

Abstract Book

2020 Symposium of the Pacific Northwest Chapter of the AVS



September 24-25, 2020

**Virtual Meeting hosted by
Environmental Molecular Sciences Laboratory at
Pacific Northwest National Laboratory
Richland WA, 99352**

Contact: Zihua Zhu, PNWAVS Chair

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The 31st Annual Symposium of the PNWAVS Science and Technology Society (www.pnwavs.org) will be a virtual meeting hosted by EMSL located at Pacific Northwest National Laboratory in Richland, WA. The meeting will consist of two days of invited talks, plenary speakers, and student presentation competitions.

The PNWAVS symposium has a long tradition of providing a stimulating interdisciplinary program in a relaxed, informal atmosphere. The meeting attracts a broad representation of government, corporate, and university researchers from throughout the Pacific Northwest, Western Canada and Alaska. The symposium provides an excellent opportunity for students and postdocs to sharpen their presentation skills. This tradition will continue as we adopt a virtual format for the 2020 Symposium due to the Coronavirus pandemic. We are focusing on student presentations and awards during this year's symposium.

Agenda for the 2020 PNWAVS Symposium			
September 24, 2020 (Thursday) Morning			
8:15-8:30	Zihua Zhu	Greetings	Pacific Northwest National Laboratory
Session 1: Advanced Materials. Chair: Vaithiyalingam Shutthanandan			
8:30-9:10	David Ginger	(Invited) TBD	University of Washington
9:10-9:25	Yujing Zhang*	Facial Synthesis of Photoluminescent Zeolitic Imidazolate Framework on Nanostructured Zinc Oxide Thin Film: A Photoluminescence-Based Carbon Dioxide Gas Sensing Platform	Oregon State University
9:25-9:40	Kevin D. Vallejo*	Self-Assembly of InGaAs Quantum Dots on InAs(111)A via molecular beam epitaxy	Boise State University
9:40-9:55	Brian Muhich**	Transition Metal Selenide-Based Electrocatalysts for Water Oxidation Reaction	Oregon State University
9:55-10:10	Maoyu Wang*	Ultrahigh Oxygen Evolution Reaction Activity Achieved Using Ir single atoms on amorphous CoO _x nanosheets	Oregon State University
10:10-10:25	Shujie Li*	Low-Temperature Processing Inkjet-Printed P-Type Transparent CuBrI Thin Film Transistor	Oregon State University
10:25-10:40	Break		
Session 2: Applied Surface Science (I). Chair Zihua Zhu			
10:40-10:55	Yanjie Shen*	Liquid ToF-SIMS revealing the oil, water, and surfactant interfacial evolution	Ocean University of China
10:55-11:10	Yuchen Zhang*	Evaluating the effect of PGPR on seedling growth potential using ToF-SIMS	Huazhong Agricultural University
11:10-11:25	Yatong Zhao*	Probing Trace Fe and Cr Incorporation During Crystal Growth of Gibbsite	Nanjing University
11:25-11:40	Ariel Whitten*	Understanding the Chemical Meaning of Information-rich XANES Spectra	Washington State University
11:40-11:55	Pedro Alzaga*	Oxidation of Amorphous Metal Alloy Surfaces Studied Using Ambient Pressure X-Ray Photoelectron Spectroscopy	Oregon State University
11:55-12:10	Hoan Nguyen*	Ambient Pressure X-Ray Photoelectron Spectroscopy Study of Thermal Decomposition of Acetic Acid on Pd(111)	Oregon State University
12:10-12:40	Break		
September 24, 2020 (Thursday) Afternoon			
Plenary Session (I). Chair: Tiffany Kaspar			
12:40-13:30	Kai-Mei Fu	(Plenary) Engineering Quantum Defects for Quantum Network Applications	University of Washington
Session 3: Advanced Material Interfaces. Chair: Tiffany Kaspar			
13:30-14:10	Song Jin	(Invited) Fundamental Studies and Optoelectronic Applications of Metal Halide Perovskite Nanostructures	University of Wisconsin-Madison

14:10-14:25	K. Mullapudi*	Synthesis of WS ₂ nanostructures using atomic layer deposition and post-deposition sulfur annealing	Oregon State University
14:25-14:40	Kathryn E. Sautter*	Tensile-Strained Germanium Quantum Dots on InAlAs(110)	Boise State University
14:40-14:55	Marcos Lucero*	High performance iron-based phosphate anode for aqueous sodium-ion batteries	Oregon State University
14:55-15:10	Tyler D. McCrea*	Synthesizing Colloidal PbSe Quantum Dots for the Investigation of Gamma Ray Spectroscopy Resolution in Semiconductor Radiation Detection Devices	Oregon State University
15:10-15:25	Carrington Moore*	Analyzing the Conversion of 2,3-Butanediol to Butene From First Principles	Washington State University
15:25-15:40	Break		
Session 4: Applied Surface Sciences (II). Chair: Xin Zhang			
15:40-15:55	K. Mullapudi*	Remote oxygen plasma-enhanced atomic layer deposition of tungsten oxide	Oregon State University
15:55-16:10	Suyun Wang*	Understanding the crystallization mechanism of copper nanoparticles during thermal decomposition of Cu-MOF using TEM techniques	Nanjing University of Science and Technology
16:10-16:25	Nurun Nahar Lata*	Physicochemical characterization of vertically resolved atmospheric particles via unmanned aerial system	Michigan Technological University
16:25-16:40	Yadong Zhou*	Molecular revealing of mixing states of aerosol particles using ToF-SIMS spectra and imaging analysis	East China Normal University
16:40-16:55	Rhenton Brimberry**	Analysis of Aerosol Composition During a Dust Event in the Northern Atlantic	Washington State University
16:55-17:10	Naseeha Cardwell*	Solvent and Coverage Effects on the Stability of HDO Relevant Aromatics	Washington State University
September 25, 2020 (Friday) Morning			
Session 5: Applied Surface Sciences (III); Chair: Zhenxing Feng			
8:30-9:10	David Harrington	(Invited) Electrooxidation and Dissolution of Pt(111) and Pt(100)	University of Victoria
9:10-9:25	Kingsley Chukwu*	Effect of co-adsorbed water on acetic acid decomposition on Pt (111) using Density Functional Theory	Oregon State University
9:25-9:40	Kofi Oware Sarfo*	The role of chloride in the initial stages of the breakdown of α -Cr ₂ O ₃ passive layer: a density functional theory study	Oregon State University
9:40-9:55	Quinn Carvalho*	An AP-XPS Study of La _{1-x} Sr _x NiO _{3-δ} Perovskite OER Catalysts: Interpretation of Mechanistic Rate Limiting Step	Oregon State University
9:55-10:10	Sri Krishna Murthy*	Probing the surface reactivity of amorphous aluminum oxide thin-films using methanol: An Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) study	Oregon State University
10:10-10:30	Break		

Session 6: Applied Surface Sciences (IV); Chair: Mark Engelhard			
10:30-11:10	Xin Zhang	(Invited) Probing the mineral crystallization and phase transformation via advanced transmission electron microscopy	Pacific Northwest National Laboratory
11:10-11:25	Jiyoung Son	Interactions between synthetic bilgewater emulsion and biofilms	Pacific Northwest National Laboratory
11:25-11:40	Xiao-Ying Yu	Molecular insights into communications of Geobacter syntrophic communities	Pacific Northwest National Laboratory
11:40-11:55	Jennifer Yao	Detection and identification of PFASs using ToF-SIMS and principal component analysis	Pacific Northwest National Laboratory
11:55-12:30	Break		
September 25, 2020 (Friday) Afternoon			
Plenary Session (II); Chair: Mark Engelhard			
12:30-13:10	Jeff Kissel	(Plenary) Astronomy's Future is LOUD: LIGO+Virgo Observations of the Universe to-Date	Laser Interferometer Gravitational-Wave Observatory
13:10-14:10	Award ceremony and closing remarks		
14:10-15:30	PNWAVS Chapter board meeting		
* = Graduate student; ** = Undergraduate student			

September 24, 2020 (Thursday) 8:15-8:30
Zihua Zhu: Chairman Greetings

September 24, 2020 (Thursday) 8:30-9:10
David Ginger: (Invited) TBD

September 24, 2020 (Thursday) 9:10-9:25
Facial Synthesis of Photoluminescent Zeolitic Imidazolate Framework on Nanostructured Zinc Oxide Thin Film: A Photoluminescence-Based Carbon Dioxide Gas Sensing Platform

Yujing Zhang¹, Tianlei Li¹, Justin Y. Lu¹, Zhong Chen², Alan X. Wang³, Ki-Joong Kim^{4,5}, Paul R. Ohodnicki^{4,6}, and Chih-Hung Chang^{1,*}

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ZnO/ZIF-8 composite thin films are prepared *via* a room-temperature facial conversion of ZnO nanorods in 2-methylimidazole precursor solution. Different composition of ZnO/ZIF-8 composite thin films is obtained by varying the reaction time. All the composite thin films exhibit yellow and green photoluminescence (PL) emissions that are of interest in PL-based gas sensing application. A novel PL-based optical gas sensing platform for CO₂ based on ZnO/ZIF-8 composite thin films is investigated in this work. The influences of ZnO/ZIF-8 composition on the PL properties of the thin films and the corresponding sensing responses toward CO₂ are studied. It is revealed for the first time that ZnO/ZIF-8 composite thin films with different compositions present different sensitivity toward CO₂. In addition, the PL sensing response based on single ZnO and ZIF-8 thin films toward CO₂ is analyzed. A hypothesis regarding the PL-based CO₂ gas sensing mechanism based on ZnO/ZIF-8 composite structure is proposed.

