

SURFACE ANALYSIS

22



Energy Sciences Center, Richland, WA 99354

September 14-16, 2022

**41st Annual Symposium on Applied Surface Analysis
and
33rd Annual Symposium of the Pacific Northwest
Chapter of AVS, The Science and Technology Society**

Welcome to Surface Analysis '22: Joint Meeting of Applied Surface Analysis and PNWAVS

On behalf of the organizing committee, we warmly welcome you to the Energy Sciences Center (ESC) on the Pacific Northwest National Laboratory campus for the Surface Analysis '22 Meeting. We hope that colleagues and friends, together with new arrivals in the field, will find the sessions stimulating and that you will create, renew, and deepen acquaintances and collaborations throughout the conference.

If there is anything we can do to improve your visit, please visit our registration desk located in the ESC lobby.

Conference co-chairs:

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Tiffany Kaspar
Pacific Northwest National Lab
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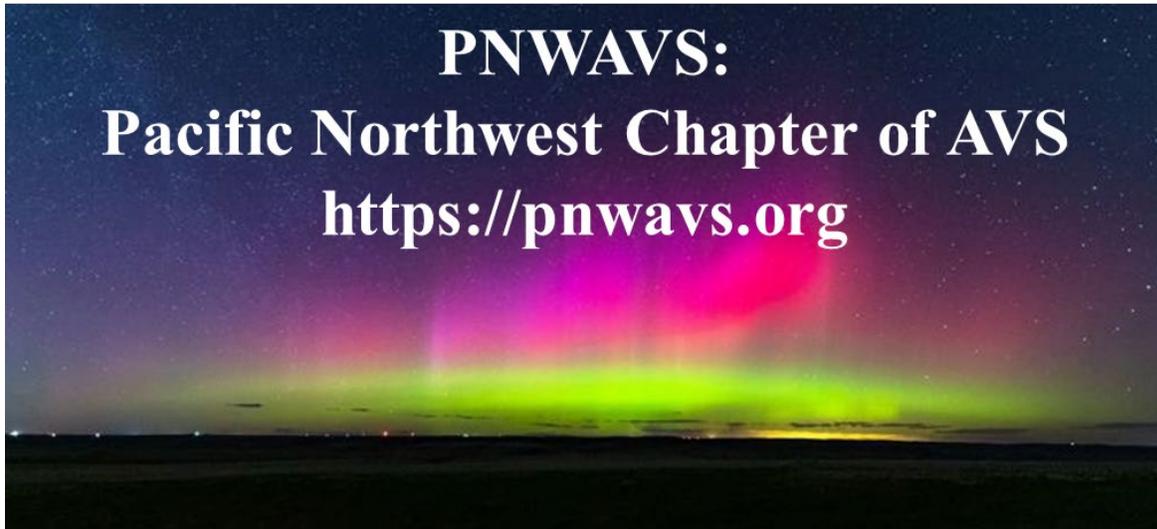
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Local Arrangements:

Lara Hastings, Jene Iceberg, and Becky Ford, Pacific Northwest National Lab
Shuttha Shutthanandan, Pacific Northwest National Lab





2022 marks the 60th anniversary of PNWAVS, which was founded in 1962 as the first local chapter of the AVS. We are a nonprofit organization which promotes communication, dissemination of knowledge, recommended practices, research, and education in the use of vacuum and other controlled environments to develop new materials, process technology, devices, and related understanding of material properties for the betterment of humanity.

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Please contact us if you are interested in getting involved in PNWAVS. We will hold a Board Meeting immediately following the Symposium on Friday afternoon.

In celebrating our 60th anniversary, we will recognize the past PNWAVS Chairs at the BBQ Banquet on Thursday night. The list of past PNWAVS Chairs includes many of the notable vacuum scientists from the Pacific Northwest region. We appreciate their dedication to keeping vacuum and surface science pursuits thriving in the region.

Name	Year(s) served	Affiliation during service (if known)
Roland R. LaPelle	1962-1964	Boeing
Edwin Srebnik	1964-1966	
Joseph L. Rumney	1967-1970	
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Kenneth W. Bird	1970-1971	
B. Michael Wareham	1972	
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Wallace C. Budke	1975-1978	
M. Tom Thomas	1979	Pacific Northwest [National] Laboratory
Virginia E. Lowe	1982	Boeing
Paul R. Davis	1983-1984	Oregon Graduate Center
Michael A. Bayne	1985	Tektronix
John F. Wager	1986	Oregon State University
Philip R. Watson	1987-1989	Oregon State University
Eric M. Stuve*	1990	University of Washington
David G. Castner*	1991-1992	University of Washington
J. Thomas Dickinson*	1993	Washington State University
Scott A. Chambers*	1994	Pacific Northwest National Laboratory
John P. LaFemina	1995	Pacific Northwest National Laboratory
Mark Bussell	1996	Western Washington University
Steve Joyce	1997	Pacific Northwest National Laboratory
Marjorie A. Olmstead*	1998-1999	University of Washington
J. Thomas Dickinson*	2000	Washington State University
Michael Henderson*	2000-2001	Pacific Northwest National Laboratory
Fumio S. Ohuchi*	2001-2002	University of Washington
Gregory S. Herman*	2002-2003	Hewlett-Packard
Theva Thevuthasan*	2003-2004	Pacific Northwest National Laboratory
David Patrick	2004-2005	Western Washington University
Kerry Hipps*	2006	Washington State University
Zdenek Dohnalek*	2007-2008	Pacific Northwest National Laboratory
Ursula Mazur	2009	Washington State University
Shuttha Shutthanandan*	2010	Pacific Northwest National Laboratory
Alex Chang	2011	Oregon State University
Tiffany Kaspar	2012	Pacific Northwest National Laboratory
Louis Scudiero	2013	Washington State University
Mark Engelhard*	2014	Pacific Northwest National Laboratory
David N. McIlory	2015	University of Idaho
Scott Smith	2016	Pacific Northwest National Laboratory
Liney Arnadottir	2017	Oregon State University
Yingge Du	2018	Pacific Northwest National Laboratory
David Y. Lee	2019	Washington State University
Zihua Zhu	2020	Pacific Northwest National Laboratory
Zhenxing Feng	2021	Oregon State University
Elton Graugnard	2022	Boise State University
* AVS Fellows		



Applied Surface Science Division Advancing the Science and Technology of Materials, Interfaces, and Processing

The mission of the Applied Surface Science Division of the AVS is to provide a forum for research and education in the preparation, characterization, modification, and utilization of surfaces and interfaces in practical applications. The current vision for implementation of the mission statement includes promotion of science and technology relevant to:

- understanding solid/gas, solid/solid, and solid/liquid interfaces of practical importance
- methods for characterizing these interfaces for composition, bonding, topology and structure
- modification of interfaces to optimize the stability, reactivity or other properties of components and/or devices

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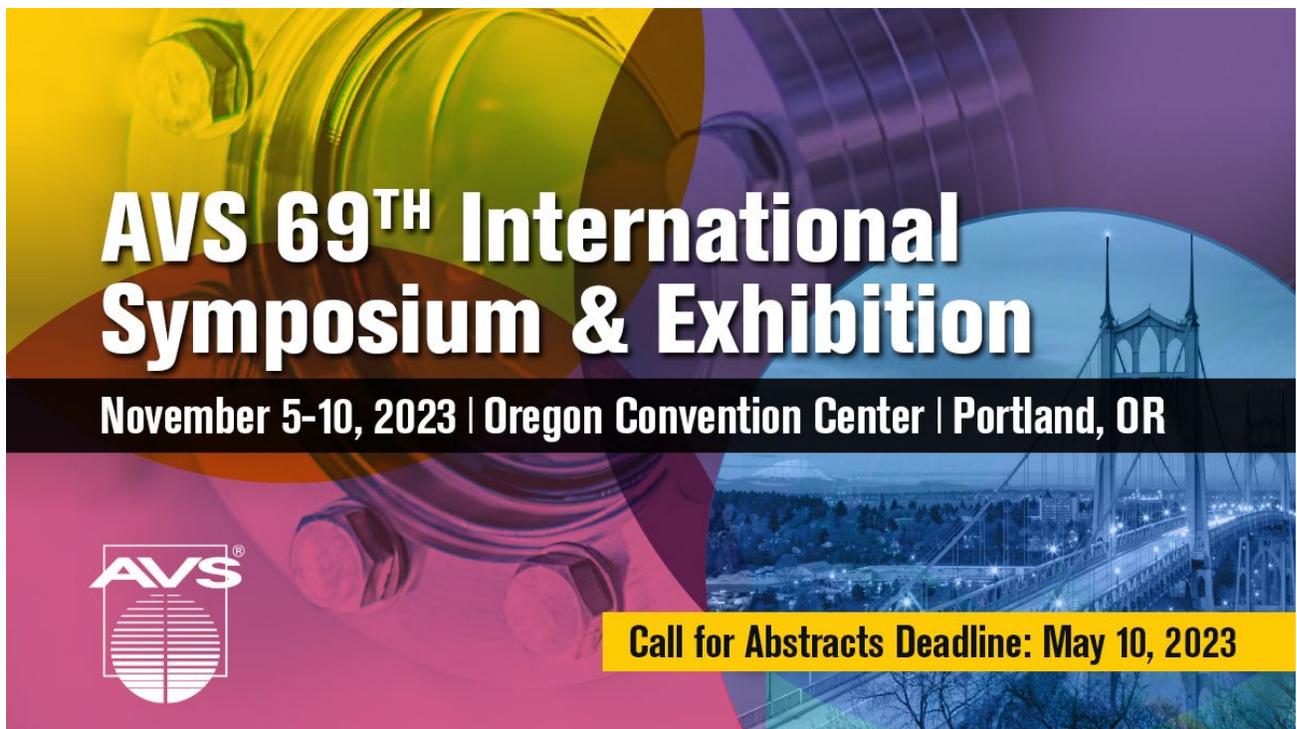
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VENDOR EXHIBITION



Surface Analysis 2022 Schedule

In person Meeting: **Platinum Room, Energy Sciences Center**

Microsoft Teams Link: [Click here to join the meeting](#)

Meeting ID: 244 558 982 63

Passcode: SjF3v8

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WEDNESDAY, 14 SEPTEMBER			
8:05-8:20	Elton Graugnard	Co-Chair Greeting	Boise State University
8:25-8:30	Lou Terminello	Associate Lab Director for Physical and Computational Sciences Directorate Opening Remarks	Pacific Northwest National Laboratory

Session 1 Chair: Elton Graugnard

8:35-9:15	David Bergsman	Invited: Atomically precise Ultrathin Films and Coatings through Atomic Layer Processing	University of Washington
9:20-9:40	Prescott Evans	Palladium Nucleation and Alloying at the WTe ₂ (001) Surface	Pacific Northwest National Laboratory
9:45-10:05	Mohammad Delower Hossain	Quantification of Oxygen Vacancies in Complex Oxides	Pacific Northwest National Laboratory

10:05-10:35 Break in Energy Sciences Center (ESC) Lobby

10:35-11:15	Shalini Tripathi	Tutorial: Explore the 'room at the bottom' Introduction to Transmission Electron Microscopy (TEM)	Pacific Northwest National Laboratory
11:20-12:00	Melissa Santala	Invited: Characterization of the Atomic-level Structure of Pt/ γ -Alumina and Pt/ θ -Alumina Interfaces	Oregon State University

12:00-1:30 Lunch in ESC Lobby

Session 2 Chair: Tiffany Kaspar

1:30-2:10	Arun Devraj	Tutorial: Atom Probe Tomography (APT)	Pacific Northwest National Laboratory
2:15-2:35	Dallin J. Barton	The Direct Observation of Oxygen and Hydrogen Influence on Model Austenitic Stainless Steel using Atom Probe Tomography	Pacific Northwest National Laboratory

2:35-3:05 Break in ESC Lobby

3:05-3:45	Ann Chiamonti	Invited: Atom Probe Tomography Using a Wavelength-Tunable Femtosecond-Pulsed Coherent Extreme Ultraviolet Light Source	National Institute of Standards and Technology
3:50-4:10	Jesse Huso	Photoluminescence Mapping of Semiconductors and Oxides	Klar Scientific/ Washington State University
4:15-4:55	Sten Lambeets	Invited: Field Ion Microscopy and Operando Atom Probe for Surface Dynamics	Pacific Northwest National Laboratory

Surface Analysis 2022 Schedule

Session 3

5:00-8:00

Chair: Shuttha Shutthanandan

Poster Session and Vendor Exhibit with Hors d'oeuvres in ESC Lobby

THURSDAY, 15 SEPTEMBER

Session 4 Chair: Liane Moreau

8:35-9:15	Qian Zhao	Tutorial: X-ray Photoelectron Spectroscopy (XPS)	Pacific Northwest National Laboratory
9:20-9:40	Christopher Lee	Investigating the Reactivity of Formic Acid on Reconstructed Fe ₃ O ₄ (001)	Pacific Northwest National Laboratory
9:45-10:05	Chris Moffitt	Developments in the Surface Analysis of Battery Materials	Kratos Analytical

10:05-10:35 Break in ESC Lobby

10:35-11:15	David Estrada	Invited: Two-dimensional and Layered Materials at the Energy-Healthcare-Water Nexus	Boise State University
11:20-12:00	Arthur Barnard	Invited: Tools for Dynamically Tuning Interactions in 2D Quantum Materials	University of Washington

12:00-1:30 Lunch in ESC Lobby

Session 5 Chair: Jean-Sabin McEwen

1:30-2:10	Stacy Copp	Invited: Developing a "Genome" for Atomic Precision: DNA-templated Luminescent Silver Nanoclusters	University of California, Irvine
2:15-2:35	Liane Moreau	Structure/Property Relationships in Actinide Oxide Nanoparticles	Washington State University

2:35-3:05 Break in ESC Lobby

3:05-3:45	Jeffrey Bell	Invited: Global Health: The push for clean energy and accessible diagnostics	Washington State University
3:50-4:10	Kelsey Stoerzinger	Understanding competitive electrochemical reactions on strained surfaces	Oregon State University/ Pacific Northwest National Laboratory
4:15-4:55	Zihua Zhu	Tutorial: Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)	Pacific Northwest National Laboratory

Session 6

5:00-6:00

Vendor Exhibit in ESC Lobby

6:00-8:00

Dinner, Plenary Talk and Award Ceremony

Plenary Talk: **Aurora Borealis and Astrophotography in Eastern Washington**, Shuttha Shutthanandan and John Cliff, Pacific Northwest National Lab

