Mapping the Ti $L_3$ $t_{2g} - e_g$ crystal field splitting across the film, we find evidence consistent with a slight reduction in Ti valence from 4+ to 3+ in the vicinity of the LCO layers, possibly the consequence of La$^{3+}$ substitution for Sr$^{2+}$ or oxygen vacancies. Measurements of the Ti $L_3$ $t_{2g} / e_g$ ratio also point toward such a trend: moving from the STO toward the LCO layers the ratio begins to decrease within the intermixed region, indicating a redistribution of electrons from $t_{2g}$ to $e_g$ states, suggesting a reduction in valence. In light of these results, our experimental STEM-HAADF measurements and accompanying $ab$ $initio$ calculations indicate that the induced polarization is robust against even sizable chemical intermixing and defect formation.
Enhanced surface chemical information using gas cluster ion source technology: cleaning just the adventitious hydrocarbon from samples

C.E. Moffitt¹, J. Counsell²

¹Kratos Analytical, Inc., 100 Red Schoolhouse Rd., Chestnut Ridge, NY 10977, USA
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Email: cmoffitt@kratos.com

Gas cluster ion sources have revolutionized the analysis of a host of organic film structures for use in surface characterization. This previously impossible capability is due to the ability of the cluster ion to sputter only the very surface of the material, causing no damage to the material beneath the sputtering location, allowing organic materials and film systems to be depth profiled for chemical analysis, which then allows profiling of a wide range of relevant materials systems analysis that.

Depth profiling of organic film systems is relevant to a wide array of modern applications, and the capability of these sources to only remove the organic contaminants from a whole host of samples has revealed the ability to analyze traditional inorganic systems and improve the information attainable in both spectroscopy and imaging techniques.

This ability to remove the very surface structure, without the damage to the underlying material that is present when using mono-atomic ion etching, also allows structures like metal oxides and glasses to be depth profiled, with much less reduction of oxide structures, or loss of light elements as the etching progresses. Chemical imaging of the sample surfaces is also improved using selective etching beams, which have only enough energy to remove adsorbed contaminants, especially adsorbed hydrocarbons that are present on the surface of nearly every material exposed to atmosphere. Effects on a range of sample types will be discussed.
Thursday Morning, September 15th, 8:20 to 10:00a  
Session I. Surface Physics and Analysis

Exploring “no man’s land” of Supercooled Liquid Water in Ultrahigh Vacuum  
with Nanosecond Pulsed Laser Heating

Yuntao Xu, Collin J. Dibble, Nikolay G. Petrik, R. Scott Smith, Alan G. Joly, Russell G.  
Tonkyn, Bruce D. Kay and Greg A. Kimmel

Physical Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999, Richland,  
Washington 99352

Abstract

To circumvent the rapid crystallization in water’s “no man’s land” and fast desorption for water films in  
ultrahigh vacuum (UHV), we have developed a pulsed laser heating system for experimental  
investigations of the dynamics and kinetics of nanoscale liquid films and liquid/solid interfaces on the  
nanosecond timescale. Combining this novel pulsed laser heating system with standard surface science  
techniques, such as the infrared reflection absorption spectroscopy (IRAS) and the temperature  
programmed desorption (TPD), we have experimentally measured of the growth rate of crystalline ice in  
supercooled liquid water have been obtained for 180 K < T < 262 K, i.e. across most of “no man’s land”.  
Because the growth rate of ice is closely related to the self-diffusion of supercooled water via the Wilson-  
Frenkel theory, these measurements provide valuable new insights into the properties of supercooled  
liquid water in “no man’s land.” It is anticipated that with this new experimental tool, experimental  
studies of a wide range of phenomena in liquids, in supercooled liquids and at liquid/solid interfaces that  
were not accessible previously will become possible.
More Accurate Adsorption Energies from First Principles: An Adaptive Sum of Energies from RPBE and vdW Density Functionals

Alyssa Hensley, Kushal Ghale, Carolin Rieg, Thanh Dang, Emily Anderst, Y. Hong, Felix Studt, Y. Wang, Charles T. Campbell, Ye Xu, Jean-Sabin McEwen

(1) The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA, (2) Department of Chemical Engineering, Louisiana State University, Baton Rouge, LA, (3) Karlsruhe Institute of Technology, Karlsruhe, Germany, (4) Chemistry and Chemical Engineering Departments, University of Washington, Seattle, WA

In recent years the popularity of density functional theory with periodic boundary conditions (DFT) has surged for the design and optimization of functional materials. However, no single DFT exchange-correlation functional currently available gives accurate adsorption energies on transition metals both when bonding to the surface is dominated by strong covalent or ionic bonding and when it has strong contributions from van der Waals interactions (i.e., dispersion forces) [1-4]. Typically, strong covalent or ionic bonding is dominant for small adsorbates (e.g. H, CO, OH and O) while van der Waals interactions contribute significantly for larger adsorbates (e.g. benzene and phenol). A number of important adsorbate systems exist where both type of adsorbates simultaneously interact with a metal surface, such as in the hydrodeoxygenation of phenolic compounds [5].

Here we present a new, simple method for accurately predicting adsorption energies on transition metal surfaces based on DFT calculations, using an adaptively-weighted sum of energies from RPBE and optB88-vdW (or optB86b-vdW) density functionals. This method has been benchmarked against a set of 39 reliable experimental energies for adsorption reactions. Our results show that this method has a mean absolute error and root mean squared error relative to experiments of 13.5 and 19.6 kJ/mol, respectively, compared to 20.4 and 26.4 kJ/mol for the BEEF-vdW functional [3]. For systems with large van der Waals contributions, this method decreases these errors to 12.0 and 18.3 kJ/mol. Thus, this method more accurately predicts adsorption energies both for processes dominated by strong covalent or ionic bonding and for those dominated by dispersion forces than any current standard DFT functional alone.

References
Multiple H₂O and NH₃ Adsorbed on Cu-SSZ-13: XANES and XES Study from First Principles

Renqin Zhang¹, Hui Li¹, Janos Szanyi², Feng Gao², Christopher Paolucci³, Trunojoyo Anggara³, Hui Li³, William Schneider³ and Jean-Sabin McEwen¹*

(1) The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA,
(2) Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, WA,
(3) Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN

Nitrogen oxides (NOₓ) are one of the main air pollutants present in the exhaust from diesel engines, which are popular for vehicle transportation due to their efficiency and durability [1]. Copper-exchanged small-pore micro-crystalline materials with the chabazite structure (Cu/CHA), such as Cu-SSZ-13, display excellent catalytic activity and hydrothermal stability in selective catalysis reduction (SCR) of NOₓ, as has been shown in a number of recent studies [2, 3].

X-ray absorption spectroscopy (XAS) is a versatile tool to determine the oxidation state and the local structure of Cu in Cu/CHA. Cu K-edge X-ray absorption near edge spectra (XANES) has been widely used to study the properties of Cu-SSZ-13 because of its high activity and selectivity in the NH₃ SCR of NOₓ. It is demonstrated that XANES is extremely sensitive to the local structure of Cu ions [4, 5]. However, the exact relationship between XANES features and local structure is still unclear. In this work, we examine how the geometry of a Cu⁺ ion with a linear configuration and Cu²⁺ ion with a square planar configuration in Cu-SSZ-13 correlate with the XANES features. When water and ammonia binds to a Cu⁺ ion with a linear configuration, a strong intensity peak around 8983 eV in Cu K-edge XANES appears. Concerning the case of Cu²⁺ ions with a square planar configuration bounded to four ammonia molecules, it is found that there are two feature peaks around 8986 and 8993 eV in their Cu K-edge XANES.

An important limitation of XANES is that it is difficult to distinguish the nitrogen and oxygen atoms in the proximity of the metal center. X-ray emission spectroscopy (XES) could overcome this limitation. It is reported that the K beta”’ peak in XES of a Cu-SSZ-13 sample presents a blue shift with the formation of Cu-N bond [6]. This can be understood by the fact that the K beta”’ peak originates from the ligand 2s to a metal 1s crossover transition and the nitrogen 2s level lies higher in energy than the one for oxygen. By comparing the XES results between H₂O and NH₃ adsorbed on Cu-SSZ-13, it is found that the K beta”’ peak of Cu-O bond appears at lower energy than that of Cu-N bond. Overall, our careful elucidation of the spectroscopic properties of Cu ions in Cu-SSZ-13 via theoretical techniques can assist us in interpreting the corresponding experimental results so as to gain a deeper understanding of the SCR of NOₓ with NH₃ throughout its catalytic cycle.

References

Developing Multi-Scale Models of Bimetallic Catalysts for the Hydrodeoxygenation of Bio-oil Compounds

Breanna Wong\textsuperscript{a}, Alyssa Hensley\textsuperscript{a}, Yong Wang\textsuperscript{ab} and Jean-Sabin McEwen\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a}The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, WA 99164

\textsuperscript{b}Pacific Northwest National Laboratory, Richland, WA 99354

Presentation Abstract

Developing an effective means of using hydrodeoxygenation (HDO) to upgrade the fuel quality of bio-oil produced from biomass is a challenge difficult to overcome through experiment alone. This is especially true when trying to elucidate the cause of synergistic interactions in bimetallic catalysts that are active for HDO. Such insight would accelerate the development of a superior HDO catalyst; however, this necessitates a thorough understanding of the nanoscale behavior of these systems in order to develop a truly predictive model on relevant time scales. We present two density functional theory (DFT) studies examining first, the interactions between a Pd/Fe surface and various O containing adsorbates; and second, the interactions between vicinal aromatic adsorbates on Pt and Pt/Sn surfaces.

Pd/Fe catalysts have been shown to exhibit a high degree of synergy and are active and selective HDO catalysts \cite{1-4}. Our investigation sought to better quantify the role of Pd through a microkinetic model of the dissociation of H\textsubscript{2}O using previously developed linear scaling relations \cite{5}. Due to a substantial decrease in the adsorption strength of O with the addition of Pd to the Fe surface, the barrier for the dissociation of H\textsubscript{2}O increases significantly. Consequently, the risk of catalyst deactivation due to the formation of a surface oxide decreases with the addition of Pd to an Fe surface, thereby promoting HDO.

Pt/Sn catalysts have exhibited a synergistic propensity to promote the lower temperature desorption of aromatic compounds like benzene when compared to Pt catalysts, which exhibit benzene decomposition \cite{6}. In order to accurately model the nanoscale behavior of such systems, the lateral interactions between adspecies need to be quantified. We have characterized the benzene-benzene lateral interactions by studying the effect of surface coverage on the adsorption energy of benzene on Pt (111) and Pt\textsubscript{3}Sn (111), modeling the temperature-programmed desorption (TPD) of benzene, and comparing our model results to experimental TPD spectra \cite{6}. We found that a mean field model is sufficient in describing these lateral interactions. Our investigation of modeling the lateral interactions of an aromatic molecule on both the Pt (111) and the Pt\textsubscript{3}Sn (111) surfaces justifies future application of our method onto systems less experimentally characterized, such as doped Fe surfaces.