September 24, 2020 (Thursday) 9:25-9:40

Self-Assembly of InGaAs Quantum Dots on InAs(111)A via molecular beam epitaxy

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In this study we have mapped the growth parameters for optimal homoepitaxy of InAs on InAs(111)A substrates using molecular beam epitaxy.[1] Increasing the substrate temperature reveals a transition from 2D flat island growth to step-flow. The optimized parameters we established (substrate temperature = 500° C, growth rate = 0.12ML/s and V/III ratio = 48) produce an atomically flat surface, free of 3D imperfections. We study material quality using photoluminescence and have established a relationship between InAs(111)A surface smoothness and light emission intensity. This work paves the way for integrating the 6.1 Å family of materials with the desirable properties of semiconductors with a (111) orientation.[2] We will then present preliminary results demonstrating the self-assembly of InGaAs quantum dots on these smooth InAs(111) surfaces, indicating new paths towards low bandgap tunable light emitters for infrared optoelectronics.

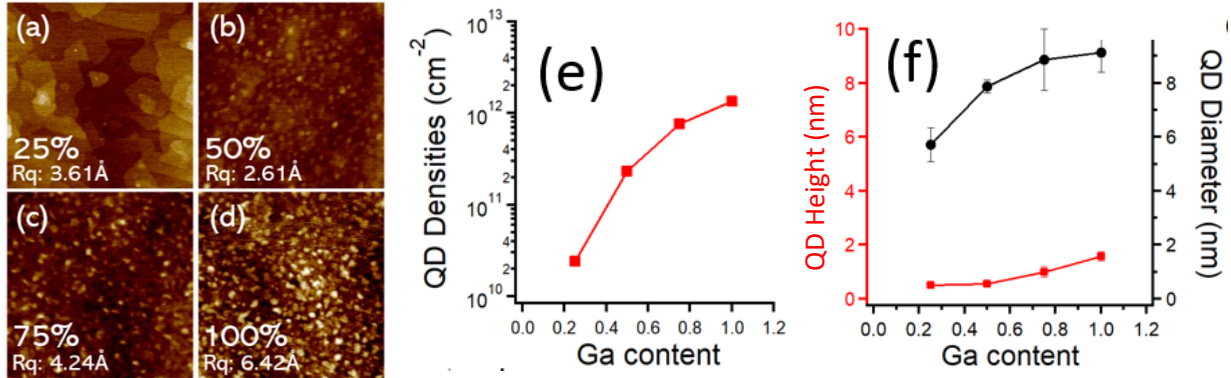


Figure 1 (a-d) 500 nm x 500 nm AFM scans of In_{1-x}Ga_xAs QDs grown on InAs(111)A with varying Ga content. R_q is the root mean squared roughness of each sample. We grew all samples at T_{sub}=410° C and deposited 3 ML of In_{1-x}Ga_xAs. **(e)** Graph of InGaAs QD density vs. Ga content. **(f)** Graph of average heights and diameters of InGaAs QDs vs. Ga content.

References:

[1] Vallejo, Kevin D., et al. "InAs (111) A homoepitaxy with molecular beam epitaxy." *Journal of Vacuum Science & Technology B*, **37** 061810 (2019).

[2] C. D. Yerino, B. Liang, D. L. Huffaker, P. J. Simmonds, and M. L. Lee, "Review Article: Molecular beam epitaxy of lattice-matched InAlAs and InGaAs layers on InP (111)A, (111)B, and (110)," *Journal of Vacuum Science & Technology B*, **35**, 010801 (2017).

September 24, 2020 (Thursday) 9:40-9:55

Transition Metal Selenide-Based Electrocatalysts for Water Oxidation Reaction

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Water splitting reactions represent a promising future avenue for clean energy storage and fuels, and the development of inexpensive and commercially friendly electrocatalysts is essential for the widespread utilization of such processes. Oxygen evolution reaction (OER), also known as water oxidation reaction, is a key component of the overall water splitting reaction, and currently, the most effective catalysts for OER are RuO₂ and IrO₂. Due to the scarcity of noble metals like Ru and Ir, effective catalysts composed of more abundant transition metals are desired. Among these transition metal catalysts, (Ni, Co)Se materials have shown significant promise as effective OER catalysts. In this project, we explore the enhanced OER activity through the use of (Ni, Co)Se catalysts and also explore different means by which to optimize this catalyst through different NiCo compositions. Through the use of electrochemical tests, we have observed higher favorable reaction kinetics at higher concentrations of Co and lower overpotentials at higher concentrations of Ni, with good stability overall. We attribute these characteristics to the *in-situ* development of NiOOH active sites and the higher conductivity of Co. This work provides insights in the development of efficient and noble metal free OER electrocatalysts based on the optimization of transition metal compositions, and future physical characterization can advance our understanding of a catalyzed water splitting mechanism and the development of chemically stable electrocatalysts.

September 24, 2020 (Thursday) 9:55-10:10

Ultrahigh Oxygen Evolution Reaction Activity Achieved Using Ir single atoms on amorphous CoOx nanosheets

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In the past decades, the renewable energy storage and energy conversion systems, such as fuel cells, water electrolysis, and metal-air batteries, have attract great attention. Oxygen evolution reaction (OER) is a key half reaction of water splitting to produce clean fuels. However, the

sluggish kinetics of OER has significantly limited the performance and commercialization of such energy conversion devices. Up to now, the most efficient OER catalysts are still noble metal and metal oxides of Ruthenium (Ru) and Iridium (Ir), which are not cost-effective catalysts and unstable under high potentials. Recently, single atom catalysts have been used to improve the surface-to-volume ratio to increase OER catalytic activity. In our work, Ir single-atom catalysts supported by CoO_x amorphous nanosheets (ANSs) for OER. Experimental results show that Ir single-atoms are anchored by abundant surface-absorbed O in CoO_x ANSs. The Ir single-atom catalysts possess ultrahigh mass activity that is 160-fold of commercial IrO₂. The OER of IrCoO_x ANSs reached a record-low onset overpotential of less than 30 mV. The *in-situ* X-ray absorption spectroscopy reveals that the Ir-O-Co pairs directly boosted the OER efficiency and enhanced the Ir stability.

References:

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2. J. Suntivich, K. J. May, H. A. Gasteiger, J. B. Goodenough and Y. Shao-Horn, *Science*, 2011, **334**, 1383.
3. P. Li, M. Wang, X. Duan, L. Zheng, X. Cheng, Y. Zhang, Y. Kuang, Y. Li, Q. Ma, Z. Feng, W. Liu and X. Sun, *Nature Communications*, 2019, **10**, 1711.

September 24, 2020 (Thursday) 10:10-10:25

Low-Temperature Processing Inkjet-Printed P-Type Transparent CuBrI Thin Film Transistor

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Thin-film semiconductors, made by solution-processed technique, offer essential cost reductions in terms of the fabrication of electronic and optoelectronic devices. Printing technology, a direct writing method, has provided several benefits, such as selective deposition, waste elimination, and precise quantities. P-type TFTs are highly desired to achieve complementary circuits with less power dissipation and high noise resistance. However, there are only a few studies on inkjet-printed inorganic p-type semiconductor TFTs. Low temperature-processed P-type copper iodide TFT was first published in 2016 by Choi et al [1]. The hole density of CuI can be turned by alloying the CuBr that also has a zinc-blende structure and $E_g \approx 3$ eV. Especially for p-type TFT application, the high hole density of as-fabricated CuI films makes it difficult to module the current leading to the high off current and thus a low on/off ratio. [2]

In this study, the hole density tunability of CuBr_xI_{1-x} ($x = 0-1$) thin films deposited at low-temperature processing was experimentally and theoretically investigated. The electronic and

optical property of $\text{CuBr}_x\text{I}_{1-x}$ alloys as a function of x was studied. Also, the alloy composition as a function of x was further characterized by X-ray photoelectron spectroscopy (XPS) analysis. The p-type $\text{CuBr}_x\text{I}_{1-x}$ thin film transistor was fabricated by inkjet printing technology. We demonstrate that the off current of the TFT can be reduced either from the TCAD simulation and as-fabricated device through inkjet printing technology. These results show that the p-type, transparent, CuBrI thin film transistor can be achieved at low temperatures with a tunable on/off ratio.

Acknowledgment: This work was supported by the US National Science Foundation [CMMI #1537196, CBET# 1449383] and the Walmart Manufacturing Innovation Foundation.

References:

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- [2] Yamada, N, Tanida, Y, Yoshida, S. Wide-Range-Tunable p-Type Conductivity of Transparent $\text{CuI}_{1-x}\text{Br}_x$ Alloy. *Advanced Functional Material*, 30(34), 2020, 2003096

September 24, 2020 (Thursday) 10:25:10:40

Break

Session 2: Applied Surface Science (I). Chair: Zihua Zhu

September 24, 2020 (Thursday) 10:40-10:55

Liquid ToF-SIMS revealing the oil, water, and surfactant interfacial evolution

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Bilgewater formed from the shipboard is regarded as a major pollutant in the marine environment. Bilgewater exists in a stable oil-in-water (O/W) emulsion form. However, little is known about the O/W liquid-liquid (l-l) interface. Traditional bulk characterization approach is not capable of capturing the chemical changes at the O/W l-l interface. Although surfactants are deemed essential in droplet formation, their roles in bilgewater stabilization are not fully revealed. We have employed novel in situ chemical imaging tools including in situ scanning electron microscopy (SEM) and in situ time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study the evolving O/W interface using a NAVY bilge model for the first time. The droplet size distribution (DSD) does not change significantly without the addition of X-100 surfactants at static or rocking conditions. Both the oil components and the water clusters are shown to evolve over time at the O/W droplet interface by in situ liquid SIMS imaging. Of particular interest to droplet

stabilization, the contribution of surfactants to the aged bilge droplets becomes more significant as the droplet size increases. The higher mass surfactant component does not appear on the droplet surface immediately while many lower mass surfactants are solvated inside the droplet. We have provided the first three-dimensional images of the evolving O/W interface and demonstrated that in situ surface chemical mapping is powerful to reveal the complex and dynamic I-I interface in the liquid state. Our observational insights suggest surfactants are important in mediating droplet growth and facilitating effective separation of bilgewater emulsion.