Surface Analysis 2022 Schedule

FRIDAY, 16 SEPTEMBER

Session 7 Chair: Arthur Barnard

8:35-9:15	Harman Khare	Invited: Scratching the Surface: Enabling Tribological Materials Development through Multiscale Tribometry	Gonzaga University
9:20-10:00	Paul Davis	Tutorial: Atomic Force Microscopy (AFM)	Boise State University
10:05-10:25	Grant Johnson	Intermolecular and Surface Interactions Influence the Properties of Supported Polyoxometalates	Pacific Northwest National Laboratory

10:25-10:55 Break in ESC Lobby

10:55-11:35	Loni Kringle	Invited: Structural Transformations in Supercooled Liquid Water	Pacific Northwest National Laboratory
11:40-12:20	Tanvi Ajantiwalay	Tutorial: Scanning Electron Microscopy (SEM) and Plasma Focused-Ion Beam (FIB)	Pacific Northwest National Laboratory

12:20-12:30 Closing Remarks

12:30-2:00 Boxed Lunch

12:30-2:00 PNWAVS Board Meeting

2:05-4:30 **Lab Tours**

Poster Session

Graduate Poster Session - Wednesday, September 14 - Surface Analysis '22		
Poster Number	Title and Presenter	Note
G 1	<p>Two-phase solvothermal synthesis of Gd-doped CeO₂ nanoparticles and their crystallographic and electronic structural characterization</p> <p><i>Shinhyo Bang, Washington State University</i></p>	Graduate
G 2	<p>In-Situ XAS Studies of Cu-S Complex Catalysts for Electrochemical CO₂ Reduction Reaction</p> <p><i>Chun-Wai Chang School of Chemical, Biological, and Environmental Engineering, Oregon State University,</i></p>	Graduate
G 3	<p>Impact of catalyst morphology and electrocatalytic hydrogenation of benzaldehyde</p> <p><i>Padavala Sri Krishna Murthy Oregon State University</i></p>	Graduate
G 4	<p>Seed-mediated anisotropic growth of UO_{2+x} nanoparticles directed by solvent conditions</p> <p><i>Natalie Yaw Department of Chemistry, Washington State University</i></p>	Graduate
G 5	<p>The application of permanent magnets for high capacitance polyaniline-modified electrodes</p> <p><i>William McLeod Washington State University</i></p>	Graduate
G 6	<p>Adsorption of H₂O derivatives and CO₂ on Lanthanum-Based Perovskites: An Analysis From First Principles</p> <p><i>Ariel Whitten Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University</i></p>	Graduate
G 7	<p>Preparation and Characterization of Model Homotopic Catalysts: Rh Adatoms, Nanoparticles, and Mixed Oxide Surfaces on Fe₃O₄ (001)</p> <p><i>Marcus A. Sharp,^{1,2} 1. Voil and School of Chemical Engineering and Bioengineering, Washington State University, 2. Physical and Computational Sciences Directorate and Institute for Integrated Catalysis, Pacific Northwest National Laboratory</i></p>	Graduate
G 8	<p>Elucidating the Influence of Structure Directing agents on the Aluminum Distribution of SSZ-39</p> <p><i>Charles Umhey, Washington State University</i></p>	Graduate
G 9	<p>Coverage Analysis of 2,3-butanediol on RuO₂ (110) using First Principles</p> <p><i>Carrington Moore</i></p>	Graduate

Poster Session

	<i>Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University</i>	
G 10	Electrocatalytic nitrate reduction to ammonium over 3d transition metals: Role of resting electronic structure on selectivity <i>O. Quinn Carvalho,1,2, 1. School of Chemical, Biological and Environmental Engineering, Oregon State University 2. Advanced Light Source, Lawrence Berkeley National Laboratory</i>	Graduate
G 11	Intrinsic Area Selective Atomic Layer Deposition of MoS₂ Thin Films <i>Wesley Jen Boise State University</i>	Graduate
G 12	Two-Steps MgMOF74 Thin Film Fabrication with Controllable Pattern via Inkjet Printing Techniques <i>TZER-RURNG SU Oregon State University</i>	Graduate
G 13	Deposition and Growth of Metal-Organic Frameworks Thin Films via a Vertical Microfluidic Probe <i>Hsin-Mei Kao Oregon State University</i>	Graduate
G 14	A millikelvin scanning probe microscope for probing emergent states in layered quantum materials <i>Chadwick Evans University of Washington</i>	Graduate
G 15	Controllable shear of a 2-dimensional magnetic <i>Morgan Sherer University of Washington</i>	Graduate
G 16	The Study of Interfacial Reactions of Layered Oxide Cathodes in Water-in-Salt Electrolytes <i>Mason Lyons School of Chemical, Biological, and Environmental Engineering, Oregon State University</i>	Graduate
G 17	Light olefine oligomerization on Ni single cations: Reaction mechanism and evolution of the active site environment <i>Julian Schmid Pacific Northwest National Lab</i>	Graduate
G 18	MOCVD Growth of Monolayer MoS₂ and WS₂ <i>Michael Curtis, Boise State University</i>	Graduate
G 19	Studying Additively Manufactured Ti-6Al-4V Using High-Resolution Nano-scale Characterization Techniques: KPFM, SEM, EBSD, and EC-AFM	Graduate

Poster Session

	<i>Olivia Maryon</i> <i>Boise State University</i>	
G 20	Additive Manufacturing of Piezoelectric Surface Acoustic Wave Thermometers <i>Nicholas McKibben</i> <i>Boise State University</i>	Graduate
G 21	Thermal Atomic Layer Etching of MoS₂ Films <i>John Hues</i> <i>Boise State University</i>	Graduate
G 22	Trace Detection of L-Dopa Utilizing a Simple 3D Printed Carbon Electrode <i>Dalton L. Glasco</i> <i>Washington State University</i>	Graduate
G 23	Laser Induced Graphene for Gas Sensing Applications in Environmental Monitoring <i>Cadré Francis</i> <i>Boise State University</i>	Graduate
G 24	Tailoring the Solvation Structure of Dilute Ether Electrolyte for Stabilized High-Voltage Cathode Interface in Li Metal Battery <i>Zheng Li</i> <i>Purdue University</i>	Graduate
G 25	Amorphous-to-Crystalline Transition of the Mixed Oxide SnO₂/TiO₂ <i>Pritha Biswas</i> <i>Department of Physics, Oregon State University</i>	Graduate
G 26	Understanding Facet-Dependent Reactivity and Selectivity of IrO₂ in Water Through Ambient Pressure XPS and Electrochemistry <i>Molly Vitale-Sullivan,</i> <i>School of Mechanical, Manufacturing, and Industrial Engineering, Oregon State University</i>	Graduate
G 27	Substrate-metal interaction as a descriptor for electrocatalytic hydrogenation of carbonylic molecules on Palladium in aqueous phase <i>Julia B. D. Moreira</i> <i>Institute for Integrated Catalysis, Pacific Northwest National Laboratory</i>	Graduate
G 28	Residual Ions Trapping at the Σ3 Grain Boundaries of Catalytic Pt Nanoparticle Assemblies <i>Jack Grimm^{1,2}</i> <i>¹Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory</i> <i>²Department of Materials Science and Engineering, University of Washington</i>	Graduate
G 29	Laser Sintering of Printed Metal Films for Flexible Hybrid Electronics <i>Ellie Schlake</i> <i>Department of Electrical and Computer Engineering, Boise State University</i>	Graduate

Poster Session

Undergraduate Poster Session - Wednesday, September 14		
Poster Number	Title and Presenter	Note
UG 1	Rh doped "29 oxide" Cu_xO Energy Barriers for H₂ Dissociation <i>Eva Arm</i> <i>Voiland School of Chemical Engineering and Bioengineering, Washington State University</i>	Undergraduate
UG 2	Hydrogenation of Carbon to Methane on Flat and Stepped Platinum Surfaces <i>Stuart Helikson</i> <i>Oregon State University</i>	Undergraduate
UG 3	Gold coated doped-iron oxide nanoparticles for multimodal radiotherapy <i>Holly Heckerman, Katherine Busiek</i> <i>Washington State University</i>	Undergraduate
UG 4	The Design of In Situ Hydrogen Charging Devices <i>Andrew "Mengkong" Tong</i> <i>Pacific Northwest National Lab</i>	Undergraduate
UG 5	Studying the Mechanical Properties Influenced by Hydrogen Interaction in Austenitic Stainless Steels Using In-situ Nanoindentation Technique <i>Cassandra L. Orozco</i> <i>Physical and Computation Sciences Directorate, Pacific Northwest National Laboratory</i>	Undergraduate

General Poster Session - Wednesday, September 14		
Poster Number	Title and Presenter	Note
1	Exploring the Complex Chemistry and Degradation of Ascorbic Acid in Aqueous Nanoparticle Synthesis <i>Debashree Roy,</i> <i>Department of Chemistry, Washington State University</i>	General

Invited Talks

Atomically-precise Ultrathin Films and Coatings through Atomic Layer Processing

David S. Bergsman^{1,*}

¹*Department of Chemical Engineering, University of Washington, Seattle, Washington, USA 98195.*

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Recent years have seen a surge of interest in the development of scalable tools for nanomaterials synthesis. Many emerging technologies, like solar cells, batteries, catalysts, and membranes, rely on atomically-precise coatings to operate effectively. One suite of tools, known collectively as atomic layer processing (ALP), is particularly interesting for nanomaterials synthesis, due to its ability to create ultrathin films with sub-nanometer thickness and compositional control. ALP has also been used in the semiconductor industry over several decades, making it easy to deploy in other manufacturing processes. However, as demand for nanotechnology increases, there is a continued need to expand the library of materials that can be made with these tools and to accelerate the pace with which these materials are deployed.

This presentation will highlight our group's work to expand the applicability of ALP to new materials and new use cases. First, the use of vapor phase infiltration (VPI) to modify polymers will be discussed, highlighting our work to make polymer membranes conductive and to upgrade their stability and performance. Next, we will review the use of molecular layer deposition (MLD), exploring our work to study how this technique differs from its inorganic older sibling atomic layer deposition. Last, we will describe how high-throughput materials testing is needed for rapid materials deployment, exploring our group's work to construct a high-throughput deposition system and to collect data on processing conditions into a database for additional analysis. Through these projects, our group expects to greatly expand the library of materials accessible to ALP and improve the speed with which these new materials can be translated into commercial technologies.

Invited Talks

Tools for dynamically tuning interactions in 2D quantum materials

Arthur Barnard

Department of Physics and Department of Materials Science & Engineering, University of Washington, Seattle, Washington, USA 98195

Two dimensional materials made by van der Waals assembly offer a unique way of building and exploring novel materials properties. The fact that electrons are primarily confined to atomically thin crystal planes grants functionalities distinct from bulk materials—proximate layers and localized probes can interface with the entire electron system rather than just the surface. This affords a new approach to materials science centered on scanning probe techniques. In this talk, I will discuss our group's development of new cryogenic scanning probe techniques to explore emergent phenomena in 2D quantum materials. In particular, I will discuss how we use various capacitively coupled tips to probe electron hydrodynamics and emergent superconductivity in graphene-based heterostructures as well as how we slide/shear 2D materials to tune interlayer interactions in layer materials such as CrI_3 .

Invited Talks

Atom Probe Tomography Using a Wavelength-Tunable Femtosecond-Pulsed Coherent Extreme Ultraviolet Light Source

Ann N. Chiaramonti, Benjamin W. Caplins, Jacob Garcia, Luis Miaja-Avila, and Norman A. Sanford

National Institute of Standards and Technology, Boulder, CO, USA

Femtosecond pulsed extreme ultraviolet (EUV) radiation has recently been demonstrated [1-3] to trigger controlled field ion emission from insulating and semiconducting specimens in a 3D atom probe microscope. However, the exact mechanism for EUV radiation-assisted field ion emission is not understood at this time. Unlike the near ultraviolet (NUV) ($E_{\text{photon}} \sim 3.5$ eV) or even deep ultraviolet bands ($E_{\text{photon}} \sim 4.8$ eV), EUV photons can have energy (~ 10 eV $\leq E_{\text{photon}} \leq 100$ eV) that is above the optical band gap or work function of any material, and the ionization potential of any element. Photons in the EUV range discussed here can break any chemical bond. Therefore, they can uniquely promote direct photoionization (i.e. to vacuum) or excite core electrons. They can also potentially offer a more local heating mechanism through fast local phonon decay. They are also absorbed within a very shallow region confined to the specimen surface due to their extremely large absorption cross section across the entire periodic table. Therefore, it is reasonable to speculate that the mechanism of field ion emission under pulsed EUV radiation may differ from the traditional *bulk* heating and cooling model or photoexcitation-based mechanisms [4] that have been proposed to occur in visible or NUV laser pulsing.

The performance of EUV versus NUV atom probe as it pertains to the compositional analysis of insulating and semiconducting materials such as SiO₂, Al₂O₃, MgO, Ga₂O₃, and GaN will be presented. The varied effects of pulse repetition rate, base temperature, and pulse energy on the measured composition will be presented and compared to similar data obtained in a conventional, near ultraviolet radiation pulsed atom probe.

[1] A.N. Chiaramonti, L. Miaja-Avila, P.T. Blanchard, D.R. Diercks, B.P. Gorman, and N.A. Sanford. MRS Advances 4, 44-45 (2019) 2367.

[2] A.N. Chiaramonti, L. Miaja-Avila, B.W. Caplins, P.T. Blanchard, D.R. Diercks, B.P. Gorman, and N.A. Sanford. Microsc. & Microanal. 26 (2020) 258.

[3] L. Miaja Avila, B.W. Caplins, A.N. Chiaramonti, P.T. Blanchard, M.D. Brubaker, A.V. Davydov, D.R. Diercks, B.P. Gorman, A. Rishinaramangalam, D. Feezell, K.A. Bertness, and N.A. Sanford. J. Phys. Chem. C 125 (2021) 2626.

[4] T.T. Tsong, J.H. Block, M. Nagasaka, and B. Viswanathan J. Chem. Phys. 65, 6 (1976) 2469.