References

\cite{1} Y. Hong, et al., Catalysis Letters (2016), \url{http://dx.doi.org/10.1007/s10562-016-1770-1}.

\cite{2} Y. Hong, et al., ACS Catalysis 4 (2014) 3335-3345.


\cite{5} C. Tsai, et al., Catalysis Letters 146 (2016) 718-724.

\cite{6} C. Xu, et al., The Journal of Physical Chemistry 98 (1994) 585-593.
Imaging mass spectrometry of biology in 2D and 3D

Lara J. Gamble
NESAC/BIO, Department of Bioengineering, University of Washington, Box 351653, Seattle, WA 98195-1653.
l gamble@uw.edu

Imaging mass spectrometry can provide sub-micron resolution images of cells, tissues, and other biomedically relevant samples with chemical and molecular specificity. These chemically specific images could revolutionize our understanding of biological processes such as increasing our understanding of biology. Applications include spatially identifying chemical changes as a function of an applied stress (delivered drug or biomaterials) or as a result of disease as well enable tracking the spatial distribution of metabolites and lipids. Chemistry of tumor microenvironments, lipid metabolomics relationship to cancer, delivery of nanoparticles to cells, and tissue repair could be visualized on a cellular and sub-cellular level. Similarly, ToF-SIMS images of biomaterials (e.g. polymer scaffolds) can give insight to the biological response to biomaterials.

In this presentation, imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis of biological samples will be presented. ToF-SIMS 2D images of cancer tumor tissues and 3D images of cells will be presented to highlight the utility of ToF-SIMS for investigating chemistry of tissue and cells. ToF-SIMS for characterization of polymer scaffolds (2D and 3D) will be presented. Challenges with sample preparation for the ToF-SIMS environment and processing of the large amount of data will be discussed (including multivariate analysis of the ToF-SIMS image data). Overlap of ToF-SIMS images with optical images of the same samples will be discussed. Such image comparisons allow researchers to visualize a molecular map that correlates with specific biological features or functions.
In situ Mass Spectrometric Monitoring of Dynamic Electrochemical Process at the Electrode-Electrolyte Interface, a SIMS Approach

Zhaoying Wang,\textsuperscript{ab} Yanyan Zhang,\textsuperscript{ab} Bingwen Liu,\textsuperscript{c} Xin Hua,\textsuperscript{c} Kui Wu,\textsuperscript{a} Suntharampilai Thevuthasan,\textsuperscript{b} Donald R. Baer,\textsuperscript{b} Xiao-Ying Yu,\textsuperscript{c} Zihua Zhu,\textsuperscript{b} and Fuyi Wang\textsuperscript{a}

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Abstract:

The \textit{in situ} characterization of reaction intermediates and products at electrode-electrolyte interfaces is central to mechanistic studies of complex electrochemical processes, yet a great challenge. The coupling of electrochemistry (EC) and mass spectrometry (MS) has developed quickly and found broad applicability in tackling challenges in analytical and bioanalytical chemistry. However, among the history of EC-MS, few accomplishments have been achieved on the truly \textit{in situ} and real-time study at electrode-electrolyte interfaces. An innovative EC-MS coupling interface named \textit{in situ} liquid secondary ion mass spectrometry (SIMS) was recently developed in our group by the match of SIMS and a vacuum compatible microfluidic electrochemical device. Here, for the first time we truly \textit{in situ} elucidated the electro-oxidation mechanism of a biologically significant organic compound, ascorbic acid (AA), at the electrode-electrolyte interface, successfully capturing its short-lived intermediate which was not detected directly. Moreover, we demonstrated the power of this new coupling technique in real-time monitoring and observed the dynamic evolution of electrical double layers at the electrode-electrolyte interface. This work implies promising applications of \textit{in situ} liquid SIMS in studying more complex chemical and biological events at the electrode-electrolyte interface.
Nanoscale Imaging of Alteration Layers of Corroded International Standard Glass Particles using ToF-SIMS

Jiandong Zhang¹,², James J. Neeway³, Joseph V. Ryan³, Tongan Jin³, Tieshan Wang¹, Zihua Zhu²*

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². W. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99354
³. Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99354, USA

Abstract: To study corrosion mechanisms, glass coupons are traditionally investigated as a model system. A major reason is that laminar alteration layers usually form on the corroded coupon surface, which are not only easy to analyze, but also simple to model. For example, secondary ion mass spectrometry (SIMS) depth profiling has been readily used to characterize the alteration layers on glass coupon surface. In recent years, glass particles have been increasingly interesting in glass corrosion research due to their fast corrosion rate resulting from relatively large surface area. However, traditional SIMS depth profiling may not work on these particles due to their irregular shapes. Two-dimensional and three-dimensional nanoscale imaging techniques are needed to characterize the alteration layers on the glass particle surfaces. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is thus considered because it can provide a lateral resolution as low as ~100 nm, which can be used to image glass alteration layers. In this work, ToF-SIMS was used to characterize the alteration layers of corroded international standard glass (ISG) particles. Unlike traditional alteration layers on coupon surfaces, non-homogeneous alteration layers were observed. Some surface locations show relatively thick (e.g., 1-10 microns) alteration layers. It was more interesting that some large size (tens of microns) glass particles could be fully altered. Alteration layers were not observed on the other particle surfaces, indicating that the thickness of these alteration layers may be too thin to observe by ToF-SIMS imaging. Above observations suggest that the defects on glass particle surfaces play an important role during corrosion process.

Key words: ToF-SIMS, Nanoscale imaging, glass corrosion, alteration layer, ISG particles,
Investigation on Noble Catalytic Material Synthesis and Chemisorption

Haiyan Zhao, University of Idaho, Idaho Falls

The synthesis of highly dispersed palladium nanoparticles on TiO$_2$ surfaces from palladium hexafluoroacety-lacetonate (Pd(hfac)$_2$) was investigated using in situ infrared (IR) spectroscopy, in situ X-ray absorption spectroscopy (XAS), and in situ pair distribution function (PDF) measurements under practical atomic layer deposition conditions. Residual surface chlorine was found to directly participate in the transformation of organometallic compounds to nanoparticles. Deligation of the Pd(hfac)$_2$, evolution of the surface species, and nucleation of the Pd nanoparticles were precisely resolved. This knowledge can help direct the future design of advanced heterogeneous catalysts from organometallic compounds.

We also investigated changes in the Pt–Pt bond distance, particle size, crystallinity, and coordination of Pt nanoparticles as a function of particle size (1–3 nm) and adsorbate (H$_2$, CO) using synchrotron radiation pair distribution function (PDF) and X-ray absorption spectroscopy (XAS) measurements.
Sub-nanometer clusters exhibit size-dependent properties that are unique from larger nanoparticles and do not scale predictably to the bulk phase. These highly tunable properties and large surface-to-volume ratio make clusters promising materials for commercial applications such as catalysis, solar energy conversion, and molecular electronics. Since “each-atom-counts” toward their properties it is necessary to develop robust scalable methods for synthesizing clusters of predetermined size and composition in solution. Although phosphines have been used for decades to synthesize gold clusters, it is not understood how the functionality at the coordinating phosphine centers affects the size and properties of ligated gold clusters. Using electrospray ionization mass spectrometry (ESI-MS) we characterize the electronic and steric effects of differently substituted phosphines on the distributions of gold cluster cations synthesized in solution. Ligand binding and fragmentation energies, which determine the stability and size evolution of clusters during synthesis, are characterized using surface induced dissociation (SID). The results of data modeling are compared to ligand binding energies determined for the lowest energy structures of clusters using high-level theoretical calculations. Collectively, the insights resulting from this work aid the directed synthesis of scalable quantities of clusters with specific properties for commercial applications.
Elucidating the Catalytic Nature of Pt Single Sites Supported on the “29” Cu₉O/Cu(111) Surface via CO Oxidation

Alyssa Hensley¹, Andrew Therrien², Renqin Zhang¹, E. Charles H. Sykes² and Jean-Sabin McEwen¹

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The ability to create highly dispersed, single-site noble metal catalysts is of significant interest as such catalysts would have the potential to significantly reduce the cost of catalysts for key reactions, such as the low-temperature oxidation of CO and the water-gas shift reactions.[1, 2] However, there is still disagreement over whether atomically dispersed metal atoms are catalytically active.[3] In order to resolve such disagreements, well-defined single-site supported catalysts with an accompanying experimentally accurate theoretical model are required. Here, we present such a model in the form of Pt single atoms supported on the “29” Cu₉O/Cu(111) surface for CO oxidation.

Via a comparison of experimental and theoretical STM images for the “29” Cu₉O/Cu(111) surface in the absence and presence of adsorbed CO, we developed an accurate model of the “29” Cu₉O/Cu(111) surface.[4] With an accurate model for the “29” Cu₉O/Cu(111) surface, we can then characterize and model the binding of the catalytically active Pt sites to the oxide surface. Experimental STM images show that the Pt exists as single atoms on the “29” Cu₉O/Cu(111) surface. Depending on the temperature used when Pt is added to the “29” Cu₉O/Cu(111) surface, two distinct Pt sites appear: an active CO oxidation site with Pt dosed below room temperature and an inactive CO oxidation site with Pt dosed at room temperature. By modeling the adsorption of CO on the single Pt sites, we determine that the binding strength of CO on the Pt single atoms is inversely proportional to the binding strength of Pt on the “29” Cu₉O/Cu(111) surface. This suggests that the catalytically active Pt single sites might be metastable, diffusing to more stable, yet inactive, sites as the temperature is raised. Overall, our careful elucidation of the chemical nature of the Pt single atom sites on the “29” Cu₉O/Cu(111) surface via both theoretical and experimental techniques can assist in the design and optimization of atom efficient Pt catalysts.