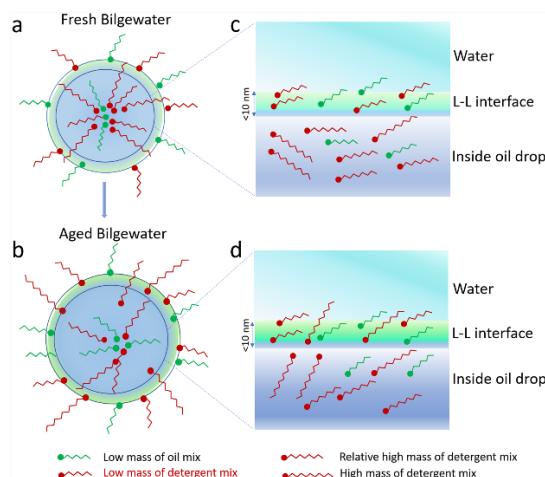


Figure 1 The schematic showing the evolution of the O/W interface in fresh and aged bilgewater.

References:

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- [2] J. Church, J. G. Lundin, D. Diaz, D. Mercado, M. R. Willner, W. H. Lee and D. M. Paynter, Identification and characterization of bilgewater emulsions, *Sci Total Environ*, 2019, 691, 981-995.

September 24, 2020 (Thursday) 10:55-11:10

Evaluating the effect of PGPR on seedling growth potential using ToF-SIMS

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Bacterial are known to use plant as hosts. The plant growth-promoting rhizobacteria (PGPR) on the plant host surface play a key role in biological control and pathogenic response.^[1]

Brachypodium distachyon (Brachypodium), a genomics model for bioenergy and native grasses, is used due to its small diploid genome, relative ease of genetic transformation, short life cycle and simple growth requirements.^[2] Two Gram-negative and Gram-positive model PGPRs, namely, *Pseudomonas fluorescens* (P.) and *Arthrobacter* (A.) were introduced to the Brachypodium seed's brush sections prior to germination, and their potential effects on seeding were studied using ToF-SIMS imaging. Specifically, delayed image extraction was used in data acquisition, in addition to high resolution mass spectral imaging, to obtain high mass and high spatial resolutions.^[3] ToF-SIMS high mass resolution spectral comparison of the seed sections shows that key plant metabolite products and biomarkers such as flavonoids, phenolic compounds and fatty acids are observable. Furthermore, principal component analysis (PCA) and two-dimensional (2D) imaging analysis reveal that the seed brush section is more sensitive to PGPR, accompanied by chemical composition and morphology change. Our results demonstrate that ToF-SIMS can be an effective tool to probe cell-to-cell interactions at the biointerface in phyllosphere and rhizosphere.

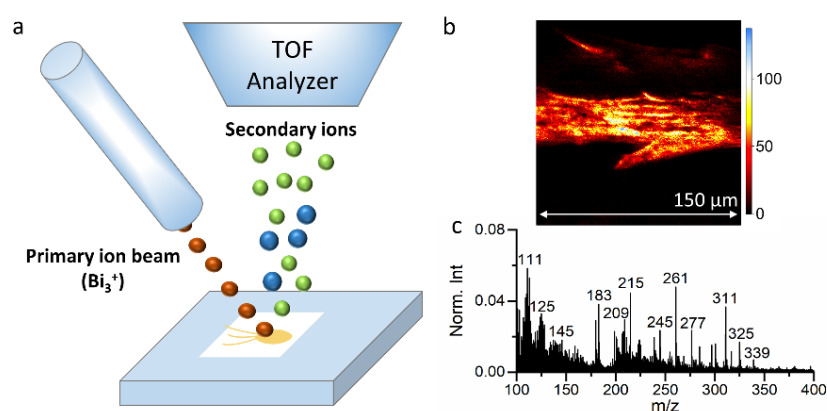


Figure 1 (a) A schematic of brush section of seed sample in ToF-SIMS analysis; (b) A representative ToF-SIMS negative 2D total ion images of *P.*-treated seed; and (c) A representative ToF-SIMS negative spectrum of the *P.*-treated seed brush in m/z^- 100–400.

References:

- [1] Ahkami, A. H., Allen White, R.; Handakumbura, P. P.; Jansson, C. Rhizosphere engineering: Enhancing sustainable plant ecosystem productivity. *Rhizosphere* **2017**, 3, 233-243.
- [2] Thomas Girin, Laure C. David, Camille Chardin *et al.*, Brachypodium: a promising hub between model species and cereals, *J. Experimental Botany* (2014), **65** (19), 5683-96.
- [3] Vanbellinghen QP, Elie N, Eller MJ *et al.*, Time-of-flight secondary ion mass spectrometry imaging of biological samples with delayed extraction for high mass and high spatial resolutions, *Rapid Comm. Mass Spectrom.* (2015), **29** (13), 1187-95.

September 24, 2020 (Thursday) 11:10-11:25

Probing Trace Fe and Cr Incorporation During Crystal Growth of Gibbsite

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Gibbsite (α -Al(OH)₃) is a widespread material in nature and various industrial processes and also are major component in the high-level nuclear waste storage tanks at the US DOE Hanford Nuclear Reservation (WA, USA), the Savannah River site (SC, USA), and the West Valley Nuclear Site (NY).^{1, 2} High-level nuclear wastes contain complex mixtures of dissolved constituents, and thus the growth of gibbsite in these wastes always incorporate with impurities.³ The incorporation of relatively minor impurity metals onto gibbsite can strongly impact its structure and stability, such the solubility in caustic solutions.⁴ Understanding the trace metal incorporation during crystal growth of gibbsite may help improve kinetics models and ultimately provide a stronger foundation for the development of robust nuclear waste processing strategies. Herein, we report the incorporation behaviors of trace Fe and Cr during the crystal growth of gibbsite. We first synthesized the gibbsite nanoplates with/without adding Cr (III) or Fe (III) (0.01%-0.5%) ions during hydrothermal treatment. We also prepared a series of Cr (III) or Fe (III) adsorbed gibbsite samples via adding as-synthetic pure gibbsite nanoplates into 5-100 ppm Cr (III) or Fe (III) solutions. Then we explored these Cr (III) or Fe (III) doped/adsorbed gibbsite samples in detail using various characterization techniques. Structural and morphological of as-prepared samples were characterized by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The ratios of Al/Cr or Al/Fe in bulk solids were quantified by inductively coupled plasma - optical emission spectrometry (ICP-OES) and Electron Paramagnetic Resonance (EPR). The surface-sensitive analysis techniques including X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) were employed to obtain the ratios of Al/Cr or Al/Fe on gibbsite surface. Comparing the samples with similar Al/Cr or Al/Fe ratio in bulk solids, the intensity of Cr in ToF-SIMS spectra was similar for both doped and adsorbed sample but the iron signal in adsorbed samples was much higher than doped samples, which indicated the Fe(III) can incorporated into the gibbsite bulk structure but Cr(III) cannot. The Cr(III) can only adsorb on the gibbsite surface and the adsorption capability of Cr(III) was much higher than Fe(III).

References:

- [1] R. A. Peterson, *et al.* Review of the Scientific Understanding of Radioactive Waste at the U.S. DOE Hanford Site. *Environ Sci Technol* 52 (2018) 381-396.
- [2] X. Zhang, *et al.* Boehmite and Gibbsite Nanoplates for the Synthesis of Advanced Alumina Products. *ACS Appl. Nano Mater.* 1 (2018) 7115-7128.
- [3] W. Cui, *et al.* Cr(III) Adsorption by Cluster Formation on Boehmite Nanoplates in Highly Alkaline Solution. *Environ. Sci. Technol.*, 53 (2019) 11043-11055.
- [4] W. Cui, *et al.* Effect of Cr(III) Adsorption on the Dissolution of Boehmite Nanoparticles in Caustic Solution. *Environ Sci Technol*, 54 (2020) 6375-6384.

September 24, 2020 (Thursday) 11:25-11:40

Understanding the Chemical Meaning of Information-rich XANES Spectra

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Reserves of shale gas contain large amounts of ethane and propane in the U.S., consequently there has been significant interest in finding ways to create olefins and aromatics from dehydrogenation and dehydrocyclization reactions.¹ Gallium can be added to zeolites to increase selectivity and catalyst stability under industrial conditions for these reactions.² Due to the poor crystallinity of gallium, X-ray absorption spectroscopy (XANES) must be used to determine local site symmetry in order to elucidate the structure of the molecule. XANES is also unique because it can measure reactivity of metal sites under *operando* conditions, but the computational cost and the non-uniformity of the catalytic materials make the interpretation of these results elusive. One solution to this problem is to implement machine learning by creating a large library of well-defined spectra to correlate specific features in the spectra to structural properties. In this work, we not only determine the dependence of the K-edge XANES spectra on the oxidation state of gallium, but also how the surrounding environment determines specific peaks.

To better understand the features of these spectra, calculations were performed using CASTEP, StoBE and the FEFF software packages. We compare these theoretical calculations to the experimental results of several well-defined Ga(III) compounds to ensure that the predictive models fit the experimental data. In doing so, we correlate the XANES features to orbital analysis of these compounds when Ga has a 3-fold or a 4-fold coordination. Once a large enough library of spectra has been measured, the goal is to use the data to predict spectra of ill-defined Ga-containing materials to better understand the reaction environment in order to promote better catalyst choices for specific reactions.