Invited Talks

Structural Transformations in Supercooled Liquid Water

Loni Kringle

Pacific Northwest National Lab

Water is a highly unusual liquid and, although it plays an important role in many chemical and biological processes, the origin of water's anomalies remains unresolved. While there has been growing consensus that the anomalies are connected to the existence of two liquid structures, validation of a leading theory, the liquid-liquid critical point hypothesis, has been limited by the experimental difficulty in examining deeply supercooled liquid water prior to crystallization at temperatures and pressures where key phenomena are predicted to occur. We have developed a pulsed laser heating technique, which rapidly heats and cools nanoscale water films on a nanosecond timescale, allowing brief, incremental excursions into this elusive temperature regime. With this approach, we have investigated the metastable, steady-state structure of supercooled water prior to crystallization, its relaxation kinetics, and its eventual crystallization for temperatures between 180 and 260 K. The results show that the supercooled liquid structure can be described by a linear combination of two structural motifs, with a reversible, temperature dependent transition centered at 210 K. (1) The out-of-equilibrium relaxation to the metastable liquid state exhibits non-exponential kinetics dependent on the initial structural configuration and occurred faster than crystallization at all temperatures examined. (2) This work was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences. This research study was performed in EMSL, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory, which is operated by Battelle for DOE.

References:

1. Kringle, Thornley, Kay, Kimmel, *Science* 369:1490 (2020).
2. Kringle, Thornley, Kay, Kimmel, *PNAS* 118:e2022884118 (2021).

Invited Talks

Characterization of the atomic-level structure of Pt/ γ -alumina and Pt/ θ -alumina interfaces

Melissa Santala

Oregon State University

Metal nanoparticles (NPs) on metal-oxides play a critical role in catalysis. The activity and selectivity of metal NPs depends on their size, shape, and interactions between the metal and the support. Gamma-alumina is an important support for catalytically active metallic NPs. The structure of γ -alumina has been the subject of numerous studies, but is still under debate partly due to its structural disorder. In this work, the atomic-level structure of Pt/alumina interfaces is studied through comparison of atomic-resolution transmission electron microscopy (TEM) experiments and density functional theory (DFT) based structural models. Model microstructures, consisting of Pt NPs in dense transition alumina, were formed through solid-state precipitation into sapphire wafers that were partially amorphized by high-energy ion implantation of Pt. Recrystallization of amorphized alumina proceeds through the transition series $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha\text{-Al}_2\text{O}_3$ with increasing temperature. Thermal annealing in air at 800°C produces γ -alumina and causes precipitation of the Pt NPs. The faceted NPs take a cube-on-cube orientation relationship with the γ -alumina and form tetrahedra bound by {111} facets and cubo-octohedra bound by {111} and {100} facets. The prevalence of {111} facets motivated the development of DFT-based models of (111)Pt|(111) γ interfaces with different chemical terminations (O, Al1, Al2) of the γ -alumina by Oware Sarfo et al. [1]. Aberration-corrected scanning TEM (STEM) was used to collect atomic-resolution images of Pt NPs in γ -alumina, which are compared to STEM image simulations of experimentally-based models of γ -alumina by Smrčok et al.[2] and Zhou and Snyder [3] and Oware Sarfo et al.'s model of Pt/ γ -alumina interfaces. The Smrčok model is a better match than the Zhou model to the bulk γ -alumina. The oxygen-terminated interface Oware Sarfo model best fits the experimental data and is expected to be the most stable for the processing conditions, based on thermodynamic calculations of the interfacial energy as a function of temperature and oxygen partial pressure. The Oware Sarfo model provides a very good match right at the interface, but the fit becomes poor beyond the third atomic layer in the γ -alumina. This is attributed to compromises required in the model to limit the cell size and computational time for DFT calculations. Understanding the limits of the structural models of γ -alumina and Pt/ γ -alumina interfaces is important to further the understanding the structure/property relationships in this system. For comparison, similar work on Pt NPs in θ -Al₂O₃ will be described. The structure of θ -Al₂O₃ is more highly ordered and well-defined than γ -alumina. The (111)Pt|(2 $\bar{0}$ 1) θ interfaces Pt/ θ -alumina were imaged with STEM and compared to image simulations of DFT models with six different chemical terminations of the θ -alumina. The model interface with Pt bonded to oxygen-terminated θ -Al₂O₃, with an underlying layer of octahedral Al, provided the best match to the experiments.

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Invited Talks

Global Health: The push for clean energy and accessible diagnostics

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Throughout the world, two major societal issues requiring profound attention are (i) the development of clean and efficient energy storing devices and (ii) access to appropriate healthcare. The synergistic relationship between the need for accessible diagnostics and clean energy stem from the recent recognition and importance of 'Global Health'. Electrochemistry, which plays an important role in a variety of scientific pursuits, is heavily relied upon in the fields of diagnostics and sustainable energy and is thus well-suited to make significant contributions to Global Health. This utility, and diversity in implementation, stems from the ability of electrochemical systems to be easily modified, miniaturized, and used in the field. This talk will focus on our group's efforts in advancing the Global Health initiative. Firstly, I will discuss a new approach for fabricating low-cost and highly selective sensors for diverse applications at the point-of-care (POC) using additive manufacturing (i.e., 3D printing) technologies. Secondly, I will discuss our recent progress towards overcoming some of the current roadblocks in the field of energy storage and conversion as it relates to (i) aqueous redox batteries, through the incorporation of internal magnetic fields and (ii) electrocatalysis, using an emerging class of quantum materials.

Invited Talks

Scratching the Surface: Enabling Tribological Materials Development through Multiscale Tribometry

Harman Khare

Gonzaga University

Tribology is the study of surfaces in contact and in relative motion. Tribological interfaces are ubiquitous in biological and engineering systems; these give rise to phenomena such as friction, wear and adhesion, which ultimately drive system performance, efficiency and reliability. Tribological phenomena are intrinsically multiscale – macroscale tribological behavior of materials is the product of mechanical and chemical interactions that occur at atomic and nano length scales. Whereas the former drive system-scale performance, the latter can provide fundamental insights into operative mechanisms for such performance. In this talk, I will briefly discuss two vignettes where fundamental mechanisms in multiscale tribology were explored using novel experimental tools. In the first, a novel metal-oxide nanoparticle was dispersed as an anti-wear additive in liquid lubricants. Using a modified technique based on contact-mode atomic force microscopy, nanoparticle-derived surface films were generated in-situ, allowing growth kinetics to be quantified in real time. In the second, I will discuss development of sliding interfaces during the macroscale, dry sliding wear of polymer composites. Nanostructured metal-oxide fillers were added to a polytetrafluoroethylene (PTFE) matrix and run against polished alloys, using custom-built tribometers. Morphological and chemical characterization of resulting interfacial films was used to develop a mechanistic understanding of the effects of filler and counterface chemistry on polymer wear.

Invited Talks

Field Ion Microscopy and Operando Atom Probe for Surface Dynamics

Sten Lambeets

PNNL

Physics governing surface chemical reactions and interfaces involved in heterogeneous catalysts fundamentally depends on the synergistic interactions between reactive gases and specific surface structures. Surface science techniques are continuously evolving to help bridge knowledge gaps between fundamental research and real-world applications. In the past decade, an increasing number of analytical techniques successfully achieved their evolution towards an in situ and operando version of themselves, and recently such approaches are being developed for atom probe microscopy (APM) techniques. In this work, we will present the recent advances in the conversion of Atom Probe Tomography (APT) to study surface dynamics of O₂/Fe using two different APM techniques and modifications: Field Ion Microscopy (FIM), and Operando Atom Probe (OAP). APM techniques are capable of imaging the apex of sharp needles with nanometric lateral resolution, which can be seen as model nanoparticles. FIM is used to image such needles with atomic resolution and to identify the crystal orientation along with the local surface reaction dynamics during oxygen interaction with Fe. The resulting FIM image corresponds to a stereographical projection of the apex and allows the identification of the crystal orientations with atomic resolution. Regular APT, from which the OAP derives, relies on the thermally assisted field evaporation of positively charged ions from a needle shaped specimen. In regular use, the APT is performed in an Ultra High Vacuum ($<10^{-11}$ mbar) while the sample is cooled at 50K. The OAP modification consists of performing the atom probe analysis in the presence of reactive gas at 300 K. Once the FIM characterization is complete the sample is maintained at 300K before starting APT analysis and introducing 1.1×10^{-7} mbar of pure O₂. As soon as the O₂ is introduced, we can measure the surface formation of Fe oxides by monitoring the local concentration of Fe₂O_n⁺ ion species extracted from the surface over time. We can track the local concentration over the different surface regions in real time. We observe the progressive surface oxidation starting from open facets structures, such as Fe{222} and Fe{112}, towards the central Fe(011) and the Fe{024} which show significantly higher resistance toward oxidation. The combination of the different concentrations allows us to reconstruct the full movie of the surface oxidation in real-time. However, since the measurements are performed in the presence of very strong electric fields (>10 V/nm), it is necessary to discuss the potential influences of it on the system as well.

Invited Talks

Two-dimensional and Layered Materials at the Energy-Healthcare-Water Nexus

Michael Curtis, Florent Muramutsa, Naqsh-e-Mansoor, Tony Varghese, Fereshteh Kouchi-Rajabi, Josh Eixenberger, Lynn Karriem, Monét Alberts, David Estrada

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The rapidly evolving field of 2-dimensional materials continues to highlight new avenues of fundamental and applied research across numerous disciplines. At Boise State University recent advances in the synthesis of 2-dimensional (2D) materials-based inks has increased the design space for additive electronics manufacturing for sensors, 2D-silicon integrated photonics, energy harvesting, and more. In particular, the Advanced Nanomaterials and Manufacturing Laboratory has undertaken several projects to help overcome obstacles facing the integration of 2D materials in applications for energy, healthcare, and water. This talk will highlight results of several ongoing studies on the integration of black phosphorus with silicon photonics, graphene for musculoskeletal tissue engineering, printable thermoelectrics for energy harvesting, and Ti_3C_2 MXenes for water purification.

In energy, black phosphorus (BP) has emerged as a promising material in photonics and optoelectronics due to its direct bandgap and photon emission in the mid- to near- infrared (IR) wavelength range. We have successfully synthesized bulk BP inks for printing of optoelectronic devices using aerosol jet printing (AJP). We also report on the solvent assisted exfoliation and formulation of a binary-alloyed transition metal dichalcogenide (TMD) inks and Bi_2Te_3 inks for next-generation printing of electronic devices such as energy storage and harvesting devices. Additionally, new techniques such as metalorganic chemical vapor deposition are highlighted as a path towards wafer scale growth of TMDs for energy-efficient computing architectures.

In healthcare, the intersection of graphene and biology has emerged as a promising area where graphene's physical properties may help elucidate fundamental insights into the chemistry of life. However, graphene's structure and properties are tightly coupled to synthesis and processing conditions, thus influencing biomolecular interactions at graphene – cell interfaces. We show the fate of C2C12 cells, a pluripotent (mouse muscle) cell line, depends greatly on the structure – property – processing – performance (SP3) correlations of graphene bioscaffolds. The type of graphene used significantly influences C2C12 differentiation, myotube formation, and gene expression, suggesting that the cell – graphene interface can be engineered to control biomolecule structure and function in adherent cells.

In water, we have developed a flowing electrode capacitive deionization (FE-CDI) system using Ti_3C_2 MXene suspension electrodes for the removal and recovery of ammonia from synthetic wastewater. The electrodes possessed favorable electrochemical properties with a high specific capacitance of 148 F/g. The system proved to be a green technology by exhibiting satisfactory charge efficiency of 58-70% while operating at a relatively low energy consumption of 0.45 kWh/kg, which is $\sim 10\times$ lower than the 4.6 kWh/kg used by commercial wastewater treatment plants. The results demonstrate that Ti_3C_2 MXene electrodes have the potential to improve the FE-CDI process for energy-efficient removal and recovery of ammonia.

Together, these results highlight a range of applications impacted by 2-dimensional materials research at Boise State University, enabled by a rapidly evolving research landscape at the university.

Invited Talks

Developing a "genome" for atomic precision: DNA-templated luminescent silver nanoclusters

Stacy Copp

University of California, Irvine

Atomically precise nanoclusters provide the ultimate control over the light-matter interactions of nanoparticles. We are investigating a uniquely programmable class of these nanomaterials called DNA-stabilized silver nanoclusters (Ag-DNAs), which possess exciting potential for bioimaging and biosensing. DNA sequence selects the atomic size and fluorescence color of the encapsulated silver nanocluster. This "genomic" property has been used to produce a diversity of Ag-DNAs with 10-30 Ag atoms and 400 nm to 1,000 nm fluorescence emission peaks. I will discuss how we are combining high-throughput experimentation, machine learning, and analytical chemistry to better understand the structure-property relations of Ag-DNAs and enable their development for bioimaging and sensing. Our chemically-informed machine learning models can map DNA sequence onto silver nanocluster color, allowing us to decode the role of DNA sequence in sculpting silver nanoclusters and to discover new NIR Ag-DNAs that are well-suited for imaging in the biological tissue transparency windows. We also find evidence that the geometry of the Ag-DNA can strongly influence the photophysical and chiroptical properties of the nanocluster. This work advances the scientific framework for DNA as a programmable template for atomically precise nanostructures.

General Talks

Investigating the Reactivity of Formic Acid on Reconstructed Fe₃O₄ (001)

Christopher Lee

Pacific Northwest National Lab

Understanding the interactions between formic acid (HCOOH) and metal oxide surfaces is important for developing fundamental knowledge in heterogeneous catalysis. Here we investigate the reactivity of formic acid on reconstructed Fe₃O₄(001) using a combination of molecular beam dosing, angular-resolved temperature programmed reaction spectroscopy, X-ray photoelectron spectroscopy, and low energy electron diffraction. Formic acid initially dissociates at low temperatures (<80 K) into formate and a bridging hydroxyl up to an initial dosage of ~2 HCOOH per Fe₃O₄(001) unit cell (u.c.). Products including CO, CO₂, H₂O, and recombinative HCOOH primarily desorb from 400-600 K. The CO formed during the reaction is ejected sharply from the surface normal direction with very little desorption observed beyond 40° tilt towards the surface azimuthal direction. In addition, the CO desorption progresses in a first lower temperature peak at ~530 K (1 HCOOH/u.c. dose) before saturating a second higher temperature peak at ~560 K (2 HCOOH/u.c. dose). This is in contrast to the general filling of desorption features observed on simple desorption from model surfaces from high to low temperature and suggests a depletion of a key surface intermediate before the full desorption of products. The data shown here highlights the complexity presented by the reaction dynamics of even simple functional groups on metal oxide surfaces.