References

The Detection of Gravitational Waves and Observation of Black Holes in the Vacuum of Deep Space

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In the early hours of September 14, 2015, our understanding of dynamical gravity changed from theoretical to experimentally confirmed. A boundary in the way we perceived of the Universe was crossed and a new way of observing the universe became available. General Relativity expanded from the province of theory to a larger realm of experiment. In this colloquium I will discuss the LIGO project, the physics behind its interferometers, and the first direct detection of gravitational-wave events.
High Oxygen Coverages on Ag(111) and Rh(111) and the Formation of Subsurface Oxygen

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Abstract

Understanding the interaction of oxygen with transition metal surfaces is important in many areas including corrosion and catalysis. Of interest to us is the formation and chemistry of subsurface oxygen ($O_{sub}$), oxygen atoms dissolved in the near-surface region of the catalytically active metal. The goal of these studies are to understand how incorporation of $O_{sub}$ into the selvedge alters the surface structure and chemistry. The oxygen – Ag system, in particular, has been studied extensively both experimentally and theoretically because of its role in two important heterogeneously catalyzed industrial reactions: the epoxidation of ethylene to produce ethylene oxide and the partial oxidation of methanol to produce formaldehyde. In addition, the O/Rh and O/Ag systems serve as models for the dissociative chemisorption of diatomic molecules on close packed metal surfaces. Despite extensive research, there remain questions about the fundamental chemistry of the O/Ag system. Rh is also used in partial oxidation reactions, and its response to adsorbed oxygen provides an interesting complement to Ag. Where Ag extensively reconstructs, Rh does not. In particular, the structure of the catalytically active surface remains poorly understood under conditions of high oxygen coverages or subsurface oxygen. To improve our understanding of this system, we use ultra-high vacuum (UHV) surface science techniques to characterize Ag and Rh surfaces after exposure to atomic oxygen (AO) to obtain O coverages in excess of 1 ML. AO is generated by thermally cracking molecular $O_2$. We then use low-energy electron diffraction (LEED) and UHV Scanning Tunneling Microscopy (UHV-STM) to further characterize the various oxygenaceous structures produced, and quantify the amount of oxygen with temperature programmed desorption (TPD). We have found that the surface temperature during deposition is an important factor for the formation of $O_{sub}$ and the consequent surface structures.
Well-defined, monodispersed catalysts supported on oxidized carbon nanotubes and nanosheets are a promising class of new materials for heterogeneous catalysis. An analogous model support, graphene, can be prepared and studied under UHV conditions with great control. We employ scanning tunneling microscopy (STM) to study chemical functionalization of supported graphene on Ru(0001) with atomic oxygen. On Ru(0001) graphene forms a defect-free moiré structure with a periodicity of 3 nm, offering variety of distinct, regularly-spaced adsorption sites. Three different regions can be distinguished in STM images: bright regions (C atop of Ru) with the largest distance to the underlying Ru metal, dark hcp regions where graphene is closest to the metal, and medium-bright fcc regions where graphene is slightly further from the metal compared to the hcp regions. Interestingly, for temperatures above 114 K, atomic oxygen (AO) is preferentially observed within the medium-bright fcc regions but in a minority of cases also in the hcp regions. The onset of AO mobility is observed at 400 K, where AO is moving within the fcc region, or away from the less-stable hcp regions towards the bordering fcc regions. At higher temperatures (450-500 K), a dramatic increase in AO mobility is observed allowing for AO transport between the neighboring fcc regions through an hcp region. Upon encounter, the AO groups cluster, forming stable immobile dimers and large clusters. The high-resolution, time-lapsed images are used to assign the AO adsorption configuration to the on-top bonded enolate groups rather than the expected bridge-bonded epoxys. Our ongoing effort focuses on quantifying the enolate diffusion barrier and understanding of the diffusion mechanism. The high thermal stability of enolate groups, and their large periodic separation (~3 nm) makes functionalized graphene/Ru(0001) an ideal model system for future studies of well-defined model catalysts.
Direct Surface and Electronic Structural Modification of a Porphyrin Monolayer using Atomic Radicals

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Direct surface and electronic structural modification of a porphyrin monolayer using gas-phase reactive radicals was examined for the first time in the molecular scale. Scanning Tunneling microscopy (STM) was used to characterize the surface structures of Cobalt (II) octaethyl porphyrin (CoOEP) before and after the interaction with atomic oxygen in ultra high vacuum. While the lattice parameters of the porphyrin adsorbates remained constant within experimental errors, the central Co atoms with half-filled d\(_{x^2}\) orbitals did not participate in the reactions with the reactive O-atoms. Instead, terminal saturated ethyl groups of the CoOEP molecules, with standing up configuration upon adsorption on Au(111), participated in a possible cross-linking reaction between neighboring CoOEP molecules. A possible reaction mechanism involving inter-molecular hydrogen bonding was proposed based on the STM data collected at different bias voltages. Furthermore, scanning tunneling spectroscopy (STS) was used to probe changes in the highest occupied molecular orbital (HOMO) and in the lowest unoccupied molecular orbital (LUMO) of the porphyrin adsorbates. Comparison of the before and after STS spectra suggested that both HOMO and LUMO structures were directly modified and the energy band gap between them was decreased by \(~10\%\). This study suggests a promising new route to straightforwardly modify the surface and electronic structures of molecular semiconducting monolayers using highly reactive gas-phase atomic species.
Functionalization of Silica Nanoparticles with Alcohol Containing Compounds

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We have tuned the surface chemistry of silica nanoparticles through co-condensation of tetraethyl orthosilicate (TEOS) and alcohol containing compounds. Controlling the surface chemistry of silica nanoparticles are of prominent interest in applications that include diagnostics and therapeutics. Significant efforts have been made towards the modification of silica nanomaterials using a wide range of surfactants, as well as the formation of monolayers through various means of attaching species containing thiol or silane reactive groups. A major bottleneck for preparing these coatings has been the potential short-term and long-term toxicity and incompatibility with biological systems. We introduce a simple means of achieving the covalent modification of silica nanoparticles with alcohol containing compounds. These compounds pose significant less toxicity compared to thiol or silane derivatives. The new strategy introduced here could provide a simple means of modifying the surfaces of a variety of silicon oxide nanomaterials with excellent compatibility in biological media.
Catalytic Reactions on TiO$_2$ and Tip-Enhanced Raman Spectroscopy of MoS$_2$

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The catalytic activity of reducible oxides is often dominated by surface defects. Employing carboxylic acid, acetone, and formaldehyde as probing molecules, we studied how reactive sites affect the chemical activity of an oxide, specifically TiO$_2$(110), using scanning tunneling microscopy (STM). The unique methodology enables us to achieve the atomic-level understanding of the key elemental reaction steps — adsorption, dissociation, diffusion, and coupling reaction — taking place in heterogeneous catalytic reactions. We studied the structure of cross-linked (1 × 2) TiO$_2$(110) through the interaction of trimethyl acetic acid (TMAA) with various sites on the surfaces. We compared three specific atomistic models, Ti$_2$O$_3$, Ti$_2$O, and Ti$_3$O$_6$. The adsorption of TMAA strongly supports the Ti$_2$O model.

Two-dimensional (2D) materials beyond graphene have unique mechanical, optical and electronic properties with promising applications in flexible devices, catalysis and sensing. Here we obtain nanoscale optical images of MoS$_2$ by using resonant tip-enhanced Raman scattering (TERS). We investigate the limits of signal enhancement.
Understanding the reaction pathways of lignin-derived molecules on catalyst surfaces is of great importance for the sustainable production of energy carriers. In this regard, the role of radicals in the reaction mechanisms leading to functionalized aromatics has been extensively argued. The involvement of radical species has been firmly established for a number of simpler reactions on high surface area oxide catalysts, such as oxidative coupling of methane and selective oxidation of propylene. However, the formation of free radicals is rarely demonstrated. In this work, the reaction pathways of simple lignin-derived aromatic alcohols, i.e. phenol, phenylmethanol, and 2-phenylethanol, on a prototypical model oxide surface, rutile TiO$_2$(110), are studied using a combination of molecular beam dosing and temperature programmed desorption (TPD). For phenylmethanol, the coverage dependent TPD data show that about 40% of molecules adsorbed on the surface at a saturation coverage are converted to reaction products indicating that the reactions proceed on regular five-fold coordinated Ti sites. This is in contrast to aliphatic alcohols where the reactions are shown to proceed exclusively on bridging oxygen vacancy defect sites. The studies of OD-labelled phenylmethanol demonstrate that a fraction of OD hydrogen is transferred to the benzyl group to form toluene that desorbs between 300 K and 480 K. In the competing reaction, the OD hydrogen is converted to water at $\sim$350 K. Once the OD hydrogen is depleted above 480 K, the remaining phenylmethoxy surface species dissociate yielding benzyl radicals in the gas phase. Combined, these results show that the conversion of phenylmethanol on TiO$_2$(110) proceeds via a unique chemistry. In contrast, both phenol and 2-phenylethanol exhibit expected surface chemistry analogous to that of aliphatic alcohols. These findings reveal for the first time the formation of free radical species from the interaction of phenylmethanol with TiO$_2$(110) and demonstrate a new direct mechanism for deoxygenation of lignin-derived benzylic alcohols to aromatics on TiO$_2$. 
We investigate the crystallization kinetics of nanoscale amorphous solid water (ASW) films using temperature-programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). ASW is a metastable form of water created by vapor deposition on a cold substrate (T<130 K). We directly measure the surface (using TPD) and bulk (using RAIRS) ASW crystallization kinetics as a function of film thickness and temperature. The results show that nucleation and crystallization begins at the ASW/vacuum interface and then the crystallization growth front propagates linearly into the bulk. The linear propagation is further confirmed by adding a thin layer of isotopic D$_2$O ice indicator at different positions in the ice. These results show that the closer the isotopic layer is to the vacuum interface, the sooner the isotopic layer crystallizes, which confirms the top-down propagation of the crystallization front. Further evidence for ASW/vacuum interface nucleation mechanism comes from experiments where a decane layer is deposited on top of the ASW film. The presence of the decane layer impedes surface nucleation and dramatically decreases the crystallization rate. By separating surface nucleation and bulk propagation processes, we are able to extract the nucleation and growth rates of ASW crystallization between 140-160 K.

This work was supported by the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. The research was performed using EMSL, a national scientific user facility sponsored by DOE’s Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated by Battelle operated for the DOE.
In-Situ Molecular Characterization of the Solid-Electrolyte Interface on Lithium Metal Anode

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Abstract:
Currently, the main stream anode material in Li ion battery industry is graphite. Though it has been a great commercial success, the energy density of graphite-based Li-ion batteries will reach their limit soon. Li metal is an ideal anode material for next generation rechargeable Li batteries because of its extremely high theoretical specific capacity and very low negative electrochemical potential. It has been over 40 years since the first attempt of using Li metal as an anode; however, large-scale commercial applications are still not achieved due to a few challenges, such as dendritic Li growth and limited Columbic efficiency. Recent years, it has been reported that highly concentrated electrolytes, such as 4.0 M lithium bis(fluorosulfonyl)imide (LiFSI ) in 1,2-dimethoxyethane (DME), can result in the dendrite-free plating of Li metal and with high Columbic efficiency. However, the detailed mechanism is not clear. In this research, in situ liquid SIMS was used to molecularly characterize the structure of the Solid-Electrolyte Interfaces (SEI) formed in 1.0 M and 4.0 M LiFSI in DME. The thickness of the SEI in 4.0 M electrolyte is thinner than that in 1.0 M electrolyte. More importantly, less solvent molecules (DME) and Li metal residuals were found in the SEI layer formed in 4.0 M electrolyte. In addition, more F⁻ was found the SEI layer formed in 4.0 M electrolyte, indicating that more LiF stays in the SEI layer formed in 4.0 M electrolyte. Our data suggest that the residual solvent molecules (DME) in the SEI layer may play an important role in formation of dendrite and decreasing of Columbic efficiency.