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September 24, 2020 (Thursday) 11:40-11:55

Oxidation of Amorphous Metal Alloy Surfaces Studied Using Ambient Pressure X-Ray Photoelectron Spectroscopy

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Amorphous metal thin films (AMTFs) are of growing interest due to their unique mechanical properties and chemical stability. For this reason, AMTFs have been investigated as potential materials for a wide range of applications such as protective layers in microelectromechanical systems, coatings for biomedical tools, and as metal-insulator-metal tunnel diode electrodes. However, AMTFs are

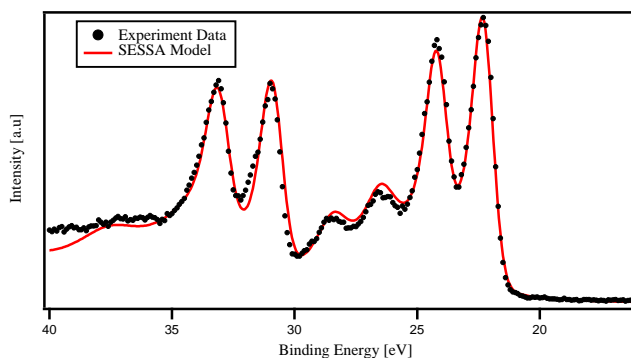


Figure 1. XPS spectrum of AMTF oxidized under 1 mbar and 25 °C compared to spectrum calculated for a model system using SESSA.

known to be structurally and chemically unstable at higher temperatures and therefore the thermal stability of these materials need to be closely studied. The present research is focused on the thermal stability in O₂ of a ternary AMTF with a composition of Ta₅₄W₂₇Si₁₉ using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). *Operando* AP-XPS allows the composition and oxidation states of the growing oxide layer to be measured as the AMTFs are heated in varying temperatures and O₂ partial pressures (P_{O_2}). Experiments were performed with P_{O_2} between 10⁻⁴ to 10 mbar and temperatures between 25 to 300 °C. XPS core levels have been measured at relatively short time intervals, which made it possible to determine the rate of oxide growth in combination with calculations using the Simulation of Electron Spectra for Surface Analysis (SESSA) software package. In Figure 1, we compare the Ta 4f and W 4f spectrum obtained from the AMTF during oxidation at P_{O_2} = 1 mbar at 25 °C to the results from SESSA for a proposed model system (i.e. oxide composition and thickness). The analysis of the AP-XPS data, along with the SESSA modeling, indicated an increase in the apparent oxidation activation energy for Ta₅₄W₂₇Si₁₉ compared to similarly prepared polycrystalline tantalum films. The results also indicated that Ta in TaWSi films was preferentially oxidized, thus forming primarily a tantalum pentoxide (Ta₂O₅) layer on the surface.

September 24, 2020 (Thursday) 11:55-12:10

Ambient Pressure X-Ray Photoelectron Spectroscopy Study of Thermal Decomposition of Acetic Acid on Pd(111)

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Acetic acid decomposition over Pd(111) is a good model for the decomposition of fatty acids and other oxygenates involved in biofuel production. Our previous density functional theory (DFT) studies on the thermal decomposition of acetic acid on Pd(111) suggested that carbon monoxide (CO) and carbon dioxide (CO₂), are produced by two different reaction pathways: decarbonylation (DCN), and decarboxylation (DCX), respectively. Without water, the DCN, producing CO, is slightly favored over the DCX pathway but in the presence of water, that shifts to mostly CO₂. To further understand these reaction mechanisms, we have studied this model system using ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and mass spectrometry (MS). During AP-XPS and MS experiments the acetic acid was dosed at several pressures: 0.001, 0.04, 0.11, 1.0 mbar on clean Pd(111) at 300K. AP-XPS allowed us to identify adsorbed reaction intermediates, including surface carbon, adsorbed CO, and physis- and chemisorbed acetate species. In order to confirm our DFT results, we introduced a 1:1 mixture of water and acetic acid at various pressures and temperatures. We found that the CO₂:CO mass peak ratios increased from 0.52 to 1.75 for 0.001 mbar to 1 mbar, respectively, when acetic acid was exposed to Pd(111) at 300K. This mass peak ratio also increases from 1.75 to 2.09 in the presence of water at 1 mbar and 300K, which suggests that more CO₂ is produced in the presence of water. AP-XPS data shows that the ratio of adsorbed acetate to adsorbed CO decreases when water is added suggesting that more acetate is converted to products other than CO but more data are needed to establish statistical significance. Future experiments include lower pressures to separate the contribution of gas phase from the surface reaction as well as varied temperatures.

September 24, 2020 (Thursday) 12:10-12:40

Break

September 24, 2020 (Thursday) Afternoon

Plenary Session (I). Chair: Tiffany Kaspar

September 24, 2020 (Thursday) 12:40-13:30

Engineering Quantum Defects for Quantum Network Applications (Plenary)

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Point defects in crystals are the solid-state analog to trapped ions. Thus these “quantum defects” have gained popularity as a qubit candidate for scalable quantum networks. I will introduce some of the basic quantum defect properties desirable for quantum network applications and give some illustrative examples of recent successes toward scalable quantum networks (for example, see Fig. 1). The talk will address both defect creation and characterization with a focus on the nitrogen-vacancy (NV) center in diamond.

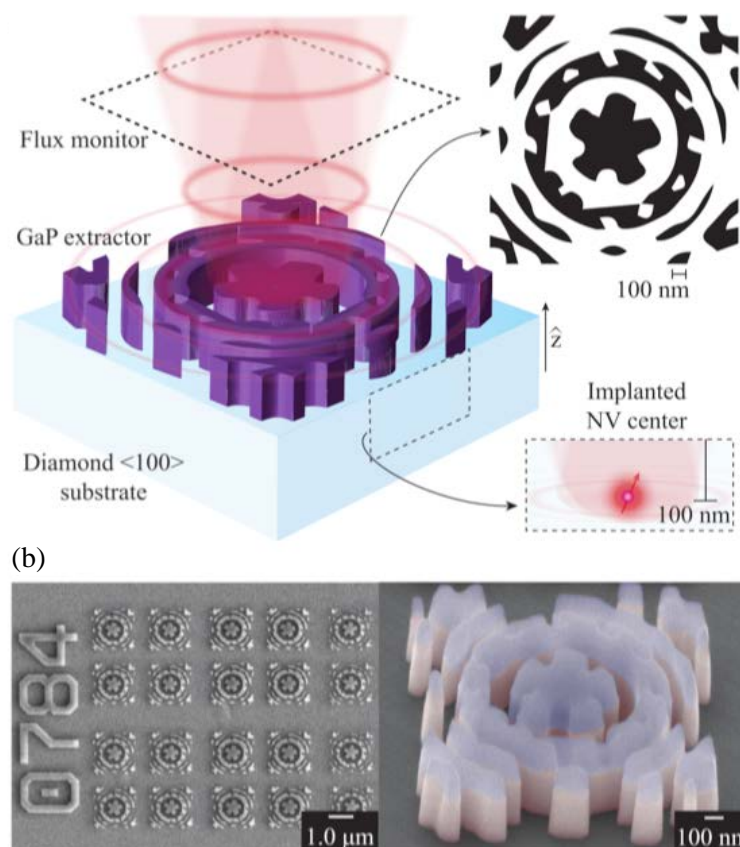


Figure 1 Example of photon extractor device designed to efficiently outcouple light from a single quantum emitter. **(a)** Schematic of gallium phosphide (GaP) photon extractor on diamond. An NV center < 100 nm from the GaP-diamond interface is coupled to the device **(b)** Scanning electron micrographs of fabricated devices [1].

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Session 3: Advanced Material Interfaces. Chair: Tiffany Kaspar

September 24, 2020 (Thursday) 13:30-14:10

Fundamental Studies and Optoelectronic Applications of Metal Halide Perovskite Nanostructures (Invited)

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The remarkable solar performance of lead halide perovskites can be attributed to their excellent physical properties that present many mysteries, challenges, as well as opportunities. Better control over the crystal growth of these fascinating materials would further enhance their applications. I will first discuss the solution growth of single crystal nanowires and nanoplates of various 3D lead halides perovskites that have demonstrated high performance room temperature lasing with broad tunability of emission. I will then discuss the growth of heterostructures of 2D Ruddlesden–Popper (RP) layered lead iodide perovskites with defined *n* phases and atomically sharp interfaces both in 2D/3D perovskite heterostructures and also as multi-layered vertical heterostructures, in which the long chain ammonium ligands serve as the barriers to prevent ion migration across the junctions; as well as lateral heterostructures with different chemical compositions. We have used these well-defined heterostructures to study the carrier transfer mechanisms between different perovskite phases. The excellent properties of these nanostructures and nanoscale heterostructures of diverse families of perovskite materials with different cations, anions, and dimensionality make them ideal for fundamental physical studies and for enabling high performance lasers, LEDs, and other optoelectronic applications.

References:

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September 24, 2020 (Thursday) 14:10-14:25

Synthesis of WS₂ nanostructures using atomic layer deposition and post-deposition sulfur annealing

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Tungsten disulfide (WS_2) has gained attention in recent years for its applications in spinFETs,¹ catalysis,² and promise as a 2D material. Atomic layer deposition (ALD) is an ideal technique for achieving highly conformal and uniform films with the layer by layer thickness control needed for these applications, but faces challenges in achieving high crystallinity. While recent efforts target improving film crystallinity, either by inducing substrate inhibited growth,³ or by post-deposition annealing,⁴ growing crystallites of the order of a few microns in size remains a challenge and new processes are needed. Here, we report ALD of WS_2 films using a novel metal-organic tungsten precursor (WSN-4) and H_2S at temperatures $\geq 290^\circ\text{C}$. Post-deposition sulfur annealing at 600°C and above improves film crystallinity (Fig 1(a)). SEM micrographs of sulfur annealed films reveal multi-layered WS_2 pyramids and flowers with sizes of up to a few microns (Fig 1(b) and (c)). The presence of WS_2 for sulfur-annealed films is further confirmed by signature Raman $2\text{LA}(\text{M})$, $\text{E}^{1}_{2\text{g}}$ and A^{1}_{g} peaks. Further XPS results and catalysis activity of these nano-structures will be discussed at the meeting.