General Talks

Palladium Nucleation and Alloying at the WTe₂ (001) Surface

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A deeper understanding of atomic-scale functionalization of transition metal dichalcogenides, especially topologically interesting variants such as WTe₂, is critical in developing deployable structures in quantum information science. Discerning the role of intrinsic surface defects as adsorption and functionalization sites is a key step towards device realization. In this study, scanning tunneling microscopy (STM), X-ray photoemission spectroscopy (XPS), and Density functional theory (DFT) were utilized to examine the initial nucleation and growth of palladium on the WTe₂ (001) surface as both a function of coverage and temperature. XPS measurements of the WTe₂ (001) surface after palladium deposition at room temperature show significant interaction between Pd and surface tellurium reminiscent of PdTe₂ in electronic structure with an absence of interaction between Pd and tungsten. Using STM, we found palladium deposited at room temperature, where Pd clusters outnumber surface defects more than 10:1, produced no change in surface defect density. This indicates a lack of interactions between deposited Pd clusters with intrinsic surface defects. The annealing temperature-dependent STM studies further show that palladium clusters are stable to about 475 K. Palladium deposition at an elevated temperature of 425 K was performed to determine that the lack of nucleation on defects is, in fact, not a result of diffusion limitations during the growth. Complementary theoretical studies predict that palladium atoms interact strongly with Te adatoms and Te vacancies, while only binding weakly on pristine WTe₂ (001). Based on these results, we conclude that the nucleation of Pd clusters is initiated by mobile Te adatoms that likely significantly outnumber other surface defects. Our high-temperature Pd deposition studies further support this assertion. Atomically resolved images of large Pd nanoparticles annealed above 475 K exhibit a superstructure on the top terrace indicating alloying with tellurium. Atomically precise, tailored heterostructures with tunable electronic, and topological properties are necessary for the growing need for quantum devices. A full account of the surfaces of these quantum materials, as in with WTe₂ (001) where excess chalcogenide complicate interactions at the surface, is vital in directing both accurate predictive theory and material synthesis efforts.

General Talks

Quantification of Oxygen Vacancies in Complex Oxides

Mohammad Delower Hossain

Pacific Northwest National Laboratory

Oxygen vacancies play pivotal roles in determining physico-chemical properties of complex oxide. For example, oxygen vacancies drive the metal-insulator transition, enhance the catalytic activity, induce magnetism in non-magnetic systems, trigger superconductivity and promote ionic conductivity in complex oxides. However, the accurate quantification of oxygen vacancies is often challenging which lead to unreliable defect-structure and property relationship. This talk will illustrate a strategy to determine the oxygen vacancy concentration in a perovskite $\text{SrFe}_{0.5}\text{Cr}_{0.5}\text{O}_{3-\delta}$ (SFCO) complex oxide that was epitaxially grown on $\text{SrTiO}_3(001)$ (STO) substrate with a plasma assisted molecular beam epitaxy method. Synchrotron based coherent Bragg rod analysis (COBRA) analysis, with subangstrom length scale resolution, illustrates gradual expansion in unit cell volume when moving from the SFCO/STO interface to the surface. The lab-based X-ray diffraction, X-ray photo electron and X-ray absorption spectroscopy analyses demonstrate that the lattice expansion primarily originate from oxygen vacancies in the crystal. The chemical expansivity are further explored with Density Functional Theory (DFT) based first principle calculations. The DFT calculations elucidate a linear expansion in the SFCO lattice as a function of the random oxygen vacancies in the structure. In addition, the spin density plot and the charge analyses supplement the experimental conclusions. Based on these experimental and theoretical findings an analytical model is used to accurately quantify the δ value in $\text{SrFe}_{0.5}\text{Cr}_{0.5}\text{O}_{3-\delta}$. The presented strategy is applicable for other complex oxide, such that a defensible structure and property relationship can be established.

General Talks

Structure/Property Relationships in Actinide Oxide Nanoparticles

Liane Moreau

Washington State University

Actinide oxides at the nanoscale are increasingly relevant for their development as accident-tolerant nuclear fuels, their role in nuclear fuel corrosion and mobility within environmental systems, and their potential for advances in nuclear medicine and catalysis. Compared with transition metal counterparts, however, actinide oxides are underexplored at the nanoscale, and size-dependent structure and properties of these materials to date remain elusive. Correlating particle size and resulting structure/property relationships within these materials requires 1) methods to control size and shape of actinide oxide nanoparticles with high monodispersity and 2) comprehensive characterization of structural attributes over multiple length scales. Work will be described which contributes new approaches to the synthesis and characterization of uranium oxide at the nanoscale. Colloidal-based methods are used to control the size and morphology of uranium oxide nanoparticles through varying solvent and molecular ligand chemistry, leading to morphologies not previously reported, including a multi-pod “nanoflower” structure. The anisotropic growth mechanisms for such particles were interrogated using timecourse electron microscopy. The synthesis of core/shell iron/ UO_{2+x} nanoparticles will also be discussed and resulting constructs are of interest to actinide deposition onto iron-based minerals as observed in environmental contamination sites. In addition to the development of new synthetic products, methodology is simultaneously underway to improve structural analysis of nanoparticles, where surface layer characteristics may differ from those within the nanoparticle core. To this end, an approach was developed to account for radially-dependent heterogeneity within X-ray spectroscopy data and used to extract surface-chemistry attributes of UO_2 nanoparticles from bulk XAFS signal. Atomic and nanometer scale structure derived from X-ray analysis and informed modeling provides insight into differences nanoscale structure compared with bulk counterparts.

General Talks

Intermolecular and Surface Interactions Influence the Properties of Supported Polyoxometalates

Grant E. Johnson, * Oliva M. Primera-Pedrozo, Brian O'Callahan, Shuai Tan, Difan Zhang, Xuebin Wang, Wenjin Cao, Eric Baxter, Patrick El-Khoury, Venkateshkumar Prabhakaran, Vassiliki-Alexandra Glezakou

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Polyoxometalates (POMs) with localized spins have potential as molecular qubits for quantum computing. POMs may incorporate magnetic atoms such as V in their structures, producing novel molecules with promising electro/magneto-optical properties. However, for eventual applications, molecular qubits need to be arranged in electronically- or optically-addressable arrays which imposes interactions with underlying supports and adjacent POMs. Specifically, spin-lattice (phonon) coupling is an influential decoherence mechanism that remains insufficiently understood for supported molecular qubits. Herein, we synthesized W-based POMs doped with V atoms and transferred them into the gas phase using electrospray ionization. Ion soft landing, a versatile surface modification technique, was used to deliver mass-selected POMs with predetermined V-composition to different self-assembled monolayer surfaces in the absence of contaminants that often confound droplet-based depositions. Alkylthiol, perfluorinated alkylthiol, and carboxylic-acid terminated surfaces on gold were selected as well-defined model supports with which to characterize POM-substrate and POM-POM interactions. We obtained insight into the properties of supported POMs, how they are influenced by V-doping, and how they are perturbed by interaction with different supports using infrared reflection absorption spectroscopy, scattering-type scanning near-field optical microscopy (s-SNOM), and density functional theoretical calculations. The effect of surface coverage on POM-SAM and POM-POM interactions was revealed using spatially-resolved s-SNOM. The electronic properties of the bare POMs were determined in the gas phase by negative ion photoelectron spectroscopy and on surfaces using cyclic voltammetry and scanning Kelvin probe microscopy. Our results provide insight into how substrate and intermolecular interactions influence the properties of potential molecular qubits, which is central to extending their coherence times for practical quantum computing applications

General Talks

Photoluminescence mapping of semiconductors and oxides

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Photoluminescence (PL) spectra with high spatial resolution provide insight into semiconductor defects, inhomogeneous composition, and surface imperfections. The method serves as a valuable tool for failure analysis. Typical PL spectroscopy is not spatially resolved. Excitation photons impinge on a sample; emitted light is collected by a spectrometer. Spatial variations get averaged into one overall spectrum. This approach is adequate for a homogeneous sample but there are many instances where one requires a spectrum at each (x,y) point on the surface as well as the ability to visualize the data.

This presentation will discuss PL mapping of several key materials and devices, with excitation wavelengths ranging from 266 to 975 nm. The sample is scanned in the x - y plane and emitted light is collected by an Ocean Insight spectrometer (detection ranges encompass 200 to 1700 nm). This system yields a map that covers an area as large as 100×100 mm. Analysis software performs rapid peak fitting on each spectrum and displays the data in a false-color image. An autofocus routine analyzes the laser spot and adjusts the objective height to keep the laser spot in-focus on the sample surface, ensuring diffraction-limited resolution.

General Talks

Understanding competitive electrochemical reactions on strained surfaces

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In heterogeneous electrocatalysis, reactants adsorb on a materials surface, and subsequently transfer electrons to or from the solid in conjunction with ionic motion, forming and breaking chemical bonds. This complex interface—between a solid surface and a reactive gas and/or liquid—can change dramatically with the electrochemical potential that drives such reactions. For example, materials can change oxidation state (where changes in the surface oxidation state are associated with adsorbates, and bulk changes require diffusion of oxygen through the material itself) or change their structure/phase. Such changes in a catalyst are intimately linked to their functionality and activity for desired electrochemical reactions.

We have been investigating how metal electrocatalysts react with species from aqueous solution by electrochemical approaches with complementary spectroscopy. We are particularly motivated by complex reaction environments where multiple species – such as oxidized reactants and reducing equivalents of protons – compete for sites on the surface, influencing the activity for reduction reactions. This competition and resultant activity depends on the applied voltage, but also characteristics of the electrocatalyst itself, such as strain. We will share how such changes in a material's bulk influence competitive processes on the surface and the formation of hydride phases under electrochemical conditions.

General Talks

The Direct Observation of Oxygen and Hydrogen Influence on Model Austenitic Stainless Steel using Atom Probe Tomography

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Stainless Steels (SS) are ubiquitous in consumer, industrial, and laboratory applications due to the combination of relatively high toughness, low cost, and especially corrosion resistance in many common aqueous environments. Stress-corrosion cracking occurs in SS while it is in tension and exposed to a corrosive environment. Understanding fundamental oxygen and hydrogen reactions and distribution in stainless steel can lead to technologies that will mitigate the deleterious effect and expand the usefulness of the alloy.

We report mechanisms of early stages of oxygen surface reactions with a model Fe-18Cr-14Ni (wt.%) austenitic stainless steel at the nanoscale. This is performed by using *in situ* atom probe tomography. A needle shaped sample is cleaned via field evaporation, which then is exposed to oxygen at elevated temperature in a reactor chamber and then analyzed in atom probe tomography afterwards while maintaining vacuum during transfer. These oxidation studies show expected Fe, Ni, and Cr nano-scale surface segregations at the surface that occur during oxidation. Furthermore, tracer O¹⁸ into stainless steel oxide confirms experimentally that at elevated temperatures, outward metal ion diffusion through an initial oxide is higher than oxygen gas diffusion inward.

We also report the direct observation of hydrogen via its isotope, deuterium, using atom probe tomography. SS is electrochemically charged in a deuterated ion solution followed by plunge quenching and transferring the sample into the APT analysis chamber via a cryo transfer system developed at PNNL. This capability to study the distribution of deuterium in model steels can provide unprecedented understanding of hydrogen embrittlement mechanisms commonly also contributing to stress corrosion cracking.

This research is supported by the Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division as a part of the Early Career Research Program FWP 76052. Pacific Northwest National Laboratory is operated by Battelle for DOE under contract DE-AC05-76RL01830.

General Talks

Developments in the surface analysis of battery materials

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Requirements for surface characterization in energy materials development have generally broadened, with demand for advanced sample treatment and handling to investigate critical interfaces and examine the development of the materials with aging.

Combining X-ray photoelectron spectroscopy (XPS) with inert ion sputtering is a common approach to study material composition and chemistry into the bulk of the materials. In Li-based batteries, the mobile Li can exhibit migration due to charge buildup when using traditional monoatomic argon sputter-etching. The development of inert gas cluster ion sources has revealed that this Li migration in solid electrolytes does not occur when profiling with argon clusters, as well as revealing that the monoatomic argon etching was also responsible for generating an artifact chemical peak. The cluster sources provide the capability to greatly improve the quantification of materials that incorporate light alkali metals.

In addition to the improved large scale depth information that the cluster sources can provide, higher energy x-ray sources offer near surface measurement depth differences that can provide insight for the progression of aging in a battery system. To fully utilize the techniques and tools of the modern XPS system for reactive materials, such as lithium metal and some structures, methods of loading samples while maintaining them in an inert environment is critical. To address this need, specialized sample holders have been developed that allow electrical connection for electrochemistry, as well as allowing heating to model accelerated aging, while maintaining the sample surface in an inert atmosphere until exposure to the vacuum of the XPS system.

Utilizing this mounting capability with deconstructed real batteries, an experiment exploring the effects of charge cycling with the Ag-La monochromatic x-ray source shows that the formation of Li_2CO_3 and LiF in the solid-electrolyte-interface (SEI) proceeds with these compounds distributing with depth.

Poster Abstracts

Exploring the Complex Chemistry and Degradation of Ascorbic Acid in Aqueous Nanoparticle Synthesis

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While ascorbic acid (AA) has been the ubiquitous choice as a mild reductant in the aqueous synthesis of noble metal nanoparticles (NPs), its role beyond the reducing powers has been mostly overlooked. Despite the fact that reduction kinetics of metal salt precursors are most susceptible to modifications by reducing agents, it has frequently been relegated to concentration and pH variations for AA, without delving into the more complex chemistry associated with the latter. The mechanism behind AA-mediated reduction is often stymied by an oversimplified presentation in literature wherein the diprotic acid is assumed to undergo consecutive oxidations via a radical intermediate to form dehydroascorbic acid (DHA). In reality, these assumptions may not accurately describe the aqueous behaviour of AA in a wide array of synthetically relevant conditions.

We show that facile degradation of ascorbic acid has considerable impacts on the formation and properties of aqueous silver NPs and discuss implications for the use of ascorbic acid in NP synthesis. Briefly, experimental evidence shows that the alkaline degradation of AA at no point converges to yield DHA, which follows an independent degradation pathway altogether. While DHA at different stages of degradation consistently results in the formation of spherical/quasi-spherical Ag NPs, it is interesting to note that AA aged for > 12h gives rise to anisotropic plate-like morphology, furthering the hypothesis that a different degradation pathway is followed for both. The role of various plausible degradation products has been additionally studied to inform AA's assumed behaviour in NP synthesis. These findings have profound implications for the understanding of AA in NP systems, and the mechanisms behind its role as a reductant and surfactant.