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Poster Abstracts

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In recent years, natural gas production is a dominant process in many countries around the world, and is projected to continue to rise in the future. However, the common long-range transportation medium for fuel gas is pipelines, which have difficulties transporting the small molecules that make up natural gas (e.g. methane). As such, the importance of converting methane to valuable hydrocarbons or other portable energies is self-evident. Methane steam reforming (MSR) over a Ni-based electrode via electrochemical cells is an attractive energy conversion technology. There are two issues facing MSR over Ni-based catalysts: (i) Coke formation; (ii) High temperatures of above 900 K. We are interested in the electric field effects on this process to address the above issues since a large electric field can rearrange the potential energy states of molecular orbitals, alter adsorbate-surface interactions, and change the overall catalytic activity of catalysts. [1, 2]

Based on the field-dependent microkinetic model and the corresponding experimental evidence of MSR, a positive electric field can importantly enhance the methane conversion and reduce coke formation over a pure Ni surface. [3-6] The reason for such improvement can be that a positive field polarizes the Ni surface with a partial positive charge and assists the first C-H bond cleavage of a methane molecule. Changing the oxygen vacancy concentration [7] and increasing the applied electric field value can largely affect the oxidation states of the Ni cluster in a Ni/YSZ cermet. Interestingly, we find that the C-H bond cleavage of methane becomes more favorable as the Ni cluster becomes more positively charged. We also find that the carbon or carbide species from the CH molecule dissociation at the triple phase boundary region of a Ni/YSZ cermet resulted in a more positively charged Ni cluster, which leads to a more kinetically and thermodynamically favorable C-H bond cleavage as compared to the scenario with no carbon or no carbide species (Fig. 1). This indicates that the initial carbon or carbide species during the methane dissociation assists in the first C-H bond cleavage of the methane molecule rather than forming coke to poison the Ni-based catalysts. Overall, this work provides valuable information for a new design of electrochemical systems to enhance the Ni-based catalytic performance of methane reforming.

References
Nanoscale Interactions Measured between Lignocellulosic Biomass and Carbohydrate-Binding Module: The Effect of Surface Lignin Coverage on Nonproductive Binding

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The lack of fundamental understanding of the type of forces that govern how cellulose-degrading enzymes interact with lignin limits the design of new strategies for efficient conversion of biomass to bioethanol. Lignin content is recognized as the most influential substrate characteristic affecting the efficacy of enzymatic hydrolysis. Specifically, the inhibitory effects of lignin by physically blocking the enzyme accessibility to the substrate or by facilitating nonproductive binding to cellulases are known to be critical. In a step to improve our fundamental understanding of such interactions, nanoscale forces acting between the model cellulase carbohydrate-binding module (CBM) of cellobiohydrolase I (CBH I) and a set of model lignocellulosic substrates with controlled composition were measured using atomic force microscopy (AFM). Three pretreatment techniques were used to prepare the model substrates. These are kraft, lignosulfonate and organosolv pulping methods. Our results indicated that the overall adhesion forces of biomass to CBM increased linearly with surface lignin coverage with kraft lignin showing the highest forces among lignin types investigated. It was also shown that hydrophobic and Lifshitz-van der Waals (LW) forces dominated the binding forces of CBM to kraft lignin whereas permanent dipole-dipole interactions and electrostatic forces facilitated the interactions of lignosulfonates to CBM. Our results indicated that the organosolv treated substrates were characterized by the least adherent forces to enzymes. This suggests that organosolv pretreatment can yield substrates with lower nonproductive binding of cellulases to lignin. Understanding how enzymes interact with lignin would allow protein engineers to design better enzymes for effective hydrolysis or researchers to develop unique pretreatment technologies to avoid nonproductive binding of cellulase to lignin by altering its structure and surface properties.
Multiscale approach to fundamental understanding of biofilm-mineral interactions

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**Introduction.** Formation of biofilms in subsurface sediments offers the potential to innovative and sustainable solutions for many geotechnical problems including soil erosion, soil stability and soil contamination by chemical compounds such as petroleum hydrocarbons. However, the lack of the fundamental knowledge of how biofilms and minerals interact together hinders advancement towards developing such solutions. Furthermore, the effects of the environmental conditions including pH and ionic strength of pore water on the cellular-level adhesion forces of biofilms to minerals is not currently well understood. Therefore, the objective of this study is to investigate the interactions acting between bacterial cells and mineral surfaces using nanoscale and macroscale approaches.

**Materials and Methods.** To reach our goal, the effect of ionic strength on the nanoscale adhesion forces between bacterial surface biopolymers and a silicon nitride (Si$_3$N$_4$) cantilever, which mimics the properties of sand, were studied using atomic force microscopy (AFM). In addition, quantitative information on the conformation of bacterial surface biopolymers was obtained from modeling the measured force data using the steric model. Electrophoretic mobilities of bacteria in a range of ionic strengths (0.0027-0.2 M) were measured using a zeta potential analyzer. In addition, a sand column was used to study the transport of bacteria in soil under variable environmental conditions.

**Results and discussion.** The adhesion of *Pseudomonas putida* to a Si$_3$N$_4$ cantilever was affected by the physicochemical properties of the surface biopolymers measured in a range of ionic strengths (0.0027-0.5 M). The biopolymers on the surface of *P. putida* experienced a conformational change from a soft to a rigid structure as the salt concentration increased. At low salt concentration, bacterial cells were negatively charged (-24.9 mV) and a large barrier to adhesion was predicted using soft-particle analysis of the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory calculations. Due to such electrostatic repulsion, the brush layer extended in the electrolyte solution. In comparison, our steric model showed collapsed biopolymers on the bacterial surface at high salt concentration and the soft-particle analysis of the DLVO theory predicted an attraction at all separation distances between bacterial biopolymers and the cantilever. This is likely due to the relatively neutral surface charge of the bacteria at high salt concentration. Therefore a compressed biopolymer layer as well as less negative electrophoretic mobility for the bacterium resulted in a higher adhesion to the Si$_3$N$_4$ cantilever. At macroscale, higher retention of the bacteria in the packed bed at high salt concentration indicated more attachment to sand compared to when no NaCl was available.

**Conclusions.** Collectively, our results indicated that at low salt concentration, cells are less adherent to the silicon nitride cantilever representative of soil compared to cells exposed to a high salt concentration. This is likely due to a higher electrostatic barrier as well as longer biopolymer brushes at the lower salt concentrations. Also both macroscale and nanoscale experiments predicted similar adhesion trends between bacteria and soil mimicking surfaces under variable NaCl concentration conditions.

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**References.**

Hindered Translator and Hindered Rotor Models for Calculating the Entropy of Adsorbed Species

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Adsorbed species on surfaces are important for a range of applications including heterogeneous catalysis, corrosion processes, and film growth. The need for a fast and accurate way to predict equilibrium constants and rate constants for surface reactions is important for understanding reaction kinetics and for building microkinetic models of catalytic reactions. Here a method to calculate partition functions and entropy of adsorbed species is presented. Instead of using the vibrational frequencies estimated from density functional theory and the harmonic oscillator approximation to calculate the partition function for all modes of motion, we use hindered translator and hindered rotor models for the three modes of motion parallel to the surface, two translations and one rotation. The energy barriers for translation and rotation were determined using density functional theory and the nudged elastic band method for four different adsorbates on a platinum surface: methanol, propane, ethane, and methane. The hindered translator model was used to calculate the entropy contributions from the two translations parallel to the surface and the hindered rotor model was used to calculate the entropy contribution from the rotation about the axis perpendicular to the surface. When combined with the vibrational entropy contributions and the concentration related entropy contributions, this gives the total entropy of the adsorbate on the surface. The total adsorbate entropies were found to agree well with experimental results, with an average absolute value of the error of only 1.1R or 8% for the four adsorbates. This new model should be useful to future researchers in surface chemistry, since it provides more accurate predictions of standard-state entropies and partition functions, and thus more accurate equilibrium constants and rate constants for surface reactions than provided by the standard harmonic oscillator approximation.
*Ab Initio* Calculations of the Interface Between $\alpha$-Al$_2$O$_3$ and Pt (111)

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The use of metal-oxide interfaces has gained a lot of interest due to the wide array of applications in fields like heterogeneous catalysis, interfacial science and thermal barrier coating. By their nature, the bonding between atoms of these interfaces are complex and this has a direct impact on the electronic and mechanical properties of the interface. For this reason, it is crucial to understand the structure and properties of the interface to be able to optimize these properties via processing conditions. This could be done by tentatively controlling temperature and partial pressure of oxygen. *Ab initio* calculations provide an effective approach to understanding and evaluating the properties of materials based on the first principle calculations via Density Functional Theory (DFT). Hence, the stability and interfacial energies of three terminations of $\alpha$-Al$_2$O$_3$ (Al-termination, Al$_2$-termination, O-termination) and Pt (111) interface were calculated using the Vienna Ab initio Simulation Package (VASP). Meanwhile, the interfacial energies were calculated as functions of temperature and oxygen partial pressure within the framework of interfacial thermodynamics using the results obtained from the DFT calculations. These were then compared with high-resolution transmission electron microscopy (HRTEM) experimental results with the conclusion that the interface under experimental conditions is most likely oxygen terminated. This is in line with the experimentally determined equilibrium structure at room temperature and atmospheric oxygen pressure. Future calculations, in collaborations with HRTEM experiments, will study the interfaces between Pt nanoparticles and different Al$_2$O$_3$ structures.
Growth and Stability of Titanium Oxide Nanoclusters on Graphene/Ru(0001)