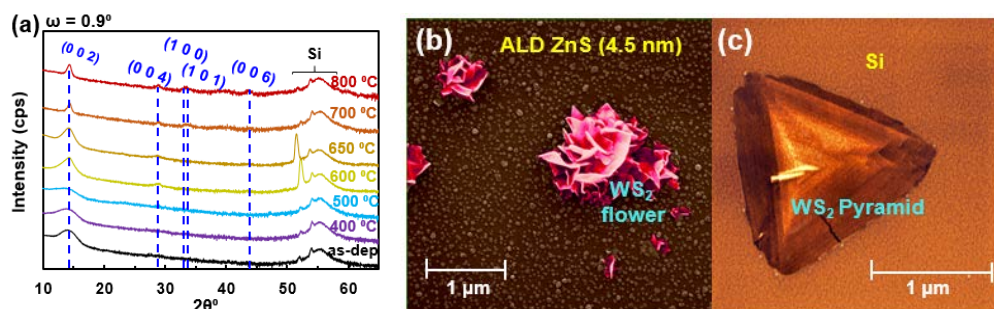


Figure 1 (a) GI-XRD scans comparing 200 ALD cycle films deposited at 330°C , as-deposited and post elemental sulfur-annealing (peaks shown from diffraction card 00-008-0237 (S) for 2H WS_2). (b) SEM micrographs (shown in false color) of WS_2 flowers grown on ALD ZnS and (c) WS_2 pyramids on Si.

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September 24, 2020 (Thursday) 14:25-14:40

Tensile-Strained Germanium Quantum Dots on InAlAs(110)

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Self-assembled quantum dots (QDs) are widely studied for their highly tunable optoelectronic properties. Until recently, the bulk of QD research relied on compressive strain to initiate the self-assembly process. Quantum confinement and compressive strain combine to greatly blue-shift QD emission, leaving longer wavelength regions of the electromagnetic spectrum nearly unattainable for QD-based technologies. Our research provides a solution to this problem: tensile strain red-shifts the emitted light, even beyond the blue-shifting effects of quantum confinement.^[1] Theory shows that tensile strain makes direct bandgaps more direct, and it can even cause germanium (Ge) to become a direct bandgap semiconductor.^[2]

In this presentation, we demonstrate the defect-free growth by molecular beam epitaxy (MBE) of self-assembled, tensile-strained germanium (Ge) QDs on InAlAs(110). We study the resulting shape of these elongated QDs, providing kinetic and thermodynamic insight into the self-assembly processes. We can tune the aspect ratio, size, and areal density of Ge(110) QDs with MBE growth parameters, and show that they grow with an unusual flat top. We show that with increasing substrate temperature, the natural anisotropy of the (110) surface is amplified. The increasing kinetic energy at higher temperature allows Ge adatoms to cross surface energy barriers towards $\bar{1}10$ easier than $00\bar{1}$. These results provide an excellent starting point from which to explore tensile Ge(110) optoelectronic properties and create future tensile-derived Ge QD-based optoelectronic devices.

References:

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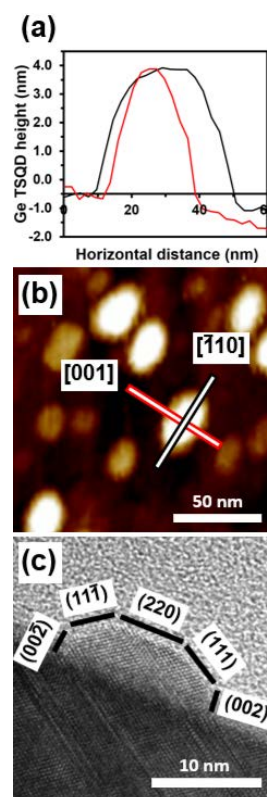


Figure 1 (a) Height profiles along $\bar{1}10$ (black) and $00\bar{1}$ (red) for a Ge QD shown in (b). (b) $150 \times 150 \text{ nm}^2$ AFM image showing Ge(110) QDs, and the z-scalebar is 5 nm. (c) High-resolution STEM image of the cross section of a Ge(110) QD with facets labelled.

September 24, 2020 (Thursday) 14:40-14:55

High performance iron-based phosphate anode for aqueous sodium-ion batteries

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Aqueous sodium-ion batteries are a promising candidate for large scale stationary energy storage, however, further development on the anode side is needed.¹ Here, we demonstrate the superior electrochemical performance of the anode $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$.² This electrode exhibits a reversible capacity of $\sim 83 \text{ mAh g}^{-1}$, excellent rate capability up to 200 C, and outstanding cycle life of 6000 cycles. *In-situ* synchrotron X-ray diffraction and X-ray absorption spectroscopy were utilized to understand the structural (e.g. crystal and electronic) evolution of the anode during charging-discharging processes. We find that the material undergoes small volume expansions upon sodium insertion ($\sim 3\%$) which enables fast charging and long-cycling capability.

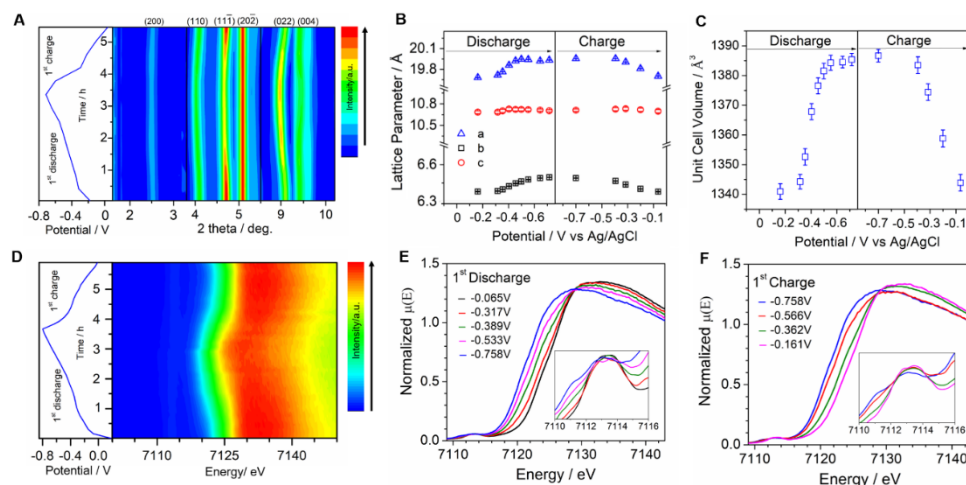


Fig. 1 | The investigation of Na-insertion mechanism in $\text{Na}_3\text{Fe}_3(\text{PO}_4)_4$. (A) Color plot of *in-situ* synchrotron XRD. (B) Lattice parameter and (C) Unit cell volume variations during the Na^+ (de)insertion process. (D) Color plot of the *in situ* XANES spectra. The Fe K-edge spectra (E) discharge. (F) charge.

References:

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September 24, 2020 (Thursday) 14:55-15:10

Synthesizing Colloidal PbSe Quantum Dots for the Investigation of Gamma Ray Spectroscopy Resolution in Semiconductor Radiation Detection Devices

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Gamma ray spectroscopy allows the identification of specific radioactive sources and not just an intensity.¹ Industry standard semiconductor diode detectors are a mature technology, but can be improved by transitioning to room temperature operation.¹ PbSe colloidal quantum dots (QDs) are a promising material for radiation detection. PbSe QDs have been shown to exhibit multiple exciton generation through impact ionization,² and if incorporated into a room temperature device, energy resolution could match or exceed the current technology that uses high-purity germanium. We have developed a microwave assisted protocol for the synthesis of PbSe QDs. These QDs are characterized by transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy, UV-Vis-NIR spectroscopy, and x-ray diffraction. In this presentation, we will show the results of material synthesis and characterization and initial results from device fabrication and testing. In Figure 1, we show initial results for synthesized PbSe QDs, where we show excellent control over nanoparticle size.

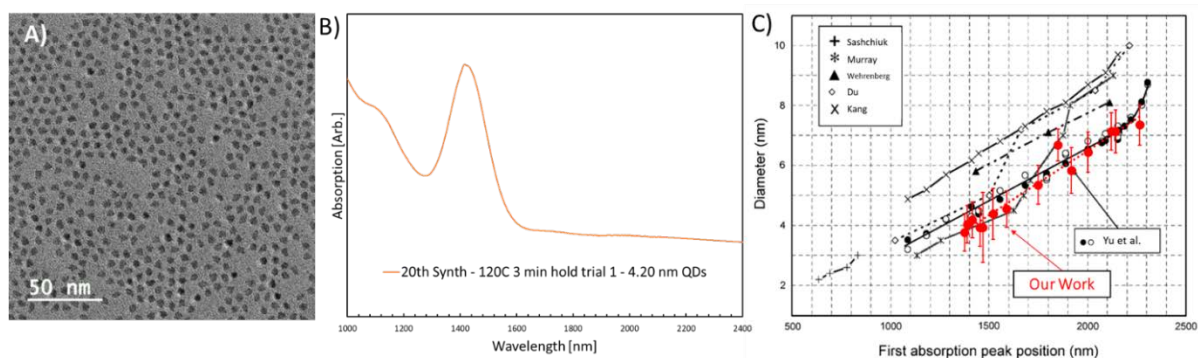


Figure 1. A) TEM image of 4.2 nm PbSe QDs grown at 120 °C for 3 mins. B) The UV-Vis-NIR spectrum for the same PbSe QDs showing a first excitonic absorption peak. C) A comparison of PbSe QD size vs. first excitonic absorption peak location.

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September 24, 2020 (Thursday) 15:10-15:25

Analyzing the Conversion of 2,3-Butanediol to Butene From First Principles

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As climate change continues to pose a threat to the Earth's carbon cycles and fossil fuel resources remain finite, more sustainable sources of hydrocarbons are being explored. 2,3-butanediol has been identified as a potential source for hydrocarbons, specifically butene since it is a biomass-derived sugar¹. Experimental research has been conducted on the conversion of 2,3-butanediol to butene. However, there is still little understanding about the fundamental reaction.

As a first step toward understanding the underlying reaction mechanism better, we performed Density Functional Theory (DFT) based calculations in the gas phase. The effect of van der Waals corrections were also determined using the optB86b-vdW functional². As can be seen in Figure 1, applying the van der Waals corrections generally reduces the overall reaction energy by ~0.5 eV. Of the butene isomers in Figure 1, 1-butene and trans-2-butene are the most thermodynamically favorable with trans-2-butene being the most abundant isomer observed experimentally¹. The overall trend remains regardless of the functional choice, with 1,3-butadiene being the most stable intermediate. As such, our DFT-based results indicate that the formation of trans-2-butene would be less likely through a 1,3-butadiene intermediate as compared to those involving 2-butanone or 2-methylpropanol.