Graduate Abstracts

Two-phase solvothermal synthesis of Gd-doped CeO₂ nanoparticles and their crystallographic and electronic structural characterization

Shinhyo Bang,
Washington State University

The supreme oxygen storage capacity of CeO₂, which forms and eliminates oxygen vacancies makes CeO₂-based materials attractive candidates for catalysts in reduction-oxidation processes. The catalytic activity of CeO₂ can be enhanced with doping impurities such as Gd³⁺ ion, which is expected to increase the concentration of oxygen vacancy defects in the matrix. The atomic-scale structure of doped CeO₂ depends on the synthetic method due to kinetic and morphology-driven energetics, which affects the electronic structure of Ce and the catalytic activity in corollary. In this research, Gd-doped CeO₂ nanoparticles were synthesized using a two-phase solvothermal method. The incorporation ratio of Gd was evaluated using XRF, and XRD/XANES were employed to extract the crystallographic and electronic structures. We find there is a saturation point to how much Gd can be incorporated into CeO₂. Phase transformation from CeO₂'s pure fluorite structure was observed beyond the saturation point, which is lower than that has been reported in the literature for bulk CeO₂. A crystallographic structural change was observed as a function of additional Gd introduced, which is evidenced by a consistent systematic change in the peak intensities indicative of site preference for Gd. XANES results from fluorite- CeO₂ nanoparticles show greater f_{1,2} character, whereas with additional Gd incorporation, the f₀ peak increases until the structure deviates from the conventional fluorite structure. Results from this work will be used to better inform the crystallographic and electronic structural connections within doped ceria as well as inform the impact on the catalytic behavior.

Graduate Abstracts

In-Situ XAS Studies of Cu-S Complex Catalysts for Electrochemical CO₂ Reduction Reaction

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Abstract

The increasing level of carbon dioxide (CO₂) has led to global warming by greenhouse effect. Therefore, it is of paramount importance to reduce the CO₂ level. Restructuring-induced catalytic activity has shown a phenomenal performance in reducing carbon dioxide to value-added products, such as methane (CH₄), ethylene (C₂H₄), etc. The present study examined the in-situ electrochemical CO₂ reduction process of a Cu-S centered metal organic complex. The Cu-S complex showed a high Faradaic efficiency for CO₂ reduction and top selectivity of 52% CO₂ -to-CH₄ and 16% CO₂ -to-C₂H₄. Combining cyclic voltammetry (CV) and in-situ X-ray absorption spectroscopy (XAS) results, we found the high performance of Cu-S complex catalysts is a result of reversibly reconstructed Cu nanoparticles formed during electrochemical reaction, instead of the molecule itself. In addition, the formed Cu nanoparticles, which are identified as the reaction active sites, are allowed to reverse back into the complex structure after the reaction. The relative intensities of interfacial H₂O/*CO obtained from operando infrared spectroscopy suggests that a higher amount of H₂O molecules is accumulated on the surface of catalysts. Moreover, time-of-flight mass spectrometry (TOFMS) indicates the structure of catalyst can be maintained after CO₂ reduction reaction (CO₂ RR) at -1.6V vs Ag/AgCl for 10 hr. Our study provides deeper understanding toward designing metal-complex molecular structures for controllably generating active species under reaction conditions to catalyze desirable chemistry.

Graduate Abstracts

Impact of catalyst morphology and electrocatalytic hydrogenation of benzaldehyde

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Benzaldehyde is a model bio-oil compound used to study the aqueous-phase hydrogenation of biomass to biofuels. Electrocatalytic hydrogenation (ECH) of benzaldehyde to benzyl alcohol can be carried out at mild conditions using electricity and water. ECH of benzaldehyde has been investigated on precious and non-precious metal catalysts in the literature. Palladium (Pd) is both very active and selective in reducing benzaldehyde (vs water to yield H₂ gas), and previous work has shown that interaction with benzaldehyde prohibits formation of palladium hydride under reaction conditions. We investigate high surface Pd nanoparticle electrocatalysts that enable quantification of adsorbed H on the Pd surface prior to hydride formation. Adsorption isotherm measurements establish relative binding strengths for H and benzaldehyde on the Pd surface. Considering gelled nanoparticles with extensive grain boundaries and residual strain, we observe changes in hydride formation and relative affinities for H and benzaldehyde. This morphology-induced change in surface (and bulk) chemistry is expected to impact activity and selectivity towards benzyl alcohol.

Graduate Abstracts

Seed-mediated anisotropic growth of UO_{2+x} nanoparticles directed by solvent conditions

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Anisotropic nanomaterials are a unique subset of nanoscale materials—such as rods, prisms, or octahedrons—that have at least one <100 nm dimension and that require multiple physical parameters to define. These materials exhibit structural dependent properties that can vary widely from their bulk counterparts, meaning that chemical, optical, and magnetic properties can be fine-tuned through controlled syntheses of different shapes/sizes. In the case of actinides, where important applications of nanomaterials span from next generation fuel to catalysis to environmental transport, few anisotropic syntheses have been reported and the mechanisms behind their anisotropic growth are poorly understood. To further explore anisotropic growth of actinide oxides, we have developed an organic-phase synthetic system wherein the morphology of uranium oxide nanoparticles can be controlled by tuning the reaction conditions. In our seed-mediated overgrowth protocol, quasi-spherical uranium oxide seeds are heated with organic surfactants and an organometallic precursor, resulting in nanoflowers, spheres, or cubes depending on solvent chemistry. Our results suggest that interactions between the seed surface and the solvent are integral in directing the growth. We suggest a mechanism wherein particular solvents, depending on structural attributes such as binding moiety, chain length, and aromaticity, can associate preferentially with certain surface facets of the quasi-spherical seed, leaving other facets open for preferential deposition of uranium from solution. This hypothesis will be further investigated by high-resolution transmission electron microscopy (HR-TEM) and small-angle X-ray scattering (SAXS) to deduce the surface faceting and growth mechanisms. This work highlights the complex surface chemistry and energies of monodisperse uranium oxide colloids and will enrich our understanding of their behavior in both engineered and environmental systems. Furthermore, these results are generally relevant, as solvent-directed anisotropic growth may be applicable beyond actinide systems.

Graduate Abstracts

Adsorption of H₂O derivatives and CO₂ on Lanthanum-Based Perovskites: An Analysis From First Principles

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CO₂ and H₂O co-electrolysis has the potential to create a new source of syngas using solid oxide electrolysis cells (SOECs). Perovskites are promising SOEC cathode materials due to their ability to reduce stable molecules, such as CO₂. The application of these materials in reduction reactions is limited by the lack of understanding of the underlying mechanisms. In this study, we aim to deepen the understanding of the perovskite surface structures and how they impact reactivity by deconvoluting experimental X-ray photoelectron spectroscopy. As such, we deconvolute the experimental XPS spectra of two La-based perovskite surfaces with different B-site cations (Ni and Co).

To deconvolute the XPS spectra of the perovskites, we utilized the GGA level Revised Perdew-Burke-Erzenhof (RPBE) functional that we theorize is sufficiently accurate to capture the required features to deconvolute the spectra. We first investigated the most favorable adsorption site of each of the water derivative species (O, H, OH and H₂O) and CO₂ adsorbed on both surfaces. We find that the dissociative adsorption of O₂ and H₂ is exothermic while the formation of OH from H₂O and H₂ is endothermic. Further the O 1s, La 4d, Co 2p (for LaCoO₃) and Ni 3p (for LaNiO₃) spectra were deconvoluted utilizing core level binding energy shift (CLBES) calculations. The O 1s spectra had the richest data and we found that compared to experimental literature binding shifts our theoretical data was comparable and the RPBE function sufficiently captured the required features. The other spectra were not affected by the adsorption of adspecies.

CO₂ adsorption on the surfaces of LaNiO₃, LaCoO₃ and LaFeO₃ was quantified using vibrational calculations to compare to the DRIFTS spectra. We further determined that the adsorption of CO₂ on these surfaces had an activation barrier for which we identified the rate limiting step.

Graduate Abstracts

Preparation and Characterization of Model Homotopic Catalysts: Rh Adatoms, Nanoparticles, and Mixed Oxide Surfaces on Fe₃O₄ (001)

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Single atom catalysts have emerged as a new catalyst frontier due to the need for improved catalyst activity and selectivity. Yet key fundamental challenges exist regarding understanding of how their activity and stability depend on their coordination environment. Surface science studies have the tools necessary to investigate such monodispersed single atom catalysts and their chemistry under well-controlled reaction conditions. Here, we have studied the behavior of Rh on the Fe₃O₄ (001) single crystal surface using X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and scanning tunneling microscopy (STM). We employ the Fe₃O₄ (001) reconstructed surface that has been shown to stabilize single 2-fold coordinated metal adatoms to elevated temperatures. By varying the Rh loading and annealing temperature, we have identified a series of model catalysts possessing unique Rh sites. These catalysts include Rh adatoms, mixed surface layers with octahedrally-coordinated Rh, and Rh nanoparticles on both mixed and pure Fe₃O₄ surfaces. STM and XPS are used to characterize the Rh coverage, species, binding, and particle size distribution. Subsequently, CO and CO₂ adsorption is employed to characterize the chemical properties of these sites. CO binds strongly with Rh adatoms and nanoparticles desorbing at higher temperatures but interacts weakly with the Rh-octahedral species. In contrast, CO₂ interacts most weakly with Rh adatoms and nanoparticles. These model systems allow us to directly investigate reaction mechanisms on different types of catalytic sites furthering our understanding of how to selectively tune catalyst sites for desired reaction pathways. Future studies are directed toward understanding the energetics and reaction pathways of the hydrogenation of unsaturated hydrocarbons and carbonyl functional groups.

Graduate Abstracts

Elucidating the Influence of Structure Directing agents on the Aluminum Distribution of SSZ-39

Charles Umhey,

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Elucidating the Influence of Organic Structure Directing Agents on the Aluminum Distribution of SSZ-39 Authors Charles Umhey, Graduate Student, Washington State University, Wegner Hall Room 105, 1505, NE Stadium Way, Pullman, WA 99164 Jiawei Guo, Graduate Student, University of California Davis, Materials Science and Engineering Davis One Shields Ave. Davis, CA 95616-5270 Zheng Cui, Graduate Student, Tulane University, 2015 Percival Stern Hall 6400 Freret St. Tulane University New Orleans, LA 70118 Ambar Kulkarni, Assistant Professor, University of California Davis Materials Science and Engineering, One Shields Ave. Davis, CA 95616-5270 Daniel Shantz, Professor Tulane University, 2015 Percival Stern Hall 6400 Freret St. Tulane University New Orleans, LA 70118 Jean-Sabin McEwen, Associate Professor, Washington State University, Wegner Hall Room 105, 1505, NE Stadium Way, Pullman, WA 99164 Despite their widespread use in industry the mechanisms governing the synthesis of zeolite catalysts are still poorly understood. This causes the synthesis of zeolites to be a largely empirical process which makes it difficult to design zeolite catalysts with desired properties or to improve upon successful zeolite catalysts. An important factor in zeolite synthesis is the aluminum distribution within the zeolite framework. Swapping a silicon atom with an aluminum atom creates a charge defect which allows for the placement of a catalytically active species such as Cu^+ or Fe^+ . During synthesis aluminum sites in zeolites are charge compensated by species in the synthesis gel such as OSDAs, sodium and hydrogen. Prior research has established the ratio of cis to trans isomers in organic structure directing agents (OSDAs) used during the synthesis of Cu-SSZ-39 from faujacite can influence the copper uptake, the catalytic activity towards NO_x reduction, and the aluminum distribution. We elucidate these phenomena by performing Density Functional Theory (DFT) calculations to evaluate how changing the charge compensating species alters the thermodynamic favorability of different aluminum pair distributions within SSZ-39. The trends observed in our DFT calculations can then be compared to experimental results to determine if thermodynamic limitations can explain the differences in Cu-SSZ-39 samples made with varying cis-trans OSDA ratios. Our computational results suggest the presence of sodium leads to the preferential uptake of trans OSDA making the most probable aluminum pair configuration one where the two aluminums occupy the same eight membered ring (8MR). In the absence of sodium our computational results suggest that cis OSDA will be uptaken preferentially leading to the most probable aluminum distribution being aluminum pairs that occupy no shared SSZ-39 subunits or where the aluminum pair is located in a double six membered ring (D6MR). These results match our experimental observations that trans is preferentially uptaken and the final SSZ structure contains both trans OSDA and sodium.

Graduate Abstracts

Coverage Analysis of 2,3-butanediol on RuO₂ (110) using First Principles

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The alcohol to jet pathway has been demonstrated to produce sustainable aviation fuel eligible as a mixing additive in commercial flights. This has been realized for the starter alcohols of ethanol and butanol, however 2,3-butanediol has been identified as a potential precursor as well as having the benefit of being less toxic to the producer microbes during fermentative digestion. In the alcohol to jet process the main reaction is the dehydration of the chosen alcohol to an olefin, for the case of 2,3-butanediol that olefin is butene. Dehydration is then expected to occur with the help of the RuO₂ (110) catalyst. Diol dehydration has been achieved with a TiO₂ (110) rutile surface however the isostructural RuO₂ was chosen as Ru atoms have a stronger Lewis acidity than Ti. An adsorption analysis of the 2,3-butanediol on the surface was conducted with assistance from the global optimizer NWPEsSe. The adsorption energy was found to be -2.66 eV and the most favorable position of the 2,3-butanediol was with both hydroxyl groups bonded to the Ru 5c surface atoms [1]. Upon conducting a coverage analysis, the most favorable adsorption energy was with two 2,3-butanediols adsorbed to the surface on separate but neighboring rows of Ru 5c surface atoms. Additionally, for coverages less than 0.667 ML we found evidence for attractive lateral interactions. This suggests that at low coverages the other 2,3-butanediols have a stabilizing effect on one another likely from the polarity of the hydroxyl group. An electronic analysis has shown that there is no dependence of the d-band center or d-band width on the adsorption energy with increasing coverage. However, a phase diagram of 2,3-butanediol on the RuO₂ surface will illuminate the most realistic coverage for the dehydration conditions. This information will allow us to begin the process of mapping the mechanism, which is likely to occur through two intermediates, methyl ethyl ketone and 2-butanol. Therefore, this work serves as a key indicator of 2,3-butanediol surface behavior on RuO₂.

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<https://doi.org/10.3389/FENRG.2021.781001/BIBTEX>

Graduate Abstracts

Electrocatalytic nitrate reduction to ammonium over 3d transition metals: Role of resting electronic structure on selectivity

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The perturbation of the nitrogen cycle via fertilizer amendment and fossil-fuel combustion has resulted in alarmingly increased nitrate concentrations in groundwater and coastal areas, with global human-health threatening consequences. Denitrification of drinking water, municipal cooling tower waste water, and industrial waste streams is a growing area of energy consumption, though still outpaced by the carbon-intensive Haber-Bosch conversion of nitrogen to ammonium for fertilizer. Electrocatalytic nitrate reduction offers a competitive, distributable, and cyclic alternative to traditional treatment approaches, using electrons as a reducing agent without the need for added chemicals or elevated temperatures and pressures. However, selective nitrate reduction to desired products (e.g. ammonium) is limited by a complex reduction pathway where nitric oxide (NO) plays a critical role in determining selectivity.