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Titanium dioxide (TiO₂) nanoparticles supported on carbon nanotubes (CNTs) present a promising materials system with many applications. While such systems have been extensively investigated in regards to heterogeneous catalysis, many questions remain regarding the density and types of defects in CNTs, their interactions with metal oxide clusters, and the system’s thermal stability. An analogous model system, graphene, can be prepared and studied under ultra-high vacuum (UHV) conditions with great control. In this study, we have investigated the growth of TiO₂ nanoclusters on a single-layer graphene on Ru(0001) using scanning tunneling microscopy and Auger electron spectroscopy (AES). TiO₂ was deposited by evaporating metallic titanium in a reactive oxygen atmosphere as a function of substrate temperature. Quartz crystal microbalance mass measurements were used to determine the oxygen pressure needed for the growth of stoichiometric TiO₂. Deposition performed at 300 K (0.03 – 2.4 monolayers, ML) resulted in the formation of nano-sized clusters nucleating on intrinsic defects in the graphene layer, with an average separation between clusters of ~11 nm. The saturation cluster density decreased slightly for depositions at 500 K, but the irregular shape of the TiO₂ clusters indicates poor crystallographic order. Depositions at 700 K resulted in significant etching of the graphene film. Thermal stability of the TiO₂ clusters was further explored with AES after annealing the clusters prepared at 300 K (2.4 ML). No chemical reduction of clusters or etching of the graphene film was observed up to ~900 K, although AES indicates significant sintering of TiO₂ clusters. Above 900 K, the clusters undergo reduction to TiOₓ (x ≈ 1.5) accompanied by the concomitant oxidation and etching of the graphene. Our ongoing effort focuses on optimizing the deposition conditions to grow well ordered TiO₂ nanoclusters without modifying the underlying graphene substrate for further catalytic studies and on the preparation of continuous, well-ordered TiO₂ films with potential applications for high-speed tunneling electronics.
Density functional theory study on the effect of OH and Cl adsorption on the surface structure of α-Fe₂O₃

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Hematite (α-Fe₂O₃) is the dominant structure for the outer layer of the iron passive film formed in alkaline environment while chloride has been suggested to play a major role in the depassivation of this passive film under the same conditions. The interactions of α-Fe₂O₃ (0001) surface with OH and Cl were studied using density functional theory (DFT). OH is slightly more stable on the surface with strong preference for atop site while Cl is stable on multiple adsorption sites but most stable on atop site. The effects of OH adsorption and Cl adsorption on the surface structure of α-Fe₂O₃ are similar and they are mostly on the first two layers causing an increasing distance between the two layers. The co-adsorption of OH and Cl causes the greatest structural change on the surface compared with the OH and Cl only adsorption at the same overall coverages. The structural changes caused by the adsorption show that the adsorptions are unlikely to initiate the depassivation process on the defect-free surface.
Surface Analysis and Functional Assay Characterization to Engineer DNA-AuNP Devices

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Abstract:

The spherical nucleic acid (SNA)—gold nanoparticle (AuNP) conjugate (a gold nanoparticle with densely functionalized oligonucleotides) has become an important platform of biomedical interest and represents an important and interesting tool for establishing nanoparticle surface tethered nucleic acid device design criteria. While these conjugates are marketed as being densely surface functionalized, surface characterization techniques are rarely used to verify the reproducibility of SNA-AuNP conjugation and account for contaminants or additional surface species. DNA strand displacement reactions form much of the basis of DNA device construction including logic gates, catalysts, and motors. Controlling the kinetics of these toehold-mediated strand displacement devices allows for autonomous molecular machinery and molecular computation. Thus, strand displacement reactions provide a unique and interesting tool for studying the kinetic behavior of nucleic acid based devices functionalized onto a nanoparticle support. By manipulating both the loading density of single-stranded DNA oligonucleotides (ssDNA) on gold nanoparticles, and the chemical linker modification (alkylthiol, alkylthiol with PEG\textsubscript{3}, and alkylthiol with PEG\textsubscript{6}) between the nanoparticle and DNA we aim to characterize and verify the resultant conjugates and device performance in terms of surface chemistry, actuation efficiency, and device kinetics.

Transmission Electron Microscopy, Dynamic Light Scattering, Ultraviolet-visible spectrophotometry, and X-Ray Photoelectron Spectroscopy (XPS) are used to characterize nucleic acid functionalized gold nanoparticles for size, shape, surface chemistry, and estimation of DNA loading/surface coverage. Hybridization efficiency for ssDNA-AuNP conjugates was determined by using a ROX fluorophore-modified and partially complementary oligonucleotide, and quantifying the fluorescence after etching the AuNPs with KCN to release bound DNA. These dsDNA-AuNP strand displacement devices were then actuated by an invading ssDNA and the displacement reaction was monitored using a fluorimeter. XPS can be used to verify relative DNA loading differences on AuNPs and chemical linker variations. Hybridization efficiency increases with a decreased DNA loading, and decreases with an increased DNA loading. The addition of PEG linker increases strand displacement rate constants in cases with high DNA loading and decreases under low DNA loading cases. Controlling hybridization efficiency and device kinetics is important in the design of nanoparticle surface-tethered nucleic acid-based biosensors or diagnostics.
Imaging ToF-SIMS of Human Breast Cancer Tissues: Results from a Clinical Trial

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Breast cancer, the most common cancer among women, is known to vary in responsiveness to chemotherapy. It is hypothesized that chemoresistant tumors will have a specific altered metabolism compared to responsive tumors that could be detected by comparing metabolites. Using time-of-flight secondary ion mass spectrometry (ToF-SIMS) provides a powerful approach to attain spatially-resolved molecular data from cancerous tissues for investigating metabolomic profiles. We use imaging ToF-SIMS and principal components analysis (PCA) to study human biopsy tissue samples to clarify links between fatty acid composition and amino acids in tumor tissues and their potential drug resistance. Tissue biopsy specimens from 10 triple negative (TN) patients (before chemotherapeutic treatment) have been studied using PCA to determine if molecular differences within tumor tissues can be correlated with patient response (or lack of response) to treatment.

Data were acquired with an IONTOF TOF.SIMS V using a Bi\textsuperscript{3+} analysis beam. Multiple 1mm\textsuperscript{2} areas per tissue section were analyzed by stitching together 25 200µm\textsuperscript{2} raster area scans. Data was acquired in both positive and negative polarities. Scores images generated by imaging PCA correlated with cellular and stromal areas were then used as masks to select regions of interest (ROI) that were reconstructed with ToF-SIMS software. Reconstructed spectral data of cellular and stromal areas was subsequently analyzed using PCA to ascertain molecular differences between tumor tissues.

ROIs were used to separate cellular and stromal regions within analysis areas followed by spectral PCA for 10 TN patient tissues. PCA of both the cellular and stromal regions separates patients that respond to chemotherapy and those that do not. Patients that respond to chemotherapy show higher loadings of sphingomyelin and saturated fatty acids, while non-responding patients correlate with loadings of cholesterol, C18:1 and C18:2. Combining ToF-SIMS data analysis with metabolic pathway databases has the potential to reveal diagnostic and prognostic biomarkers, an expanded understanding of the metabolism of carcinogenic tissues with the potential to improve patient outcomes.
Hollow silica nanoparticles (HSNPs) are regarded as a promising material for anti-reflective coating (ARC) due to their tunable void space and cage-structured shells. By applying the coating methods such as spin coating and dip-coating, HSNPs thin film can be created and reach a prominent enhancement of transmittance. However, the conventional coating technologies hardly fit in diverse substrates and satisfy the increasing demand of patterned thin film. Herein, we introduced the inkjet printing to accurately control the thickness, morphology and pattern of ARC thin film by managing the printing temperature, the drop spacing and the substrate wettability. The ink was prepared by mixing HSNPs (~28nm) and binder solution which enable each layer of HSNPs film have an outstanding mechanical resistance. With the precisely control of the thickness and the composition of each layer, a gradient ARC thin film can be created to achieve the optimized anti-reflective performance. With computer-designed patterns in millimeter scale, the ARC thin film can be applied to different substrates or devices like phone screen, camera lens and solar panels.
A Multi-technique Approach for Studying the Effect of Protein G B1 Orientation on Antibody Binding

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The orientation of adsorbed proteins on surfaces plays a vital role in the function and performance of biomaterials. Development of diagnostic tools such as sandwich ELISAs have focused on controlling the orientation of each protein layer. A full understanding of adsorbed proteins on surfaces, especially at the molecular level, is therefore essential. Our research addresses the challenges for characterizing protein orientation by developing new methods to study multilayer protein systems.

The aims of this study were to control and characterize the orientation of protein G B1, an IgG antibody-binding domain of protein G, on well-defined surfaces and measure the effect of its orientation on antibody binding using a variety of surface-sensitive tools and simulations. We hypothesize that binding selectivity would increase for well-ordered protein films due to higher availability of binding domains.

The surface sensitivity of time-of-flight secondary ion mass spectrometry (ToF-SIMS) enables us to distinguish between different proteins and their orientation by monitoring the changes in intensity of amino acid mass fragments. We have developed ToF-SIMS methods for analyzing the orientation of five different cysteine mutants of protein G B1 covalently attached to a maleimide surface. This technique was further extended by studying multilayer protein systems, specifically the binding of IgG antibodies to the protein G B1 films.

To study the effect of protein orientation on antibody binding, we utilized self-assembled monolayers (SAMs) to form protein G B1 films with both random and well-defined orientations. Using complementary techniques, such as X-ray photoelectron spectroscopy and quartz crystal microbalance with dissipation monitoring (QCMD), the ratio of bound IgG antibodies to protein G B1 increased from 0.06, when chemisorbed onto bare gold, to 0.2, when covalently attached to the surface. Further analysis revealed structure/orientation rearrangement of protein G B1 upon adsorption onto bare gold, which is likely responsible for decreased antibody binding.

Additionally, we developed and applied Monte Carlo (MC) simulations to predict protein orientation on a surface. The MC simulations showed that the outermost b-sheet of protein G B1 interacts most frequently with a hydrophobic surface. The predicted orientations were verified using molecular dynamics simulations, QCMD, and sum frequency generation. The model systems explored in this study are a first step in developing methodology using state-of-the-art tools that can be applied to more complex systems and expand our knowledge and control of biomolecules on surfaces.
Localized Surface Plasmon Resonance Enhanced Infrared CO₂ Sensing Using Room-Temperature, Solution-Processed Copper Sulfide Nanostructured Thin Films

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CO₂ gas sensing is important for energy reservation, environmental, agricultural and medical applications. Various gas sensors have been developed for CO₂. Among many approaches, Infrared (IR) gas sensors provide many benefits including high selectivity, high sensitivity and quick response time. Typical IR gas sensors, however, are expensive and difficult to miniaturize. Therefore it is necessary to develop a new concept of sensing technology that could alleviate these issues. The use of NIR gas sensing could utilize the low cost optical fiber, light source and light detector as a result of significant R&D efforts for telecommunication industry. Unfortunately, the NIR signals from most gases are typically weak in comparison with the mid-IR signals. To resolve this issue, the gas sensing of CO₂ with CuxS nanostructured thin films was studied in this work. CuxS is a non-toxic and low-cost semiconductor that possesses a localized surface plasmon resonance (LSPR) throughout the near-IR region. This feature makes CuxS an ideal amplifier for infrared gas sensing that work in the shorter wavelength region in which the absorption band of gases is typically low. Devices with different thicknesses of CuxS thin films were fabricated on glass using a modified successive ionic layer adsorption and reaction at room temperature. AFM, SEM, XRD and Raman spectroscopy were performed to characterize the films. Nanostructured CuxS thin films were obtained after a low temperature annealing process. The annealed CuxS films acquired a nanoplate-shape morphology that exhibited a strong LSPR. The CO₂ sensing of the devices was carried out at room temperature. The characteristic absorption band of CO₂ at 2.7 um was investigated using a FT-IR for CO₂ gas at various concentrations (0.6%, 2%, 4%, 10%, 22.5%, 30% and 100%). Significant signal enhancement was observed from CuxS thin films with 2D nanoplate-structure. This enhancement was attributed to the high carrier concentration and high surface-area-to-volume ratio of CuxS.
Scalable fabrication of patterned nanostructures by using microreactor-assisted nanoparticle deposition process and microfluidic channels