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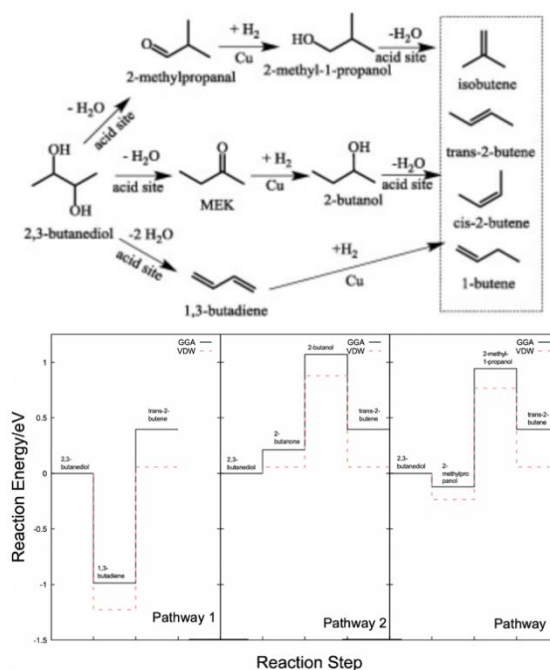


Figure 1. Reaction energies of 2,3-butanediol to butene for all three represented pathways¹ from a GGA-level of theory and using the optB86b-vdW functional.

September 24, 2020 (Thursday) 15:25-15:40

Break

Session 4: Applied Surface Sciences (II). Chair: Xin Zhang

September 24, 2020 (Thursday) 15:40-15:55

Remote oxygen plasma-enhanced atomic layer deposition of tungsten oxide

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Tungsten oxide (WO_3) has garnered interest lately for its resistive switching properties.¹ Resistive switching requires films of high electrical quality with excellent conformality, uniformity, and thickness control for which atomic layer deposition (ALD) is the method of choice. While early reports of ALD WO_3 films employed the use of halide-based precursors,^{2,3} this resulted in self-etching in addition to toxic byproducts such as HF. There has been a push in recent years towards developing ALD processes based on new metal-organic precursors such as $\text{W}_2(\text{NMe})_6$,⁴ $\text{WH}_2(\text{IPrCp})_2$,⁵ and WNBURE.⁶ In this work we study the properties of ALD WO_3 deposited using a novel metal-organic tungsten precursor WSN-4 provided by EMD Performance Materials and remote O_2 plasma in a Sunale Picosun® R200 PE-ALD reactor. A plot of thickness vs. temperature for 300 cycles of a 2/15/40/30 s WSN-4/ N_2/O_2 plasma/ N_2 pulse sequence shows film growth over a wide window of temperatures ranging from 150°C to 300°C (Fig 1a) while GI-XRD scan of as-deposited film at 250°C shows a broad $\langle 002 \rangle$ peak around 24° suggesting the presence an amorphous film. Further film properties, growth per cycle studies, and analyses will be discussed.

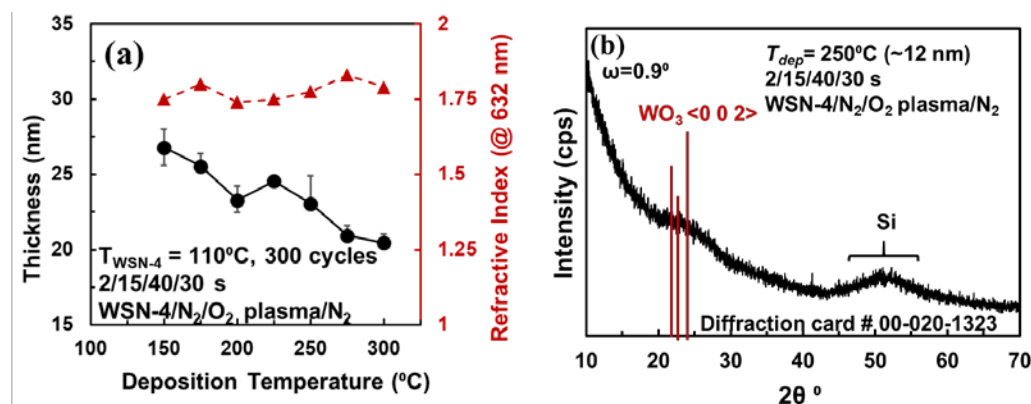


Figure 1 (a) Plot of thickness vs. temperature for ALD 300 cycles. (b) GI-XRD scan of ALD WO_3 on silicon showing an amorphous film with a broad $\langle 002 \rangle$ peak at ~ 24°.

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- Acknowledgement** - The authors thank Daniel Moser, Charles. L. Dezelah, Ravindra. K. Kanjolia, and Jacob Woodruff of EMD performance materials for supplying the metal-organic precursor used in this work.

September 24, 2020 (Thursday) 15:55-16:10

Understanding the crystallization mechanism of copper nanoparticles during thermal decomposition of Cu-MOF using TEM techniques

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Metal-carbon materials have triggered substantial interest over the last several decades due to their applications in catalysts, energy storage, environmental engineering, biomedicines, etc.^{1,2} One of the most popular methods to prepare the metal-carbon materials is decomposing metal-organic frameworks (MOFs), which always serve as both the precursor of metal nanoparticles and the template of carbon materials.³ Moreover, metal-carbon materials derived from the newly emerging MOFs usually own several advantages such as large surface area, highly ordered pore structure, and superior tailorability.⁴ Particularly, well-dispersed metal nanoparticles with controllable morphology are of great significance to their applications.^{5,6} Understanding the crystallization mechanism of metal nanoparticles during thermal decomposition of MOF materials is critical to achieve effective dispersion and control of the nanoparticles in final products. However, there is limited works to report the crystallization mechanism in detail. Herein we report the crystallization mechanism of copper nanoparticles during thermal decomposition of Cu-MOF materials using advanced *in situ* and *ex situ* transmission electron microscopy (TEM) techniques. The results demonstrated that Cu nanoparticles formed very fast after heating the Cu-MOF materials to 400 °C and then attached together through lattice mismatched aggregation. The Cu nanorods formed in the carbon matrix when increasing calcination temperatures above 600 °C. The combination of the *ex situ* high resolution scanning TEM and *in situ* heating TEM indicated the transformation of Cu nanoparticles to nanorods is a classical Ostwald ripening process not the oriented attachment. This work provides a theoretical basis for the crystallization mechanism of metal particles in the solid phase transformation process during calcination, which is conducive to the design and performance optimization of new metal-carbon materials.

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September 24, 2020 (Thursday) 16:10-16:25

Physicochemical characterization of vertically resolved atmospheric particles via unmanned aerial system

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Physicochemical properties (e.g. morphology, composition and mixing states) of atmospheric aerosols play an important role in estimating Earth's radiation budget. Though, ground based observations of the mentioned properties are abundant but only limited measurements are available for vertical profiles of the aerosols. Aircraft observations can provide useful data for high-altitudes measurements but have limited temporal coverage. The unmanned aerial systems now a days become an important platform in atmospheric measurements because of less risk, reduced cost, and higher temporal coverage involved in atmospheric research area. To understand the vertical profile of the aerosols, the tethered balloon system was deployed at the Southern Great Plains (SGP; DOE ARM mega site) at Oklahoma and Oliktok point site at Alaska located on the coast of Arctic Ocean, 2m above sea level. The aerosol particles were collected at boundary layers (10m, 500m) and free-troposphere layer (1,500m). The aerosol samples were collected employing 4-stage cascade impactor at different altitudes during July, August and October of 2019. The morphology, chemical composition and mixing states of the collected particles were analyzed using multi-modal micro-spectroscopy techniques such as computer-controlled scanning electron microscopy with energy dispersive X-ray spectroscopy and scanning transmission X-ray microscopy with near edge X-ray absorption fine structure spectroscopy. The results show a clear difference in aerosol chemical compositions at various altitudes on the same day. We observed a significant percent of dust particles at different heights and days. We classified the dust particles and observed variation in dust mineralogy at different altitudes. From STXM/NEXAFS analysis, we observed changes in carbon functionalities at different altitudes. This research can provide us with better understanding about the short-range, long-range transportation of atmospheric particles and vertical profile of atmospheric particle composition via unmanned system with long term observation.

September 24, 2020 (Thursday) 16:25-16:40

Molecular revealing of mixing states of aerosol particles using ToF-SIMS spectra and imaging analysis

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Fine particulate matter (PM), especially PM_{2.5} (PM with the aerodynamic diameter less than 2.5 μm), has been raising concern due to its potential health risks. Many analysis tools have been used

to study chemical components of PM_{2.5} particles, elucidating that PM_{2.5} particles are made up of complex chemical components. However, determination of the fine structure of the PM_{2.5} particles, such as mixing states, has been challenging. For example, popularly-used Particle into Liquid Sampler (PILS) and Aerosol Mass Spectrometer (AMS) are bulk analysis tools, which can't provide enough information for the fine structure. Sophisticated imaging tools, including Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) can provide high lateral resolution (a few nm to sub-nm level) topographic and elemental images. However, only limited chemical information, such as bulk elemental information, is available. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful surface analysis tool. It can simultaneously provide elemental, isotopic and molecular information with part per million (ppm) sensitivity. More importantly, it is very surface sensitive, and its information depth is less than a few nanometers. Also, ToF-SIMS can provide molecular imaging with submicron lateral resolution. Such capabilities are unique in aerosol research. In this work, a combination of ToF-SIMS surface analysis and traditional bulk analysis provided critical information to elucidate the mixing states of aerosol particles. PM_{2.5} aerosol samples in a typical Beijing winter pollution case were used as a model system. Our data show that chemical components of the PM_{2.5} hardly change from low to medium pollution situations, and only single-component particles form (external mixing). Under severe pollution situation, the major chemical component change is increasing of (NH₄)₂SO₄, which can form relatively large particles (5+ microns); while external mixing is still the dominant mixing state for all chemical components.