Here we utilize *in situ* ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) to probe the solid-gas interface for a series of polycrystalline 3d transition metal (TM) surfaces (Cu, Ni, Co, and Fe) exposed to nitric oxide (< 100 mTorr). Consistent with more favorable free energies of nitric oxide adsorption and N-O bond cleavage, adsorbate affinity and selectivity towards more reduced nitrogen adsorbates increase as TM *d*-band center energy (E_d) approaches the Fermi level (E_F). Contextualized with *ex situ* ammonium selectivity measurements and theoretical calculations,¹ these findings suggest N-O bond cleavage plays a critical role in the selective reduction of nitrate towards ammonium. This combination of *in situ* X-ray spectroscopy, *ex situ* electrochemistry, and theoretical calculations provides fundamental mechanistic understanding of selectivity-limiting steps, suggesting the electronic structure of Co as optimal for the selective reduction of nitrate to ammonium.

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Graduate Abstracts

Intrinsic Area Selective Atomic Layer Deposition of MoS₂ Thin Films

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As the critical dimensions in today's semiconductor devices continues to shrink, new methods for device fabrication are paramount for continued reduction in scaling. These fabrication processes must be adaptable in order to evolve with future technology nodes and scales, while providing flexible material integration techniques within the high complexity of device structures. Area selective atomic layer deposition (ASALD) is a deposition technique that utilizes a bottom-up patterning approach for self-alignment of deposited materials. ASALD operates on the basis that functional groups either present or absent on a growth surface will promote or inhibit nucleation. This contrast can lead to selective deposition. In addition to compatible processing techniques, next generation materials also need to be studied. Layered two-dimensional (2D) molybdenum disulfide (MoS₂) is a semiconducting material that shows great promise due to its atomically thin structure and impressive electrical properties. In this work, we report the ASALD of MoS₂ on patterned template substrates of common dielectric materials versus thermal silicon oxide and nitride. Growth and non-growth surfaces were initially screened with X-ray photoelectron spectroscopy (XPS) characterization of blanket MoS₂ films after numerous ALD cycles. The selectivity parameter between surfaces was calculated using XPS, revealing a high selectivity of $S = 0.85$ after 20 ALD cycles for growth on ALD alumina versus thermal silicon oxide. These results identified contrasting surfaces that were then patterned to investigate area selectivity. MoS₂ ALD was performed at 200 °C on patterned surfaces that were then annealed at 650 °C for 30 minutes. Samples were characterized using Raman spectroscopy maps of crystalline MoS₂ modes which confirmed ASALD. These results hold promise for advancing the integration of 2D materials into device manufacturing.

Graduate Abstracts

Two-Steps MgMOF74 Thin Film Fabrication with Controllable Pattern via Inkjet Printing Techniques

TZER-RURNG SU

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Two-steps MgMOF74 thin film fabrication and controllable pattern via Inkjet printing technique
Metal-organic frameworks (MOFs) possess many unique features, such as large surface area, tunable porosity and designable frameworks, which result in a broad area of application, including gas separation/storage, catalysis, etc. Among all of the MOFs, MgMOF74s have been capturing great attention for a decade because of their excellent performance in CO₂ absorption. Due to the great gas uptake of MgMOF74 and demand for porous coating in several areas, MgMOF74 thin film fabrication has been widely developed and several techniques have been introduced. In these methods, however, pattern control is still a challenge in terms of applying to electrical or electronic devices. Moreover, MgMOF74 is a type of MOF that requires external energy to possess its crystallinity. In this work, we demonstrated a two-step method to form MgMOF74 film by combining inkjet printing technique with vapor-assisted crystallization (VAC) process. MgMOF74 film pattern and growth layer can be simply controlled via inkjet printing. Following the VAC process, the MOF thin film could be fabricated in an hour on different substrates. Our work indicates a potential two-step pathway on controllable MOF thin film pattern for those MOFs that usually involve temperature heating to assist crystal formation.

Graduate Abstracts

Deposition and Growth of Metal-Organic Frameworks Thin Films via a Vertical Microfluidic Probe

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Metal-organic frameworks (MOFs) show outstanding properties of high surface area, and high porosity, making them gained significant attention due to their potential applications such as gas storage/separations, optoelectronics, smart coatings, and sensors¹⁻³. Recently, zeolitic imidazolate frameworks 8 (ZIF-8), as a subclass of MOFs, have extreme thermal and chemical stability, which are an ideal material for CO₂ capture, separation, and storage^{1,4,5}. While simultaneously enhancing the existing deposition methods, microfluidic control of several parameters, including reaction time, temperature, and etc..., could be utilized to improve the reaction condition of ZIF-8 thin films. The quality, surface morphology, and crystalline structure of the ZIF-8 thin film fabricated by the developed automated microfluidic deposition system will be characterized in this work. The deposition system used a vertical microfluidic probe (vMFP) directed by a pen-plotting instrument, which takes advantage of providing a non-contact depositing while confining precursors between the probe head and the deposition surface. Due to the microscale mixing of precursors facilitated by the microfluidic device, lesser chemicals are needed, which reduces cost and speeds up experimental time. The associated vMFP enables precise control of deposition to fabricate patterned thin film, extending ZIF-8 potential applications of chemical sensors.

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Graduate Abstracts

A millikelvin scanning probe microscope for probing emergent states in layered quantum materials

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Van der Waals (vdW) materials—those that are formed by stacking of 2D crystals—have recently been found to exhibit superconductive, correlated, and topologically nontrivial states. The most paradigmatic vdW material is magic angle twisted bilayer graphene (MATBG) since it hosts several emergent states that are tunable by interlayer twist angle. The 2D nature of MATBG and other layered quantum materials offer an exciting platform for probing emergent states because their charge density can be electrostatically tuned with proximate gates and, more crucially, they offer unprecedented access for local probes to interface with and study the internal electronic states.

Here we discuss our millikelvin scanning probe microscope and our progress towards studying emergent states in MATBG. Our microscope uses a homebuilt vibration isolation stage housed inside a commercial dilution refrigerator and enables nanometer-scale positioning of local scanning probes while simultaneously carrying out conductivity measurements. To study MATBG, we are developing novel probes to better understand the role of electrostatic coupling in emergent superconductivity—an open question in the field that may aid in our understanding of high-temperature superconductivity. For this, we are developing flat, planarized probes enabling us to systematically and locally tune electrostatic interactions in MATBG. Beyond MATBG, we envision our microscope and our novel scanned probes to be broadly applicable to a wide spectrum of layered quantum materials.

Graduate Abstracts

Controllable shear of a 2-dimensional magnetic

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The macroscopic electronic and magnetic behavior of materials is governed by their atomic and crystal structure. Subtle structural changes in inter-atomic distances, crystal symmetries, and bond-angles can intrinsically impact materials properties and as such, new approaches to systematically control structure can be an effective way of probing and understanding structure-property relationships. This has motivated the use of uniaxial strain measurements, wherein crystals are stretched along one axis while their magnetic, electrical, and thermal properties are measured. This has been applied to quantum materials to help elucidate the nature of emergent states that are challenging to probe otherwise. In our work, we draw from the benefits of this approach, and develop a complementary means of tuning structure-property relationships, wherein we shear crystals rather than stretch them.

We use our new approach to apply shear deformations to the 2D layered magnet, CrI_3 , which undergoes an anti-ferromagnetic (AFM) to ferromagnetic (FM) transition based on crystal symmetries. It appears that few layer samples of CrI_3 are AFM with a monoclinic crystal structure, but upon various perturbations (e.g. pressure), they irreversibly shift to a FM state associated with a rhombohedral structure. Since these crystal structures are related by an interlayer shift, shearing may help elucidate the energetics of the exchange coupling that leads to the changes in magnetic state and may even enable the discovery of exotic, thermodynamically unstable magnetic states. Here we detail our various approaches of shearing 2D crystals in conjunction with our wide-field magneto-optic Kerr effect (MOKE) measurements used to study crystal magnetism. Beyond 2D magnetics, our shear techniques will be applicable to a broad class of 2D and bulk crystals.

Graduate Abstracts

The Study of Interfacial Reactions of Layered Oxide Cathodes in Water-in-Salt Electrolytes

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Water-in-Salt electrolytes (WiS) have been and are still being widely explored to decrease toxicity and flammability compared against organic electrolytes. Current studies on WiS electrolytes are mostly focused on performance comparison and lack fundamental investigation on the reactions at the electrode/electrolyte interfaces. Utilizing an epitaxial thin film model system of layered oxides such as $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811), the processes occurring at the well-defined electrode-electrolyte interface, i.e. electrolyte decomposition/deposition or surface restructuring, can be studied using suitable scattering and spectroscopy techniques to markedly improve surface sensitivity, thus providing insights to understand the reaction mechanism for rational design of advanced aqueous batteries. NMC811 is an attractive candidate as a high energy-density cathode of lithium-ion batteries due to its high specific capacity (~200 mAh/g) and low Co content. To ensure the transformative study of our model systems, we compare the electrode surfaces of powder-slurry and thin-film NMC811 electrodes under reactions in 21 m LiTFSI. Our electrochemical tests and microscopy characterizations provide interesting results in the first step for systematic studies of these systems.

Graduate Abstracts

Light olefine oligomerization on Ni single cations: Reaction mechanism and evolution of the active site environment

Julian Schmid
Pacific Northwest national Lab

Light olefine oligomerization on Ni single cations: Reaction mechanism and evolution of the active site environment. Metal organic frameworks (MOFs) are highly ordered porous materials with a complex but well-defined chemical environment that can host a variety of homotopic active centers. Thus, MOFs are an interesting and versatile class of materials for catalyst design. Defect sites at nodes are terminated by hydroxy groups and aqua ligands that act as anchoring sites for metal cations during ion exchange procedures. We took advantage of this feature of MOFs to graft Ni single atoms on UiO-66 synthesized with one linker missing per node. We hypothesized that such Ni catalysts could selectively catalyze the dimerization of light olefins without side reactions promoted by strong acid sites. Thus, we correlated the structures of the active Ni sites with their activity and selectivity in the oligomerization of ethene, propene, and butene. We also characterized the Ni species before, during, and after the reaction, which allowed us to describe their morphological changes and the consequences for catalytic performance. Hence, our study provides fundamental insight into synthesis of well-defined active sites on MOFs and into mechanisms of C-C coupling reaction of olefins on Ni catalysts. We used an approach that combines chemical grafting with solvent replacement to prepare a single cation containing Ni-UiO-66 material with a Ni loading of 2.5 wt%. We performed kinetic measurements in a flow reactor at temperatures ranging from 200°C to 250°C and at ethylene, propene and 1-butene pressures ranging from ambient to 50 bar. Characterization of the as-prepared, working and spent catalyst included ex situ and in situ Fourier transform infrared (FTIR) spectroscopy and X-ray absorption spectroscopy (XAS). The structure of active sites and reaction mechanism were interrogated by Kohn-Sham density functional theory. The reaction of propene on these materials showed excellent selectivity to n-hexene (76%) and methylpentene (24 %). When using 1-butene as a substrate, the main products were n-octene and methylheptene. With ethene as a reactant, we also obtained mainly dimers such as 1-butene, cis-2-butene, and trans-2-butene. Interestingly, the activity profiles for C₆ formation from propene and C₈ from 1-butene changed significantly with time on stream depending on the reaction conditions; The catalyst goes through an activation period that is followed by a decrease in activity after extended time on stream. The first-order dependence of the reaction rate in 1-butene and the apparent activation energy of 62 kJ/mol are consistent with a Cossee-Arlman cycle calculated by density functional theory. We propose that the active site (i.e., a nickel hydride) is formed in situ during the induction period from a precursor present after the pretreatment in inert atmosphere. FTIR and XAS spectroscopy showed that such a precursor is a Ni oxidic species with different hydration degrees (e.g., Ni-(H₂O)-OH at 250°C and Ni-OH at 300°C) that forms from a hexa-coordinated octahedral Ni hydroxyl species (Ni-(H₂O)₄-OH) in the as-prepared material. Our work advances the development of heterogeneous catalysts for the selective production of linear alpha olefins (raw materials for high performance polymers) by describing how to precisely control the structure of Ni sites and the reaction mechanisms that they promote.

Graduate Abstracts

MOCVD Growth of Monolayer MoS₂ and WS₂

Michael Curtis, Chen Chen, Nicholas Trainor, Joan Redwing, David Estrada

Since the discovery of graphene in 2004, 2-dimensional materials research and engineering of advanced structures have become prevalent. 2D transition metal dichalcogenides (TMDs) are intrinsic semiconductors that show promise in overcoming the scaling limits of current silicon-based devices. In the monolayer limit, semiconductor 2D TMDs have also been shown to transition from indirect to direct band gaps in the near-infrared to the visible spectrum, which makes them excellent candidates for optoelectronic applications. However, the synthesis of these materials is not a trivial exercise, and the method of mechanical exfoliation, that jumpstarted the field, is not well suited for deeper research into the properties of these materials. Additionally, mechanical exfoliation has the potential to degrade the crystalline structure of the layers and is the source of significant defects. Interface quality and layer integrity are of vital importance when producing heterostructures, which is a key step in the functionalization of next-generation devices. To this end, direct epitaxial growth techniques such as metal oxide chemical vapor deposition (MOCVD) facilitates improved control of growth conditions by precise delivery of precursor gases at consistent reactor temperature and pressure, which enables the modulation of material properties. In this study, we demonstrate wafer scale growth of MoS₂ and WS₂ in a horizontal MOCVD reactor as part of the National Science Foundation's 2-dimensional Crystal Consortium. We use molybdenum hexacarbonyl, tungsten hexacarbonyl, and hydrogen sulfide precursors and grew MoS₂ at 9, 10, and 11 minutes at 50 torr reactor pressure. We also reduced the metal flow rate by 20% while increasing growth time. For WS₂ we grew for 12 and 15 minutes at 200 torr without varying the metal flow rate. Samples were characterized via Raman Spectroscopy and Atomic Force Microscopy to analyze the quality of the growth and bilayer coverage coverages. Using imaging processing techniques in MatLab, we found that the percent of bilayer coverage of MoS₂ varied between 57% and 24%. For WS₂, the 15 minute growth yielded a fully coalesced monolayer with approximately 16% bilayer coverage while the 12 minute growth did not fully coalesce. Raman spectroscopy of the MoS₂ samples also revealed an average 21.4 cm⁻¹ difference between the A1g and E2g phonon modes, confirming monolayer growth. Our results provide fundamental insights into the conditions for nucleation and growth of wafer scale 2-dimensional growth kinetics which will be translated to a new AIXTRON Close Coupled Showerhead MOCVD system anticipated to come online at Boise State University in Spring 2023.