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In this study, we developed a method to fabricate a patterned films by using a combination of microreactor-assisted nanoparticle deposition (MAND) process and microfluidic channels. The MAND process is capable of generating nanoscale building blocks with controlled sizes, ranging from molecule clusters to nanoparticles, which allows for a more controlled and precise growth of nanostructures. Those nanomaterials serve as building blocks that can be delivered to the substrate surface through the microfluidic channels for a patterned film growth. The microfluidic channels are made of cured polydimethylsiloxane (PDMS) by using a replication from a patterned SU-8 photoresist-coated glass. By combining the two process together, CuO nanorod, ZnO nanorod, and silver nanoparticles were successfully deposited on glass substrate. The scaling up for the MAND was achieved by numbering-up the microchannel unit operations in parallel, allowing for the deposition of the films on various scales.
Microwave Assisted Covalent Surface Modification of Silicon Oxide Surfaces with Alcohol Compounds

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We demonstrated the use of microwave radiation as a tool to rapidly modify the surfaces of silicon oxides with alcohol containing compounds. Advantages of using alcohols as building blocks for the formation of self-assembled monolayers (SAMs) include their widespread availability, ease of handling, and stability against side reactions. Previous challenges to preparing monolayers of aliphatic alcohols on silicon oxide surfaces include the relatively high temperatures and slow reaction kinetics required by the alcohol condensation reaction. Microwave radiation delivers sufficient thermal energy for the condensation reaction to occur in a fast and efficient manner. We have successfully achieved the formation of uniform monolayers with aliphatic alcohols with water contact angle values up to 110° and typical hysteresis values of less than 2° on a series of different types of silicon oxide substrates. The techniques introduced herein can be applied to tune surface properties of silicon oxides using a number of alcohol containing compounds to create oleophobic, hydrophobic, hydrophilic, and/or charged surfaces.
Microreactor-Assisted Continuous ZnS Thin Film Deposition and Characterization

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As a wide band gap semiconductor, ZnS thin film has been employed as optical window or lens for infrared and phosphor in electroluminescent panels for a long time. In photovoltaic sector, ZnS can partially replace CdS buffer layer in thin film solar cell which make the whole process more environment friendly. Recent study suggested ZnS can be used as a precursor for CZTS thin film absorber layer.

Microreactor assisted thin film deposition has been applied to solution-based ZnS thin film deposition which has been proved to radically improve the throughput efficiency. In order to gain a better fundamental understanding of the growth kinetics of ZnS thin film by solution-based processes, snapshots of scanning electron microscopy (SEM) have been sequentially acquired and analyzed which provide the guide line for further improvement of the design of microreactor.
Microreactor-Assisted Fabrication of ZnO-Ag Hybrid Structure

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Abstract:
ZnO-based films doped with various metals such as Ferrous(Fe), gallium(Ga), Silver(Ag) is a promising alternative Conductive Transparent material for Indium Tin Oxide (ITO) due to its mechanic strength, high transmittance, low electric resistivity and less expense. ZnO-Ag hybrid structure has been achieved by microwave-assisted polyol-process reaction and hydrothermal method. We are trying to achieve a sandwich like structure by using microreactor-assisted batch reaction. Compare to the traditional method Microreactor-Assisted Nanoparticles Deposition (MAND) process is controllable and a better mixing can be provided. We are not only able to get various layer thickness by applying different deposit time, but get amorphous structure to improve film’s optical and electrical properties. Meanwhile, the usual deposition on a 1” x 1” substrate only takes several minutes comparing to the conventional hydrothermal film fabrication process the whole MAND process can be neglected. Which make the industrial fabrication much more effective.
A Protein Solid Electrolyte with Decoupled Ion Transportation

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Solid ion-conductors are well-known by ceramic and polymeric solid electrolytes. A combination of the advantages of them is critical to achieve not only high electrolyte performance, but also good material processability and mechanical flexibility. However, this has been extremely challenging due to the distinct conduction mechanisms in the two systems. Here, we report a new solid electrolyte based on a type of protein-ion complex, which realizes a ceramic-like or decoupled ion-transport in a polymeric matrix. It is found that the ion-conductivity of this protein electrolyte is extremely sensitive to the loading of lithium salt and the temperature for the complex formation. For an optimized protein electrolyte, it shows ionic conductivity of \(\sim 10^{-5} \text{ S/cm}\), transference number of 0.94 and modulus of 1 GPa at room temperature. Molecular simulations indicate that these unique properties are due to appropriate manipulation of the protein-ion complex configuration. The new insights can be utilized to provide guidelines for design, fabrication and optimization of high performance bio-solid electrolytes.
Molecular Analysis of Bacterial Collagen-Like Proteins by Time-of-Flight Secondary Ion Mass Spectrometry

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Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a highly sensitive surface analytical technique for chemical mapping at the molecular level. This technique was used to analyze collagen-like proteins (CLPs), a prerequisite to biofilm growth on plant roots, in order to provide chemical imaging of the interface between plant roots and biofilms under extreme conditions. Having a molecular understanding of this interface will help to show whether a localized water cluster microenvironment at this interface influences bacterial attachment. Results were acquired on dried, mixed, and packed powder CLPs, and on immobilized in situ liquid CLPs in a vacuum compatible microfluidic reactor. Spectral principal component analysis (PCA) results display the key peaks for two CLPs, which are consistent throughout different methods of analysis. In the future, these data will be used as a part of the data set in order to investigate the effect of extreme conditions (i.e., high salinity or RH) on bacterial attachment using in situ liquid SIMS molecular imaging.
Characterization of microbial aggregates using ToF-SIMS

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Abstract:

Microbial aggregate formed by Geobacter metallireducens and Geobacter sulfurreducens were capable of interspecies electron transfer. However, the key component that facilitates the aggregate formation is unknown. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) as a powerful surface analysis tools can help us solve this problem. Analysis of a series of dry co culture, pure culture and medium controls was conducted. Spectral Principal component analysis (PCA) was used to understand the key differences among such samples. We found some peaks that have higher abundance in all three types of biofilm cultures including possibly polymer, fatty acid and other organic molecules. Our preliminary results show that ToF-SIMS can be a powerful tool to study the biofilm surface at the molecular level and providing valuable information of the chemical component that is important in electron transfer and aggregate formation.

Key words: ToF-SIMS, aggregate, chemical component, Geobacter metallireducens, Geobacter sulfurreducens
Aqueous surfaces after photochemical and dark reactions of glyoxal and hydrogen peroxide (H$_2$O$_2$) have been studied by a microfluidic reactor coupled with in situ liquid Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) for the first time. Both positive and negative ion mode mass spectra provided complementary information of the surface reactions. Compared with previous results using bulk solutions, our unique liquid surface molecular imaging approach made it possible to observe glyoxal hydration (i.e., first and secondary products, hydrates), oxidation products (i.e., glyoxylic acid, oxalic acid, formic acid, malonic acid, tartaric acid.), oligomers(i.e., glyoxal dimer.), and water clusters (i.e., (H$_2$O)$_n$H$^+$, (H$_2$O)$_n$OH$^-$.) with sub-micrometer spatial resolution. Spectral principal component analysis was used to determine similarities and differences among various photochemical aging and dark reaction samples and controls. Observations of oxidation products give the physical foundation to deduce new reaction pathways at the aqueous surface. The first chemical mapping of water cluster changes between dark and photochemical aging provides the direct physical evidence that glyoxal oxidation affects the hydrophobicity and water microenvironment at the surface. SIMS three-dimensional chemical mapping enables visualization of the surface mixing state at the molecular level. Furthermore, our UV aging system suggested that the UV reaction has a highest rate at a certain reaction time. Compared with the short reaction time (i.e., 1-2 hr.), we found that water clusters tend to grow larger and larger cluster ions appear more dominant in the long reaction time (i.e., 4-6 hr.). We potentially provide a new way to investigate complex surface reaction mechanisms as an important source of aqueous secondary organic aerosol (SOA) formation in atmospheric chemistry.

**Key Words:** glyoxal, hydrogen peroxide, secondary organic aerosol, SALVI, liquid SIMS, aqueous surface reactions, water cluster, cluster ion, carboxylic acid.
Development of Microwave-assisted Catalytically Green Route from Low Density Polyethylene (LDPE) to Hydrocarbon Fuels

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Abstract:

Polyethylene (PE) is the major component of the total plastic content of the municipal solid waste (MSW). In this study, low density polyethylene (LDPE) was paralyzed over carbon catalysts using microwave-assisted in situ catalytic pyrolysis system at an ambient pressure. The influences of catalyst types and reaction conditions including reaction temperatures, ratios of catalyst to LDPE feed were investigated for an optimum condition. Greater cracking was observed across all operating temperatures, and a light liquid product with a narrow range of chain lengths was produced and compared to the non-catalytic pyrolysis. The non-condensable gaseous components of the pyrolysis was collected and analyzed by Micro-GC. The liquid product obtained from catalytic pyrolysis was characterized by physical and chemical tests. GC/MS analysis results showed that the condensed liquid product had a carbon chain length profile matching petrol and diesel fuels ranged from C5 to C21. Even though simple straight chain alkanes and alkenes still made up a significant fraction of the pyrolysis oil, there was a dramatic increase in aromatic compounds, and the presence of other types of hydrocarbons (cycloalkanes and branched alkanes and alkene) was also observed. The interpretation of FT-IR spectra also showed the formation of aromatic compounds and substituted aromatic compounds. It could be concluded that microwave assisted catalytic pyrolysis of LDPE resulted in a narrowly targeted pyrolysis products with a high potential commercial value, which could be used in combustion engines or as feed stock for refinery process.