September 24, 2020 (Thursday) 16:40-16:55

Analysis of Aerosol Composition During a Dust Event in the Northern Atlantic.

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Atmospheric aerosol plays a large role in many biogeochemical cycles that have implications on the world's climate. Deposition of aerosols to the ocean is a source of limiting nutrients like fixed nitrogen and iron [1], which increases primary productivity [2]. The purpose of this presentation is to better illustrate the characteristics of aerosols, especially dust particles in the Northern Atlantic. Aerosol samples were collected at Pico Island in the Northern Atlantic, in the Azores, Portugal. Unlike other studies done in the Canary Islands, which receive dust plumes directly from the Sahara, dust is cycled through the atmosphere for a longer period before it reaches Pico Island. The samples were analyzed using computer-controlled scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) capabilities to determine the physiochemical properties of the samples. These Samples have considerably high dust counts compared. We further investigated characteristics of dust particles. Most Fe rich particles were 0-2.5µm in size which have been shown to be more soluble than particles larger than 2.5µm [2].

From this information, we can further understand the aerosol composition in the Northern Atlantic.

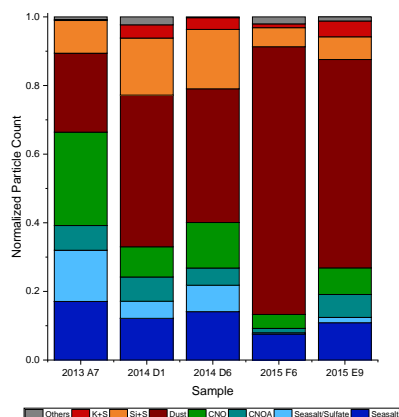


Figure 1: this figure shows the class composition of aerosols across dust events at Pico Island

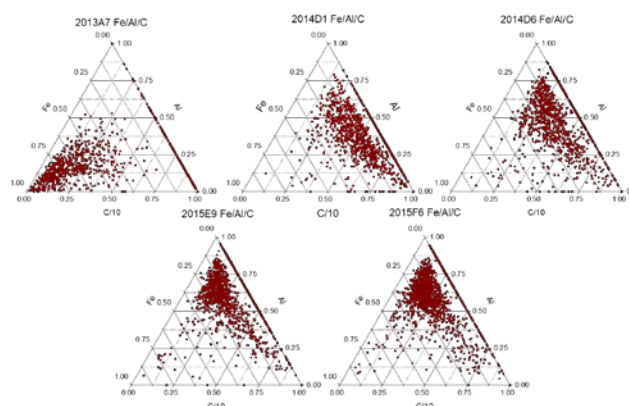


Figure 2: this figure shows the Fe, Al, and C concentrations of the samples taken from Pico Island

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September 24, 2020 (Thursday) 16:55-17:10

Solvent and Coverage Effects on the Stability of HDO Relevant Aromatics

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There has been a push for more renewable energy sources; one kind comes from the catalytic conversion of bio-oils to usable biofuels. The quality of these biofuels can be upgraded through the process of hydrodeoxygenation (HDO) where the C-O bond is cleaved¹. This process can be computationally modeled, and the physical descriptions of these systems can be altered to study a vast array of catalyst models. In our previous work², we found that the adsorption of phenol could be described using a mean field model, where its adsorption energy is an analytical function of coverage. The aim of this project is to determine the effect of coverage on the adsorption energies of aromatics (benzene, phenol, phenoxy, guaiacol, and guaioxy) on Pt(111), Pd(111),

Ru(0001), and Fe(110) in the presence of solvents (water, methanol, ethanol, acetonitrile, and cyclohexane) and whether their coverage dependence can be described within a mean field model.

We hypothesize that the adsorption energies follow the *d*-band properties of the catalyst surface and that the higher the polarizability of the adspecies, the greater the solvent affect would be with coverage since solvents increase the lateral interactions between the species. Comparing different catalyst systems allows for the analysis of the effect of solvents. Interestingly, mean-field tests of guaioxy on Ru(0001) and phenoxy on Ru(0001) show that these adspecies have flat slopes, meaning that there is a minimal coverage effect on these systems. The adsorption energies of phenol on Pt(111)², at various coverages was determined as well (Figure 1). Consistent with our hypothesis, the presence of a water increases the lateral interactions between the phenol adsorbates as compared to the corresponding case under vacuum.

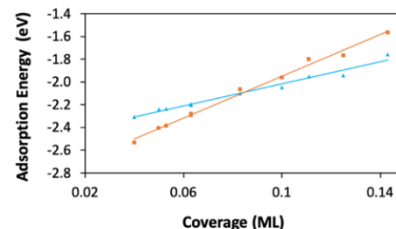


Figure 1. Binding energy as a function of solvent coverage. The orange squares represent the solvated system and the blue triangles represent the vacuum system.

References:

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- [3] This work was primarily supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences within the Catalysis Science program, under award number DE-SC0014560.

September 25, 2020 (Friday) Morning

Session 5: Applied Surface Sciences (III); Chair: Zhenxing Feng

September 25, 2020 (Friday) 8:30-9:10

Electrooxidation and Dissolution of Pt(111) and Pt(100) - (Invited)

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The electrochemical formation of Pt oxide plays a key role in Pt electrocatalysis, where its formation and reduction can lead to catalyst restructuring and dissolution, factors that limit the lifetime of Pt catalysts in PEM fuel cells. The initial stages of oxidation on Pt(111) and Pt(100) are studied by *in situ* Surface X-ray Diffraction. For Pt(111), the results refine the known "place exchange" (PE) process, in which a surface Pt atom moves to 2.4 Å above its original site, which is now occupied by an oxygen atom. This process is reversible: if the potential does not exceed 1.1 V vs RHE, then the Pt atom returns to its original when the potential is decreased [1].

Pt(100) is more reactive, in that the Pt atoms restructure at a lower potential, and it is irreversible: the Pt atoms do not return to their original sites when the potential is decreased [2]. The "PE" Pt atom moves laterally as well as up, but its height is much less than on Pt(111), indicating bonding to nearby oxygen atoms but without an oxygen atom below. The lateral motion displaces another Pt atom (adatom), and initiates removal of adjacent PE atoms, leading to a 1D stripe structure on the surface, with adatoms at each end.

Sensitive ICP-MS measurements of dissolved Pt²⁺ ions show that the dissolution coincides with the point at which the oxidation becomes irreversible, 0.15 V higher on Pt(111) than Pt(100) [2]. These observations are confirmed by DFT calculations, which show that the small number of displaced Pt adatoms are those that dissolve [2]. On cycling to higher potentials, the surface undergoes more extensive restructuring. The evolution of the nanoscale islands formed is studied by grazing incidence small angle X-ray scattering (GISAXS) [3,4].

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- [5] We thank the European Synchrotron Radiation Facility for provision of SXR facilities, and the ID03 and ID31 beamline staff for experimental assistance. We acknowledge financial support from NSERC (Canada), DFG (Germany), and MICIUN (Spain).

September 25, 2020 (Friday) 9:10-9:25

Effect of co-adsorbed water on acetic acid decomposition on Pt (111) using Density Functional Theory.

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The influence of water on acetic acid decomposition over Pt (111) is a good model system for the study of the role of co-adsorbates and solvent effects in catalytic reactions of small oxygenates. Experimental studies show that solvents influence the selectivity and rate of heterogeneous catalytic reactions. Fundamental understanding of how water affects OC-O, C-OH, CO-H, C-H and C-C bond cleavages will give us valuable insight into how and why water influences selectivity of oxygenates decomposition, enabling bottom up design of effective catalyst and catalyst system. Here we present a density functional theory (DFT) calculations of how co-adsorbed water affects the elementary reaction steps involved in acetic acid decomposition over Pt (111), focusing on the critical elementary reaction steps that influence the selectivity between carbon monoxide (CO) and carbon dioxide (CO₂) formation. Our results suggest that in the absence of co-adsorbed water, for the most favorable decarboxylation (DCX) and decarbonylation (DCN) pathway, the dehydrogenation of CH₂COO ($E_a = 0.59$ eV; DCX) and deoxygenation of CH₂COO ($E_a = 1.00$ eV; DCN) are the critical steps that separates the two pathways, which suggest that the DCX pathway is favorable than DCN pathway. The presence of co-adsorbed water increases the barrier for the deoxygenation of CH₂COO to CH₂CO ($E_a=1.23$ eV; DCN) and dehydrogenation of CH₂COO to CHCOO ($E_a=0.74$ eV; DCX), suggesting that the DCX pathway becomes more favorable than the DCN pathway because the increment is larger for deoxygenation of CH₂COO to CH₂CO. Additionally, co-adsorbed water increases the activation barrier for the OC-O bond cleavage of (CH_xCOO; x=0,1,2,3), important reaction steps in CO formation. While co-adsorbed water reduces the activation barrier for the CO-H bond cleavage of (CH_xCOOH; x=1,2,3) through hydrogen shuttling or stabilization of the transition state, important reaction steps in CO₂ formation. These calculations give insight into how water can make acetic acid decarboxylation (formation of CO₂) more favorable than acetic acid decarbonylation (formation of CO) by influencing various elementary reaction steps differently, changing the selectivity of a complex decomposition mechanism.

September 25, 2020 (Friday) 9:25-9:40

The role of chloride in the initial stages of the breakdown of α -Cr₂O₃ passive layer: a density functional theory study.