Graduate Abstracts

Studying Additively Manufactured Ti-6Al-4V Using High-Resolution Nano-scale Characterization Techniques: KPFM, SEM, EBSD, and EC-AFM

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Scanning probe microscopy (SPM) is a characterization technique that enables nano-scale resolution of surface features and properties under various modes of operation including kelvin probe force microscopy (KPFM) and electrochemical atomic force microscopy (EC-AFM). KPFM measure the volta potential between the surface and the probes potential. This technique was done in an inert atmospheric glovebox to decrease surface reactions with the ambient environment that can reduce resolution. EC-AFM measures the topographical changes on the sample's surface during an accelerated corrosion reaction. By co-localizing KPFM with elemental mapping via energy dispersive spectroscopy (EDS) and electron backscatter diffraction (EBSD), specific microstructural features in metal alloys can be tracked during the initiation and propagation of corrosion. For an electron beam meted (EBM) additively manufactured (AM) titanium alloy, Ti-6Al-4V, the KPFM Volta potential data suggested that corrosion initiation sites would likely form at boundaries between different phases in the alloy and that certain grain orientations were likely more favorable for oxidation. These findings help determine the likelihood of different microstructures corroding preferentially and help to understand how printing parameters and post-processing treatments affect the structure and properties of 3D printed Ti-6Al-4V alloys. After studying the influence the different microstructures have on the corrosion properties, the current focus of this work will be to use EC-AFM to see surface changes in real-time during a corrosion reaction and to co-localize EC-AFM with the other spectroscopy and microscopy techniques.

Graduate Abstracts

Additive Manufacturing of Piezoelectric Surface Acoustic Wave Thermometers

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Additive Manufacturing of Piezoelectric Surface Acoustic Wave Thermometers Surface acoustic wave (SAW) devices are a subclass of micro-electromechanical systems (MEMS) that generate an acoustic emission when electrically stimulated. A typical SAW transducer consists of one or more sets of interdigitated electrode pairs deposited onto the surface of a piezoelectric material. Driven by an electrical voltage, one interdigitated transducer (IDT) launches a SAW, which is later transformed back to an electrical signal by the same or a different IDT. These devices are promising for the development of sensor technology because SAWs are non-dispersive and propagate in a single wave mode. Ambient environmental factors like temperature, pressure, and even structural health of the substrate surface can be determined by monitoring the time of flight, insertion loss, or frequency drift of the SAW. In this work, we utilize an innovative aerosol jet printer to directly write consistent, high-resolution, silver comb electrodes onto a Y-cut LiNbO₃ substrate. The printed, two-port, 20 MHz SAW sensor exhibited excellent linearity and repeatability while being validated as a thermometer.

Graduate Abstracts

Thermal Atomic Layer Etching of MoS₂ Films

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2D materials can offer promise for a wide range of application within semiconductor manufacturing. Of these materials, molybdenum disulfide (MoS₂) is of great interest due to its high mobility, measured on/off ratio, tunable band gap, and a film thickness ideal for scaling. In order to get this material closer to integration with semiconductor manufacturing, a great amount of processing control is required. Atomic layer processing techniques can accommodate this needed precision, where both the deposition and removal of MoS₂ has been studied. In this work we report a thermal atomic layer etching (ALE) process using MoF₆ and H₂O as precursor reactants. Here, we will discuss atomic layer etching of both amorphous as-deposited and crystalline MoS₂ films. In-situ quartz crystal microbalance measurements (QCM) indicate removal of as deposited films when switching from a deposition chemistry (MoF₆ + H₂S) to the proposed etching chemistry (MoF₆ + H₂O). Saturation curves for the etching process were additionally identified with QCM by studying the mass change per cycle vs the precursor dose time. Films deposited on planar coupons were then measured with ellipsometry and X-ray reflectance to determine the etch per cycle. We propose half-cycle chemical reaction equations for the etching process as guided by Fourier transform infrared spectroscopy, residual gas analysis of byproduct formation, and Gibbs free energy calculations. With the many applications of both amorphous and crystalline MoS₂, this work helps to identify and expand current atomic layer processing chemistries.

Graduate Abstracts

Trace Detection of L-Dopa Utilizing a Simple 3D Printed Carbon Electrode

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Parkinson's disease (PD) is a progressive neurological illness that routinely presents with tremors. With approximately 60,000 Americans diagnosed each year, the number of patients with PD in the United States is forecasted to increase to 1.2 million by 2030. By disturbing cognitive behavior and motor function of the body, the diagnosis and treatment of PD has significant implications on a patients' quality of life. L-Dopa is the most common drug used for treating PD symptoms. With the ability to cross the blood-brain barrier, L-Dopa can be converted to dopamine in PD patients to regulate cognitive and motor functions throughout the body. Unfortunately, patients with long-term exposure to L-Dopa require an increased dosage which often leads to adverse side effects such as dyskinesia (extra movements), frozen gait (loss of movement), and mental symptoms. The need for reliable methods of at-home (i.e., point-of-care (POC)) monitoring of L-Dopa is therefore highly important. Through the use of 3D printing, this work discusses a simple detection method for L-Dopa using mass-producible electrochemical sensors. Fused deposition modeling, a filament-based additive manufacturing technique, has shown to be extremely useful in fabricating carbon-based electrodes. Herein, we discuss the fabrication of carbon-based electrodes using conductive PLA filament, its activation protocol, and demonstrate the ability to detect L-Dopa in trace quantities. This method provides a pathway for realizing low-cost POC devices for monitoring patients' L-dopa levels without the need of medical facilities.

Graduate Abstracts

Laser Induced Graphene for Gas Sensing Applications in Environmental Monitoring

Cadré Francis
Boise State University

Laser-induced graphene (LIG) is a graphitic material synthesized by laser writing a pattern on a carbon precursor. Different wavelengths of lasers are used in this direct-writing process; in this work we used a 450 nm wavelength benchtop laser to create graphene from a polyimide precursor. This present study examines the effect of the intensity and focus of the incident beam on the morphology and electrical properties of the synthesized material. We also consider the effect of the polyimide film thickness and substrates of varying thermal resistance and its effect on the thickness of the synthesized material. Polyimide tape of 50 microns required approximately 1.2W under ambient conditions (25°C, 1 atm) to synthesize LIG with a thickness of 50-80 micrometers. A higher laser power (2.3W) was necessary to synthesize 3-5 micrometers of LIG on 10 micrometers of polyimide spin-coated on SiO₂. Raman analysis of the samples show a highly defective graphene with a crystallite size of around ten nanometers. This shows that the high level of disorder within the LIG structure, along with the porous nature of the material provides a good surface for gas adsorption. Scanning electron microscopy (SEM) was conducted to characterize the surface of the synthesized LIG. The micrographs revealed a highly porous structure with a large surface-area-to-volume ratio providing many sites for solid-gas interactions allowing gases to adsorb and desorb from the material. Initial characterization of the material has shown an analyte response in the presence of volatile organic compounds (VOCs) found in sagebrush plants. The synthesized pattern has a great effect on its response to VOCs. A resistance change of 3-5% is observed in the presence of sagebrush leaves. The synthesized LIG material saturates in 30 seconds and needs the same time to regenerate. The structure-property-processing-performance (SP³) correlations of LIG provide a good foundation for gas sensing studies.

Graduate Abstracts

Tailoring the Solvation Structure of Dilute Ether Electrolyte for Stabilized High-Voltage Cathode Interface in Li Metal Battery

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Developing high energy density electric energy storage systems is heavily demanded to mitigate the upcoming energy shortage. Li metal battery (LMB) with high-voltage cathode and lithium metal anode (LMA) have been recognized as one of the most promising candidates. To overcome the famous dendritic Li deposition behavior and continuous solid electrolyte interface accumulation, ether electrolytes are developed for better LMA compatibility. However, regular ether-based electrolytes are prone to be oxidized and fail to passivate the highly oxidative cathodes. Severe anodic parasitic reactions cause quick battery failure. In our works, we successfully demonstrated that by rationally controlling the solvent coordinating power in the dilute ether electrolyte, its intrinsic challenge of oxidation instability can be overcome. We found the critical interfacial behaviors of electrolyte on the cathode surface including the decomposition pathways and reaction products are largely governed by the locally controlled and dynamically changing solvation structure. In the dilute nonfluorinated ether electrolytes, the interfacial decomposition order of solvate species is completely rearranged when the Li⁺-solvent interaction strength is significantly decreased. The oxidation of vulnerable ether molecules can be circumvented by the preferential decomposition of salt ion clusters. A robust inorganic-rich cathode electrolyte interface (CEI) can be selectively generated to passivate the high-voltage cathode and kinetically stabilize the interface so that protect electrolyte from side reactions. The tailored electrode interface can largely prolong the cycled life of LMB under stringent testing conditions. It also suggests a novel pathway to create a stabilized high voltage cathode interface via a facile but effective approach, compared to the conventional strategies including high salt concentration, cosolvent or molecular fluorination.

Graduate Abstracts

Amorphous-to-Crystalline Transition of the Mixed Oxide SnO₂/TiO₂

Pritha Biswas¹, Tamara Koledin², Melissa K. Santala², and Janet Tate¹

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Amorphous-to-Crystalline Transition of the Mixed Oxide SnO₂/TiO₂ Pritha Biswas¹, Tamara Koledin², Melissa K. Santala², and Janet Tate¹ ¹ Department of Physics, Oregon State University, Corvallis, Oregon, USA ² Department of Mechanical, Industrial, and Manufacturing Engineering, Oregon State University, Corvallis, Oregon, USA The incorporation of Sn into an amorphous TiO₂ precursor film influences which polymorph forms upon annealing. We sputter amorphous TiO₂ precursor films in an oxygen-rich environment, and they invariably crystallize into anatase TiO₂ upon annealing. In this report, we have introduced a few nm thick layer of metallic Sn between two layers of this amorphous TiO₂ in two ways – as metallic Sn and as SnO_x – and observed different behavior after annealing. When metallic Sn is introduced, X-ray diffraction reveals the final product to be anatase TiO₂ at low Sn concentration and a mix of rutile TiO₂ and rutile SnO₂ at higher Sn concentration. When Sn is introduced as SnO_x, the final product is a mixture of anatase TiO₂ and rutile SnO₂ at all concentrations thus far studied. Preliminary transmission electron microscopy of the precursor with metallic Sn indicates that Sn islands form and are oxidized to SnO₂. One possible mechanism for the formation of rutile TiO₂ in this situation is that Sn scavenges oxygen from the Sn/TiO₂ interface, stabilizing the rutile structure of TiO₂ that can accommodate oxygen vacancies.

Graduate Abstracts

Understanding Facet-Dependent Reactivity and Selectivity of IrO₂ in Water Through Ambient Pressure XPS and Electrochemistry

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Rutile IrO₂ electrocatalysts reduce the energy barrier to drive water oxidation and chlorine evolution reactions. Thus, realizing commercial scale (sea)water electrolysis hinges on the development of electrocatalyst materials that improve the efficiency of the oxygen evolution reaction (OER) over the chlorine evolution reaction (CER). We choose a highly active and stable electrocatalyst, IrO₂, to study the relationship between crystallographic orientation and stabilization of critical OER intermediate species. Surface-specific information on the affinity of key reaction intermediates for model, epitaxial thin films allow us to directly relate trends in reaction rate to the electronic structure and coordination environment of these well-defined surfaces. Here we probe polycrystalline, (100)-, and (110)-oriented IrO₂ by ambient pressure x-ray photoelectron spectroscopy (AP-XPS) in oxidizing, humid environments (3e-5 to 0.4 % relative humidity [RH]) at the Advanced Light Source Beamline 9.3.2. We used soft X-rays (<2 keV energy) to observe differences in surface hydroxylation and Ir 4f core levels for these two orientations. Electronic structure and reaction intermediate affinities are then related to OER activity in alkaline electrolyte to provide fundamental insight into electroadsorption of reaction intermediates and kinetics of rutile oxides for oxidative processes. Measurements in acidic, chloride-containing electrolytes relate crystallographic orientation with selectivity between the OER and CER. Together, core level and electrochemical techniques provide new insight into the behavior of these surfaces under electrocatalytically relevant conditions to better understand how to rationally design active and selective next-generation OER electrocatalysts.

Graduate Abstracts

Substrate-metal interaction as a descriptor for electrocatalytic hydrogenation of carbonylic molecules on Palladium in aqueous phase

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Electrocatalytic hydrogenation (ECH) is a promising approach for energy conversion utilizing renewable electricity to transform biogenic carbon sources into valuable products. Carbonyl groups are one of the most abundant and highly reactive functionalities of biomass-derived organic molecules. In the present work, we explore the relationship between substrate structure and catalytic behavior by comparing the rates of aromatic and aliphatic carbonylic compounds on Pd/C catalyst. Furthermore, we associate the different reactivities to the adsorption strengths of the organics on the catalyst. Our main conclusion relies on the influence of the organic-metal interactions on the rates and selectivity of hydrogenation.

We performed ECH reactions of aromatic (benzaldehyde, acetophenone, furfural) and aliphatic (cyclohexanone and butyraldehyde) carbonyl compounds on a Pd/C catalyst as working electrode (cathode) in a two-compartment batch cell varying the applied potential between -0.1 and -0.3 V_{RHE}. A Pt mesh was used as counter electrode (anode) and an Ag/AgCl electrode was used as reference. Sodium acetate buffer (3 M, pH 5.2) was used as electrolyte. In addition, we evaluated the adsorption of the organic substrates via the concentration-dependent inhibition of the deposition of adsorbed hydrogen in the underpotential region (i.e., H_{UPD} region) during cyclic voltammetry (CV) measurements in the presence of varying concentrations of organics on a rotating disk electrode (RDE).