Keywords: Hydrocarbon Fuel, LDPE, Microwave, Green Route
A Density Functional Theory Study of Adsorbate-Adsorbate Interactions as a Function of Coverage and Hubbard $U$ on RuO$_2$

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Density Functional Theory (DFT) has become widely used in the field of surface science as an approximation to the many-bodied Schrödinger equation and as the canonical tool for chemical modelling. When modelling transition metal oxide (TMO) surfaces, a Hubbard energy $U$ is used in conjunction with DFT for the treatment of $d$-orbital electrons. Addition of the Hubbard $U$ in the DFT Hamiltonian explicitly factors in on-site Coulombic repulsion of electrons, and has been shown to model the band-structures of strongly correlated systems with better empirical agreement than previous methods. Although the DFT+$U$ approach is common for calculating band-gaps and reaction mechanisms on TMO surfaces, the effects of the Hubbard $U$ on surface-adsorbate interactions are not yet fully explored. For example, Xu et al. (J. Phys. Chem. C 119(9) 4827-4833, 2015) found that adsorption energies on TMO surfaces vary with $U$ value, while Huang et al. (J. Phys. Chem. C 120(9) 4919-4930, 2016) showed that although DFT+$U$ improves band gap predictions, it also effects the surface energy calculations and bulk properties. It remains unclear how the addition of $U$ affects adsorbate-adsorbate interactions within the same TMO system. In this study we analyze how the addition of the Hubbard $U$ affects adsorbate-adsorbate interactions of adsorbed O on rutile RuO$_2$, as a function of adsorbate coverage and $U$ value.
Synthesis of Cu$_3$SbS$_4$ Nanoparticles for Solution Processed Thin Film Solar Cells

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As single p-n junction solar cells approach the Shockley-Queisser limit of 33% efficiency, new types of solar cell devices must be developed to provide improvements in solar energy collection efficiencies. Multijunction solar cells are a potential solution to improve efficiencies, where the multi-junction Shockley-Queisser limit has a maximum efficiency of 68%. Multijunction solar-cells are typically very expensive due to the need for precise control of film composition, structure, and the minimization of defects. Epitaxial growth on single-crystal substrates is the primary method to fabricate multijunction solar cells, which results in very high costs for these high-efficiency solar cells. Our efforts focus on the development of new thin film materials that may be directly integrated with current bulk silicon solar cells, and provide efficiency improvements while keeping manufacturing costs low.

High-efficiency single junction thin film solar cells commonly have absorber layers containing indium, gallium, selenium, cadmium, or tellurium, which are rare, toxic, or both. Furthermore, these absorber layers do not have optimal band gaps for tandem solar cells, when integrated with bulk silicon solar cells. A potential thin film absorber layer which eliminates these issues is copper antimony sulfide (CAS). CAS contains only earth-abundant and less toxic elements, making this material a viable candidate for sustainable solar cells manufacturing. Certain compositions of CAS are superabsorbers due to their very high absorption coefficients in the near-infrared/visible region of the solar spectrum, where these compositions have bandgaps between 0.74 to 0.98 eV. Both the high absorption coefficient and band gap make CAS a promising tandem solar cell material when integrated with silicon, or other thin film solar cell technologies. Chalcostibite (CuSbS$_2$) and famatinite (Cu$_3$SbS$_4$) are the most feasible phases for tandem solar cell applications due to the ease of phase pure synthesis and excellent optoelectronic properties.

In this study, Cu$_3$SbS$_4$ nanoparticles were synthesized using a hot injection approach under an inert argon atmosphere. These nanoparticles were spin coated on molybdenum coated glass substrates, followed by an air anneal. A second anneal in a sulfur rich atmosphere was used to crystallize the Cu$_3$SbS$_4$ nanoparticle films, and to increase the grain-size. We have characterized the resulting nanoparticles and films using X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy. The analysis of these results will be the primary focus of this presentation.
Characterizing the Solid Electrolyte Interface of Lithium-Sulfur Batteries using \textit{in situ} XPS

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Lithium-sulfur (Li-S) batteries are getting lots of attention in recent years because of their high theoretical specific capacity and energy density. The Li-S battery is a promising candidate to replace the Li-ion battery. However, there are some hurdles to overcome before they can be used in practical applications. One of the most critical challenges in Li-S batteries is the shuttling of long chain lithium polysulfides (LiPS), which results in the formation of non-uniform solid-electrolyte interface (SEI) layer on the electrodes. This SEI layer can cause the battery capacity to fade, hence it is important understand the properties of different SEI layers. It was suggested that the application of \textit{in-situ} or \textit{in-operando} techniques can capture the dynamic changes in the SEI layer during the battery cycling. Thus, our aim was to study the fundamentals governing the formation and subsequent evolution of SEI layer of various electrode-electrolyte systems in their working environment using \textit{in-situ} XPS and imaging XPS. In order to achieve this, we have developed an \textit{in-situ} XPS capability at Environmental Molecular Sciences Laboratory located in Pacific Northwest National Laboratory. Using this \textit{in-situ} configuration, we were able to determine the chemical state and composition of SEI layers formed on Li anode and graphite cathode in Li/ionic liquid/graphite battery system during the various charging/discharging cycles. The elemental and chemical state distribution of SEI layer was also studied using imaging XPS. The results obtained from this study will be discussed in detail.
Effect of Water on DME and Platinum Interactions

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Dimethyl ether (DME) has been widely used in fuel cells due to its non-toxic nature, inexpensive cost, high cetane value, quiet combustion, and relative ease of production. A platinum metal catalyst is commonly used to enhance the oxidation of DME at the anode. DME arrives at the anode surface after solvation in water and is then oxidized at the surface by water and its dissociation products. Previous experimental studies have suggested DME adsorption to be the rate limiting step and recent combined experimental and theoretical studies have suggested a formation of CHOC$_{ads}$ intermediates to be a critical step in the structure sensitivity of the reaction. In this study, we report density functional theory calculations of the effect of water on the interaction between DME and the Pt catalyst and the role of water in the reaction mechanism of DME oxidation. This is in contrast to the many other computational studies which exclude water, having DME react at the anode in vacuum.
Exploration of the Site-Pairing Preference of Framework Aluminum in ZSM-5 from its Reaction with Ga(CH₃)₃

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ZSM-5 is a zeolite catalyst marked with great versatility in catalytic application as a result of its flexibility in cation incorporation. Due to this property, the structure of ZSM-5 has been under question for its ability to accept divalent cations, implying that the substituted aluminum sites exist in paired configurations at specific locations within the zeolite structure. Trimethylgallium was used to probe these sites, as the dimethyl gallium fragments that exist in these locations following impregnation were thought to bridge via the terminal methyl groups. Experimental extended x-ray absorption fine structure (EXAFS) spectroscopy data supported this bridging configuration due to the presence of potential Gallium-Gallium scattering signals. Zeolite cluster models were created containing potential sites for aluminum pairings with dimethyl gallium fragments, with optimized geometrical conformations obtained from first principles using the Perdew-Burke-Ernzerhof (PBE) functional. The bridging was found unfavorable due to framework oxygen bonds dominating any possible methyl interactions, in addition to electronegativity effects with oxygen. Methyl bridged gallium is considered strongly unfavorable in the literature, so optimizations of dimeric trimethylgallium were performed, including van der Waals interactions, as well as methyl bridging configurations on silica. Using these, alternative models were developed to potentially explain the Gallium-Gallium scattering path reported by the EXAFS. Computation x-ray absorption near edge spectra (XANES) of some possible alternatives were computed using CASTEP for comparison with experimental data.

Biological Sensing using Transparent In-Ga-Zn-O Thin-Film Transistors on Curved Substrates

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Amorphous In-Ga-Zn-O (a-IGZO) semiconductors have a wide range of applications in high performance electronic devices, including the active material in thin film transistors for flat-panel displays and as the switching element for resistive random access memories. A key benefit of a-IGZO over amorphous silicon is that it enables low processing temperatures, while retaining relatively large electron mobilities, low operating voltages, and very low off currents. Herein, we present a facile, low-cost methodology to fabricate high-performance, transparent a-IGZO thin-film transistors (TFTs) on curved substrates by soft lithography. The IGZO channel and indium tin oxide source and drain were patterned using microcontact printing of an octadecylphosphonic acid self-assembled monolayer (SAM). A polymer stamp was used to transfer the SAMs to the thin film surface, and the SAMs were used as a chemical protection layer during wet etching. This approach allowed us to pattern a-IGZO TFTs on glass tubes with a diameter of 2.0 mm. The fabricated transistor has an on/off drain current ~1.3×10^6, an average electron mobility > 7.4 cm^2/Vs, an on/off hysteresis ~0.6, V and low gate leakage currents ~10^{-10} A. For sensing applications we have functionalized the back-channel a-IGZO surface with several sensing enzymes. We found that the functionalized a-IGZO provides a very high sensitivity to subtle changes in chemical concentrations in physiological buffer solutions. These results provide insight into new methodologies for low-cost manufacturing approaches of a-IGZO-TFTs for a range of applications including flexible and transparent sensing catheters, and can potentially lead to continuous roll-to-roll processing of IGZO-TFTs under ambient conditions.
Infrared Nanospectroscopy for Visualization of Heterogeneity in Soft Matter and Biological Systems

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Super resolution microscopy has revolutionized biological imaging, as evident by 2014’s Nobel Prize in Chemistry1. However, nanoscale chemically-specific information is necessary to address open questions on the structure-function relation in complex biological systems. A promising approach is Infrared Scattering-type Scanning Near-Field Optical Microscopy (IR-s-SNOM)2,3, which combines atomic force microscopy (AFM) with IR spectroscopy. IR spectroscopy is widely used to identify chemical compounds and molecular species, and can provide information about molecular interactions and local environment through small changes in vibrational modes. In IR s-SNOM, we can then probe nanometer-scale variations in aggregation, crystallinity, and conformation, in a wide range of soft matter and biological systems, with close to single biomolecule sensitivity.

Our initial studies on polytetrafluoroethylene (PTFE) demonstrate the ability to resolve differences in IR vibrational modes with nanoscale spatial resolution. We resolve significant changes in linewidth of the C-F vibrational mode, which reflect local heterogeneity even in a homopolymer system2. We extend these studies to the study of secondary structure and conformation in biological systems. Specifically we probe the Amide I and II absorption bands, which are sensitive reporters of protein structure and organization4,5. We investigate conductive pili nanofilaments produced by the soil bacterium Geobacter sulfurreducens, where the mechanism of electron transport is not well-understood. Recent studies6 have suggested that aromatic amino acids tyrosine (TYR) and phenylalanine (PHE) are closely packed in pili, enabling intermolecular electron delocalization due to π-stacking that can give rise to metallic-like conductivity7,8. Changes in pH are correlated with changes in secondary structure, as determined through the Amide bands, and also a large increase in conductivity. By probing the secondary structure of small numbers of pili proteins, and its variation depending on local environmental conditions, we will determine how the conformation of pili affects electron transfer8. This will aid in development of models of the structure of pili nanofilaments and an understanding of the mechanism of conduction.

Our work demonstrates that IR s-SNOM is an intrinsically label-free tool for investigating organization and interaction of molecules in soft matter systems. s-SNOM has strong potential for elucidating the structure-function relationship for many biology applications, in particular for proteins which cannot be studied by any other existing structural methods due to their small size (< 5 nm) and difficulty in crystallization.

REFERENCES:
Adsorption Characteristics of Hydrogen on RuO$_2$(110) Surface

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Ruthenium oxide is used extensively as a co-catalyst in a wide range of photocatalytic water splitting systems. As such, understanding how it promotes the evolution of hydrogen and oxygen is of high importance. In this study, we employ scanning tunneling microscopy (STM) to study adsorption and reaction of hydrogen on a model stoichiometric RuO$_2$(110) surface. Following the adsorption of low H$_2$ coverages (H$_2$/Ru $< 0.2$) at 5 K, the atomically-resolved images reveal asymmetric features occupying both ruthenium and bridging oxygen surface sites. Based on the STM bias-dependent studies, the asymmetric features are interpreted as heterolytically dissociated H$_2$ forming hydride-hydroxyl pairs. These features adopt (2$\times$1) and c(2$\times$2) long range order, with the latter one being preferred. At higher coverages (H$_2$/Ru $> 0.2$), new features centered on Ru sites neighboring the hydride-hydroxyl pairs appear. These features are interpreted as chemisorbed molecular hydrogen which with further coverage increase forms linear chains along the Ru rows. Upon annealing to 120 K, most of the chemisorbed H$_2$ desorbs and further temperature increase above 250 K yields fully hydroxylated surface. This fully hydroxylated surface does not adsorb H$_2$ even at 5 K. No H$_2$ adsorption and dissociation is observed on bare RuO$_2$(110) at room temperature. These studies demonstrate for the first time the adsorption and dissociation mechanism of H$_2$ on the model RuO$_2$(110) surface.
Development of a XRF detection unit for capillary electrophoresis

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On-line species separation and detection is an essential way to elucidate elemental mobilization parameters. Separation techniques, such as capillary electrophoresis (CE), have been used in for elemental separation and is most commonly coupled with UV-visible spectrometry, a non-destructive on-line detector technique. However, UV-vis does not provide elemental information. To resolve this limitation, MS coupled with suitable ionization sources or optical emission spectroscopy has been used, but this method requires physical access to the mobile phase. Non-destructive on-line detection is feasible by X-ray fluorescence spectrometry (XRF). The viability of this approach has been shown previously using Synchrotron XRF (SR-XRF) and micro-XRF set-ups. However, application of XRF detection for liquid separation has remained limited because the laboratory XRF, though having elemental sensitivity, was not competitive to UV-vis detection regarding cost and maintenance efficiency, as well as laboratory footprint. Hence, only a few analyses on highly specific applications requiring the most sophisticated instrumentation, like SR-XRF, were realized. Recently, new developments in XRF low-power tube and electrically cooled detectors have allowed the miniaturization of XRF instrumentation, and made it more cost- and maintenance efficient (e.g. led to commercializing of hand held XRF equipment). Accordingly, it is likely that on-line elemental detection in CE and HPLC can be cost efficiently enabled using XRF instrumentation. Our project aims to set up a low power XRF-detection system for CE in order to develop an elemental sensitive non-invasive detector for liquid-based separation technique. Key parameters will be evaluated, such as windows, flow, detection limits, precision, and accuracy. Here we present the outline of the set up and first results on the custom built CE instrumentation, as well as static detection limits from a micro-XRF instrument newly build at WSU. Because of the cost- and maintenance-efficient nature of modern XRF analysis, the research will involve graduate and undergraduate students in “hands-on” research of instrument development. Once the laboratory set up is successfully established, it will allow for a sensitive and accurate probing of elements in the liquid phase and provide excellent conditions for the study of dynamic change in oxidation state during elemental migration.
Surface Expression of Adhesion Proteins on Differentiating Adipose Stem Cells Grown with Biochemical and Mechanical Stimuli
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Introduction: Articular cartilage (AC) is a smooth tissue at the end of bones in a moving joint. It supports loads and acts as a lubricant. Because AC is avascular, it lacks the ability for self-repair. This complicates clinical therapies for repairing damaged tissues resulting from trauma or the degenerative disease osteoarthritis. The inadequacies of current treatments have prompted research with focus on the regeneration of AC using tissue bioengineering techniques. In this project the aim is to engineer an AC tissue with functional properties similar to native AC by differentiating human adipose-derived stem cells (hADSCs) in our novel centrifugal bioreactor (CBR) with chondrogenic medium (CM) and oscillating hydrostatic pressure (OHP). We hypothesize that CM and OHP will result in engineered AC with mechanical properties closer to those of native cartilage and that the cell surface density of β1-integrins will be greater in samples with insufficient extracellular matrix.

Materials and Methods: hADSC-derived tissues were cultured as micromass, pellet or in the CBR for 21 days. Atomic force microscopy (AFM) was used with gold-coated colloidal cantilevers to scan a 10 µm × 10 µm area with at least 256 points on 3 scan areas per sample. The Young’s moduli of the tissues were determined from fitting the Hertz model of contact mechanics to the force-indentation profiles. Surface adhesion molecules were located using a gold-coated sharp cantilever modified with monoclonal antibodies specific for β1-integrin and N-cadherin. As the cantilever contacts the cell surface, specific adhesion interactions can be identified from specific signatures that represent antibody-antigen bindings. These events were collected for each treatment group and compared among treatments.

Results and Discussion: The Young’s moduli of tissues increased by 44-fold when grown with OHP compared to static cultures and further increased by 1.8-fold with the addition of CM. N-cadherin was expressed more than 2-fold in CBR samples compared to static cultures which may be a result of shear stress and OHP induction of N-cadherin expression to differentiate the hADSCs into chondrocytes. β1-integrin counts were 2- to 5- fold larger in static cultures compared to samples with OHP which may be explained by the function of β1-integrins to attach the cells to the extracellular matrix (ECM). When ECM is insufficient, such as in static cultures, the cell expresses more β1-integrin to attach to the little ECM that is present.

Conclusions: The addition of OHP increases the Young’s modulus of tissues grown from hASCs and that gets further increased with the addition of CM. β1-integrin surface expression is higher in cultures with weak ECM.

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In situ Characterization of Green Rust in Ionic Liquids by Liquid ToF-SIMS and SALVI

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Abstract:

Ionic liquids as green solvents have wide applications in material synthesis, catalysis, and separation. A model switchable ionic liquids (SWILs) consisting of 1, 8-diazabicycloundec-7-ene (DBU) and 1-hexanol (Hex) loaded with CO₂ gas was chosen to synthesize nanocrystalline green rust. Iron acetate was used initially dissolved in methanol. Green rust was formed after the mixture undergoing solvent exchange in the DBU and Hex SWILs. The structure and oxidation state of nanocrystalline green rust were confirmed. More importantly, the molecular structure change of the ionic liquid leading to green rust formation was characterized using in situ liquid using time-of-flight secondary ion mass spectrometry (ToF-SIMS) coupled with a vacuum compatible microfluidic reactor, SALVI (System for Analysis at the Liquid Vacuum Interface). Principal component analysis (PCA) was conducted to identify the key components of the solvated iron acetate in methanol and the green rust synthesized in the SWILs. Our results show that liquid SIMS can be a useful tool to study complex liquids at the molecular level providing insights in predicative synthesis of nanomaterials using environmentally friendly solvents.
Annealing behavior of hydrogen in H$_2^+$ ion implanted polycrystalline Tungsten

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Abstract: Due to its outstanding physical properties, tungsten has been proposed as a plasma-facing material in fusion reactors. Degradation of the material properties is expected to occur as a result of hydrogen implantation and trapping in W. It is necessary to study H retention and release in W and develop an understanding of the associated processes. In this study, a polycrystalline tungsten plate was implanted with 80 keV H$_2^+$ ions to a fluence of 2×10$^{21}$ H$^+$/m$^2$ at nominally room temperature. H depth profiles are investigated in situ as a function of annealing temperature using time-of-flight secondary ion mass spectrometry (ToF-SIMS). Surface topography and lattice defects in the implanted sample are also studied using scanning electron microscopy (SEM) and x-ray diffraction (XRD). Two groups of blisters are formed in the implanted tungsten with mean sizes of ~0.7 and 2 µm. No changes in the surface topography are observed after thermal annealing at 600°C. ToF-SIMS results show that the implanted H atoms diffuse into a deeper region. In general, there is a rapid release of H from W at temperatures below 150°C, followed by a more gradual release at higher temperatures during one-hour isochronal annealing. A possible release stage between 400 and 500°C is observed. Isothermal annealing at 500°C does not lead to further H release after 30 min. In addition, the trapped H atoms in W are stable at room temperature after a period of 4 months. Possible effects of a thin carbon layer deposited onto the sample surface during ion implantation are also discussed.

Key words: Hydrogen trapping, thermal annealing, polycrystalline tungsten, ToF-SIMS

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Fish scales are one example of a biological structure that provides physical protection without restricting the flexibility or mobility of the bearer. These types of structures are often complex composites and have attracted interest in the field of biomimetics, including the areas of personal armor and protective equipment. Elasmoid fish scales consist of mineral and organic materials, including hydroxyapatite, calcium carbonate and collagen fibers. Scales from pirarucu (Arapaima gigas), tarpon (Megalops atlanticus), and carp (Cyprinus carpio) were fixed, dehydrated, mounted in epoxy and micromotmed to expose cross-sections. These sections were analyzed using ESCA to characterize the variations in composition through the scale thickness. Elemental images were obtained for a qualitative evaluation, and spectra from small area analyses provided information for a complementary quantitative analysis.
Investigation of the broadening of the bandgap of monolayer graphene supported on Cu(111)

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There has been great attention payed to graphene by researchers recently, due primarily by a push for better 2-D conducting and semiconducting materials for application in nanoelectronics. However, graphene is a zero bandgap material which complicates its usefulness in electronics. We investigate the broadening of the bandgap of monolayer graphene supported on Cu(111) via the adsorption of atomic oxygen radicals using the scanning tunneling microscopy (STM) and spectroscopy (STS) techniques. We observe an immediate bandgap opening of ~200 meV with as little as 5% coverage while a sample with much higher coverage (~25%) has a bandgap of ~400 meV. As a $p$-type dopant, radical oxygen tends to lower the Fermi energy relative to the Dirac level, an effect that is seen in the higher coverage sample but not in the lower dosed sample (by ~180 meV). This shows that oxidation of monolayer graphene is a powerful tool for creating a tunable 2-D semiconductor, to the maximum bandgap of 1.6 eV.