The aromatic carbonylic compounds showed significant reactivity toward hydrogenation to the respective alcohol, whereas the aliphatic ones exhibited small or negligible reduction rates. The H₂ evolution reaction (HER) was the prevalent side reaction during ECH and the total current (HER + ECH) of all reactions increased exponentially with negative potential. However, the faradaic efficiency, i.e., the fraction of the current utilized to reduce the organic compound, decreased with increasing overpotential. The reduction rate for benzaldehyde increased almost linearly with potential (from 782 h⁻¹ at 0.1 V_{RHE} to 2376 h⁻¹ at -0.3 V_{RHE}), and less so for furfural (from 194 h⁻¹ at 0.01 V_{RHE} to 659 h⁻¹ at 0.14 V_{RHE}). For acetophenone, the rate also increased linearly at low overpotential (from 407 h⁻¹ at 0.1 V_{RHE} to 1363 h⁻¹ at -0.2 V_{RHE}), but plateaued at potentials more negative than -0.2 V_{RHE}. Using a two-site Langmuir model, the experimental organic coverages from the CV measurements were fitted and the adsorption constants and Gibbs free energies determined. The corresponding Gibbs free energies of adsorption on Pd were -42 kJ/mol, 39 kJ/mol, -37 kJ/mol and -35 kJ/mol for benzaldehyde, furfural, acetophenone, and cyclohexanone, respectively. Interestingly, these values corroborate the observed rate differences between the reacting organic substrates, showing a correlation between their adsorption strengths, i.e., their surface abundance, and ECH reactivity.

In summary, the ability to evolve H₂ and to hydrogenate the carbonyl group correlates with organic interaction strength with the Pd electrocatalyst (cyclohexanone < acetophenone < furfural < benzaldehyde). Our hypothesis is that this is related to the high coverage and reactivity of the organic compounds for hydrogenation, resulting in a lower availability of surface adsorbed hydrogen, which in turn affects the rates of H₂ evolution.

Graduate Abstracts

Residual Ions Trapping at the $\Sigma 3$ Grain Boundaries of Catalytic Pt Nanoparticle Assemblies

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Platinum catalysts are vital for applications that rely on chemical conversions, including hydrogen sensing. The current generation of Pt-based catalysts require high temperatures ($\sim 500^\circ\text{C}$) to achieve acceptable levels of hydrogen sensing activity, and this high temperature renders the catalyst susceptible to “poisoning” by other gasses, such as H_2S and SO_2 .^[1] Recent research has shown that the efficiency of catalysts can be enhanced through an increased grain boundary density, particularly $\Sigma 3$ twin boundaries.^[2] A new synthesis method has been developed that promotes the density of $\Sigma 3$ grain boundaries through orientation attachment of sodium citrate (NaCA)-capped Pt nanoparticles via electroreduction of water.^[2] While it is believed that the high pH induced near the cathode, where the nanoparticle assembly forms, removes the NaCA ligands, there is the possibility for trace amounts of ions to be trapped between nanoparticles during gelation. Such entrapped ions may then influence the energetics and performance of the catalyst. Laser pulsed atom probe tomography (APT) is uniquely poised as a characterization tool to investigate the composition of these grain boundaries within nanoparticle assemblies, as it has both the sensitivity (nominally ppm) and spatial resolution (~ 1 nm) in three dimensions to locate trace residuals. We report on the chemical identities, spatial distribution, and concentration of impurities at the surface and interfaces of Pt nanoparticles before and after the assembly process. Specifically, we compare the local ion concentrations on the surface of individual nanoparticles and in the grain boundaries between assembled nanoparticles. Such near atomic scale compositional insight is essential to develop predictive processing-structure-performance models for improved platinum nanoparticle assembly catalysts.

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Graduate Abstracts

Laser Sintering of Printed Metal Films for Flexible Hybrid Electronics

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Flexible hybrid electronics (FHE) have a large potential for in-space manufacturing. NASA aims to incorporate additive manufacturing of FHE on the International Space Station (ISS) while reducing power consumption and post-processing time. Direct-deposition printing of inks or colloidal suspensions is the primary process in FHE fabrication to produce various device features on flexible substrates. Unfortunately, printing technologies do not provide a consolidated thin film of the desired material; but only deliver the ink in the form of nanoparticles, or nonconductive clusters, to the substrate.

Laser sintering is an effective post-processing method to sinter nanoparticles while reducing power consumption. An incident laser beam is exposed to the printed film's surface to coalesce particles and evaporate solvents. The surface of the laser sintered film is sensitive to various laser parameters such as power, intensity, wavelength, scanning speed, and pulse duration. These parameters also change with the substrate and the pretreatment of the substrate. Finally, the inherent ink properties, such as absorption cross-section, film composition, and film thickness, modify the laser parameters to create a perfectly sintered film.

In our work, we will present the results from laser sintering of aerosol jet and nScrypt printed silver on glass and Kapton substrates. We will show how the film's surface quality and resultant conductivity vary with different laser parameters and pretreatment conditions. We will compare this with traditional thermal sintering methods and showcase that laser sintering is highly effective and will improve the conductivity and surface quality of printed films.

This work was supported by NASA [grant number ID-19-EPSCoR 0021]

Graduate Abstracts

The application of permanent magnets for high capacitance polyaniline-modified electrodes

William McLeod
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Supercapacitors are energy storage devices useful for their rapid charging and discharging but held back by poor total energy density. Electrode conductivity and surface area are often increased to improve the energy storage of supercapacitors. Polyaniline (PANI) is an electroactive polymer used in supercapacitors for its high conductivity and ease of electrochemical deposition. It has also been shown that the application of a constant magnetic field can alter both the morphology of electrodeposited polymers and the rates of radical-based reactions. Additionally, the application of a strong magnetic field over a net movement of ions, such as is induced by an electric field or concentration gradient, induces rotational convective motion via the Lorentz force. In this work, we used a permanent magnet as a zero-energy-input method to influence the deposition of PANI for high capacitance electrodes with improved energy storage. The polymer was deposited onto glassy carbon or platinum electrodes using cyclic voltametric, potentiostatic, and pulsed potential techniques, and the capacitance of the fabricated electrodes was measured by cyclic voltammetry. When the polymer was deposited under potentiostatic conditions, no difference was found between electrodes fabricated under a magnetic field and those fabricated under no magnetic field. When the polymer was deposited using cyclic voltammetry, the application of a magnetic field improved the capacitance over electrodes fabricated under no magnetic field. This improvement increased under slower scan rates but decreased again at ultra-slow scan rates. Under the pulsed polymerization method, longer pulse time and downtime pairs were found to yield the greatest influence from the magnetic field. With an optimized method, the application of a magnetic field increased the electrodes' capacitance by more than 50% over the control. This presents a method for the fabrication of higher energy density supercapacitors with no additional energy input.

Undergraduate Abstracts

Rh doped “29 oxide” Cu_xO Energy Barriers for H_2 Dissociation

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Numerous chemical processes produce poisonous carbon monoxide gas from partial combustion reactions. This gas is usually removed through the use of a catalyst that oxidizes the gas to form carbon dioxide. Copper-based catalysts on which precious metals are atomically dispersed have shown promise for greater reactivity at lower temperatures. Recently, there has been a great deal of research done on single-site catalysts on which Pt is atomically dispersed on copper oxide thin films, which has shown potential for the preferential oxidation of CO [1]. In a comparative study with Pt, here we present preliminary research on a novel catalyst with the same copper oxide support, but doped with Rh instead. As both Pt and Rh are precious metals, it is informative to analyze and compare their surface reactivity on the selected substrate. To determine its potential as a catalyst for the preferential oxidation of CO, we modeled the dissociation pathway of H_2 and compared it with previous research done with Pt [1,2]. We performed Density Functional Theory (DFT) calculations using the Vienna ab initio Simulation Package (VASP). The Nudged Elastic Band method (NEB) was used to determine the kinetic barriers with three proposed Rh atom site locations on the Cu_xO structures—analogue to the structures of the previous research done with Pt. The configurations investigated were atomically dispersed Rh in and just below the oxide layer, and a cluster of Rh atoms also just below the oxide layer, all centered in one of the open six-membered copper oxide rings of the “29 oxide” Cu_xO structure. Comparing the results to Pt, we find that H_2 reaction pathway on atomically dispersed Rh in the oxide layer is slightly less exothermic and has a slightly larger energy barrier to overcome for its dissociative adsorption. We also find that both atomically dispersed Rh and the Rh cluster just below the oxide layer results in more favorable dissociation conditions than with Pt. With the atomically dispersed and cluster sites under the oxide layer, Pt atom sites are endothermic while Rh atom sites in these positions are exothermic. The energy barriers with Rh were also significantly lower than that with Pt. Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) data confirms these calculation results. When comparing the activity of these catalysts, the dissociative adsorption on H_2 seems more favorable with Rh as compared to Pt, when Rh is under the oxide layer.

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[2] ACS Catal. 10 (2020) 4215.

Undergraduate Abstracts

Hydrogenation of Carbon to Methane on Flat and Stepped Platinum Surfaces

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The introduction of nanoparticles (NPs) into the medical field opens doors for exciting opportunities in medical treatments, especially regarding cancer treatments that utilize radioactive agents. The drawback of traditional therapeutic radioisotopes is the indiscriminate damage they cause to the body, unintentionally generating negative short- and long-term effects, including tissue damage and disruption of normal cell function. A safer and more efficient method to deliver radioisotopes to the site of treatment could help ease these concerns. NPs provide a solution; because of their small size, NPs can penetrate cells (including tumor cells) that more commonly used medications and treatments cannot target specifically, leading to additional unnecessary cellular damage. Within our research project, we are aiming to develop a multimodal cancer therapy by incorporating relevant medical isotopes into iron oxide NPs and creating a gold surface coating which enables the addition of oligonucleotides through gold-thiol linkages. These two aspects will allow the medical isotope to cause less damage within the body as it travels to the tumor site by limiting non-preferential release of the radioisotope, as well as allow for a more targeted delivery system, with the surface oligonucleotides acting as a recognition and attachment system for the tumor. To date we have been able to develop a general synthetic method for iron oxide NPs, explore the role of various surface stabilization species, incorporating a nonradioactive Lu-175 surrogate for the active medical isotope Lu-177. We have also begun the process of gold coating the iron oxide NPs and exploring the ligand exchange between the oligonucleotides using a surrogate Thiol. We are using TEM to interrogate NP morphology UV-vis spectroscopy to characterize the optical properties of the gold coating and performing X-ray fluorescence spectroscopy to determine the extent of isotope dopant incorporation. Moving forward, work will be extended to probe isotope surrogate incorporation for other radioisotopes of interest, including Tc-99 and Th-227 and to verify stability in biological media. Overall, we present a construct for multi-modal radiotherapy, which proves maximally tailorable to individual treatment needs

Undergraduate Abstracts

Gold coated doped-iron oxide nanoparticles for multimodal radiotherapy

Holly Heckerman, Katherine Busiek
Washington State University

The introduction of nanoparticles (NPs) into the medical field opens doors for exciting opportunities in medical treatments, especially regarding cancer treatments that utilize radioactive agents. The drawback of traditional therapeutic radioisotopes is the indiscriminate damage they cause to the body, unintentionally generating negative short- and long-term effects, including tissue damage and disruption of normal cell function. A safer and more efficient method to deliver radioisotopes to the site of treatment could help ease these concerns. NPs provide a solution; because of their small size, NPs can penetrate cells (including tumor cells) that more commonly used medications and treatments cannot target specifically, leading to additional unnecessary cellular damage. Within our research project, we are aiming to develop a multimodal cancer therapy by incorporating relevant medical isotopes into iron oxide NPs and creating a gold surface coating which enables the addition of oligonucleotides through gold-thiol linkages. These two aspects will allow the medical isotope to cause less damage within the body as it travels to the tumor site by limiting non-preferential release of the radioisotope, as well as allow for a more targeted delivery system, with the surface oligonucleotides acting as a recognition and attachment system for the tumor. To date we have been able to develop a general synthetic method for iron oxide NPs, explore the role of various surface stabilization species, incorporating a nonradioactive Lu-175 surrogate for the active medical isotope Lu-177. We have also begun the process of gold coating the iron oxide NPs and exploring the ligand exchange between the oligonucleotides using a surrogate Thiol. We are using TEM to interrogate NP morphology UV-vis spectroscopy to characterize the optical properties of the gold coating and performing X-ray fluorescence spectroscopy to determine the extent of isotope dopant incorporation. Moving forward, work will be extended to probe isotope surrogate incorporation for other radioisotopes of interest, including Tc-99 and Th-227 and to verify stability in biological media. Overall, we present a construct for multi-modal radiotherapy, which proves maximally tailorable to individual treatment needs.

Undergraduate Abstracts

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Upon exposure to hydrogen, many metals undergo a loss of ductility in a phenomenon called hydrogen embrittlement (HE). HE will cause premature failure and is a problem in many engineering projects. Studying and characterizing HE is crucial to create alloys that resist this phenomenon. In a laboratory setting, samples are 'charged' with hydrogen in an electrochemical cell where the sample is placed in a salt solution with an inert electrode and a negative potential is applied to the sample. Due to the negative charge on the samples, hydrogen is reduced via water electrolysis and either evolves H₂ gas or permeates into the steel. After charging the samples with hydrogen, they can then be characterized; however, the hydrogen may escape between the charging and testing. It has been reported that hydrogen diffuses out in as little as seconds, necessitating a different approach to testing and charging samples. In this report, we present the creation of electrochemical cells for in situ charging and testing of model austenitic stainless-steel samples. These cells enable the in situ investigation of deformation behaviors during hydrogen charging using synchrotron X-ray diffraction and scanning electron microscopy.

Undergraduate Abstracts

Studying the Mechanical Properties Influenced by Hydrogen Interaction in Austenitic Stainless Steels Using In-situ Nanoindentation Technique

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Tanks and pipeline systems for transporting liquid hydrogen are commonly composed of 316 type austenitic stainless steels (SS). The combination of subjected stresses and the presence of hydrogen are known to make 316SS susceptible to hydrogen embrittlement. Previous studies demonstrated a relationship between deformation mechanisms in the presence of hydrogen, and reduction in its load-bearing capacity. However, a correlation between the microstructure and mechanical properties needs to be formed. Small-scale mechanical testing (SSMT) can be advantageous to evaluating local-hydrogen effects by measuring location-specific mechanical properties in a dimensional range between nanometers to micrometers. In this study, this was achieved using an in situ nanoindentation technique inside the plasma focused ion beam/scanning electron microscope (PFIB/SEM) system. The orientation and hydrogen dependence on hardness of three single crystals of 316SS samples in [001], [011], and [123] directions were explored. Such a fundamental study on hydrogen effects in stainless steels using SSMT techniques will be helpful for material developments on a commercial scale.