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Stainless steels are widely used as primary piping material in the nuclear industry because of their high corrosion resistance largely due to the formation of a protective, metal-oxide passive film (e.g. Cr₂O₃). Aggressive ions such as chloride can cause the breakdown of the oxide film, leading

to loss of protection. The breakdown of the passive film has been studied experimentally for decades but many of these studies focus on industrial alloys with large surfaces exposed to complex electrolytes, making it hard to understand the role of different stages of the breakdown mechanism. The ion exchange¹⁻² and point defect models³ are two prominent proposed models describing the role of anions, such as chlorides, in the breakdown of the passive oxide films. Here, we use density functional theory to study the thermodynamic feasibility of the critical steps in the initial stages of Cl-induced breakdown of a hydroxylated α -Cr₂O₃ (0001) passive layer. The effect of the surface concentration (coverage) of chloride on the two degradation models were investigated. Both models begin with chloride surface adsorption, i.e., chloride substitution for hydroxyl/water, which becomes less favorable with increasing Cl coverage. At low Cl coverages, neither Cl insertion, a critical step following Cl substitution in the ion exchange model nor Cr-vacancy formation, a critical step following Cl substitution in the point defect model, is thermodynamically feasible, except in the presence of an oxygen vacancy near the surface which can facilitate Cl insertion. At high coverages, the Cl-induced degradation process is first activated through a vacancy formation mechanism which is thermodynamically feasible at $\geq 10/12\text{ML}$, but both Cl insertion and vacancy formation would be feasible at the full ($12/12\text{ML}$) Cl coverage. This suggests that the initial stages of the degradation of the hydroxylated Cr₂O₃ passive layer depend on Cl coverage and the presence of O vacancy near the surface.

References:

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September 25, 2020 (Friday) 9:40-9:55

An AP-XPS Study of La_{1-x}Sr_xNiO_{3- δ} Perovskite OER Catalysts: Interpretation of Mechanistic Rate Limiting Step

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In situ spectroscopic methods allow direct interrogation of catalysts in environments similar to their operating environment. In this way, researchers are able to extract key determinants – (electronic) band structure, valence state, coordination chemistry, reaction intermediates/adsorbates, product speciation, etc. – for the activity and selectivity of a material. By harnessing these techniques, we aim to develop descriptors for the informed engineering of future catalyst designs. Our talk focuses on *in situ* ambient pressure x-ray photoelectron spectroscopy (AP-XPS) and applications to oxygen evolution reaction (OER) perovskite (ABO₃) oxide catalysts.

Aliovalent substitution of non-reducible elements into the A site of perovskites tunes the perovskite electronic structure via transition metal (B-site) redox, where OER activity trends with O 2*p* location relative to the Fermi level.¹ AP-XPS can measure the occupied valence band structure and speciation of adsorbates during H₂O and O₂ exposure to relate the electronic structure of a material *in situ* to its catalytic activity. We measured the water dissociation affinity by AP-XPS (1.6×10^{-5} – 0.11 % relative humidity) of Sr-substituted LaNiO_{3- δ} (La_{1-x}Sr_xNiO_{3- δ} , LSNO) perovskite thin films grown by molecular beam epitaxy. Here we relate the quantitative coverage of OER-relevant adsorbates to trends observed in OER activity with Sr incorporation,² suggesting a rate-limiting step for the vacancy-mediated OER reaction mechanism observed on certain transition-metal perovskite oxides.³

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September 25, 2020 (Friday) 9:55-10:10

Probing the surface reactivity of amorphous aluminium oxide thin-films using methanol: An Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) study

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The dissociative adsorption of methanol can be used to quantify the active sites of an oxide, and the oxidation products indicate the nature of this active site. Herein, we study the adsorption and oxidation of methanol on amorphous $\text{Al}_{(1-x)}\text{M}_x\text{O}_y$ ($\text{M}=\text{Fe}, \text{Mn}$) oxide thin films to ascertain the nature of the surface active sites. We use AP-XPS to identify and compare adsorbates at varying methanol:oxygen ratios and temperatures on $\text{Al}_8\text{Fe}_2\text{O}_y$, $\text{Al}_4\text{Fe}_6\text{O}_y$, and $\text{Al}_6\text{Mn}_4\text{O}_y$. The ratio of adsorbed methoxy:hydroxy species varies with composition, suggesting that dissociative adsorption occurs on different surface sites. The conversion of methanol with increase in temperature is evident by the decrease in adsorbed methoxy groups. Shifts in the binding energy of gas phase species with temperature illustrate changes in the surface dipole as methanol oxidation occurs. These findings provide guidance for the design of amorphous oxide layers with tailored chemical reactivity for a given application.

September 25, 2020 (Friday) 10:10-10:30

Break

Session 6: Applied Surface Sciences (IV); Chair: Mark Engelhard

September 25, 2020 (Friday) 10:30-11:10

Probing the mineral crystallization and phase transformation via advanced transmission electron microscopy (Invited)

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Understanding mineral crystallization and phase transformation is critical to geoscience, material synthesis, catalysis, energy storage, environmental conservation, biological medicine, etc.¹⁻³ Using a combination of advanced in situ transmission electron microscopy (TEM) techniques and computational methods, we are investigating these phenomena for several mineral systems and their relationship to interfacial structure in vacuum and water vapor. Here we discuss three cases. In the first, we use high resolution TEM and scanning TEM (STEM) to explore the aggregation behaviors of hematite nanocrystals with different exposed facets including {001}, {012}, {104} and {116}. The experimental data indicates that hematite nanoparticles aggregation-based crystallization is orientation dependent (along the [001] direction), not relies on exposed facet. We then compare the results to the predictions of density functional theory (DFT) to relate the behavior to surface interactions. In the second, we reveal the thermal transformation of akaganéite ($\beta\text{-FeOOH}$) to anhydrous iron oxide polymorphs in vacuo via in situ heating TEM. We observed the crystal structure of $\beta\text{-FeOOH}$ first undergoes disordering upon heating to 200 oC, and then the morphology evolved from solid nanowires to highly nanoporous nanowires composed of maghemite, the grain size of which is inversely related to density of the pores. Furthermore, we found that phase outcomes strongly depend on the initial size of the $\beta\text{-FeOOH}$ nanowires. In the third case, we report measurement of anisotropic forces between rutile TiO_2

(001) nanocrystals as a function of their azimuthal orientation and surface hydration extent using a combined environmental TEM-atomic force microscopy (AFM) technique.^{4, 5} At tens of nanometers of separation, the attractive forces are weak and show no dependence on azimuthal alignment nor surface hydration. At separations of approximately one hydration layer, attractive forces are strongly dependent on azimuthal alignment and systematically decrease as intervening water density increases. Measured forces closely agree with predictions from Lifshitz theory and show that dispersion forces are capable of generating a torque between particles to align them.

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September 25, 2020 (Friday) 11:10-11:25

Interactions between synthetic bilgewater emulsion and biofilms

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Bilgewater, an oil-in-water (O/W) emulsion, is a persistent pollutant released to the ocean from the lowest part of ships. Microbes play an important role in the ocean. It is hypothesized that microbes release organics that can act as surfactants that affect bilgewater formation or weakening. We present the first systematic study of emulsions and biofilms and investigate the effects of biofilms on bilgewater emulsions. Three strains were selected *Pseudomonas*, *Arthrobacter*, and *Cobetia marina*. A Navy O/W emulsion consisting of three oils and a detergent mixture was used as the synthetic bilgewater model [1]. Biofilms were cultured in a microchannel to allow healthy culture [2]. Once a thick layer of biofilms was formed, the medium solution was changed to a mixture consisting of 50 % bilgewater emulsion. Dispersed biofilms were collected at 24 hrs. and 48 hrs. after emulsions were introduced into the channel. Bilgewater emulsions, biofilms, and mixtures of bilgewater emulsions and biofilms were analyzed using multiple *in situ* and *ex situ* techniques including time-of-flight secondary ion mass spectrometry (ToF-SIMS), confocal laser scanning microscopy, and optical microscopy. Our findings indicate that biofilms change the chemical makeup of the emulsion surface

compositions and emulsion droplet size distribution, confirming the hypothesis that extracellular polymeric substance (EPS) related components released from biofilms can function as surfactants and change the oil-in-water interfaces.

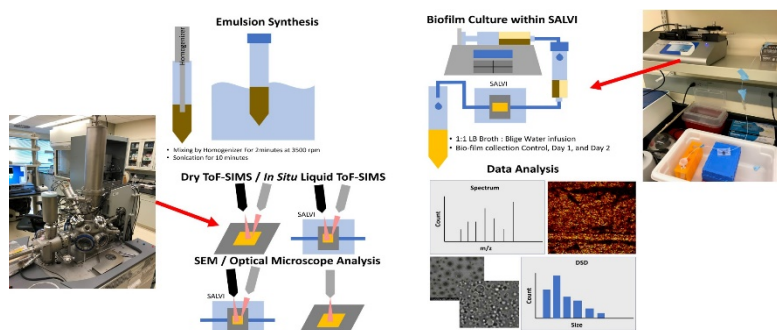


Figure 1 Schematic showing bilgewater and biofilm culture experimental setup.

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September 25, 2020 (Friday) 11:25-11:40

Molecular insights into communications of Geobacter syntrophic communities

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Direct interspecies electron transfer (DIET) has been considered as a novel and highly efficient strategy in both natural anaerobic environments and artificial microbial fuel cells. A syntrophic model consisting of *Geobacter metallireducens* and *Geobacter sulfurreducens* was studied in this work. We conducted in vivo molecular mapping of the outer surface of the syntrophic community as the interface of nutrients and energy exchange. System for Analysis at the Liquid Vacuum Interface (SALVI) combined with time-of-flight secondary ion mass spectrometry (ToF-SIMS) was employed to capture the molecular distribution of syntrophic *Geobacter* communities in the living and hydrated state. Principal component analysis (PCA) with selected

peaks revealed that syntrophic *Geobacter* aggregates were well differentiated from other control samples, including syntrophic planktonic cells, pure cultured planktonic cells, and single population biofilms. Our in vivo imaging indicated that a unique molecular surface was formed. Specifically, aromatic amino acids, phosphatidylethanolamine (PE) components, and large water clusters were identified as key components that favored the DIET of syntrophic *Geobacter* aggregates. Moreover, the molecular changes in depths of the *Geobacter* aggregates were captured using dynamic depth profiling. Our findings shed new light on the interface components supporting electron transfer in syntrophic communities based on in vivo molecular imaging.[1]

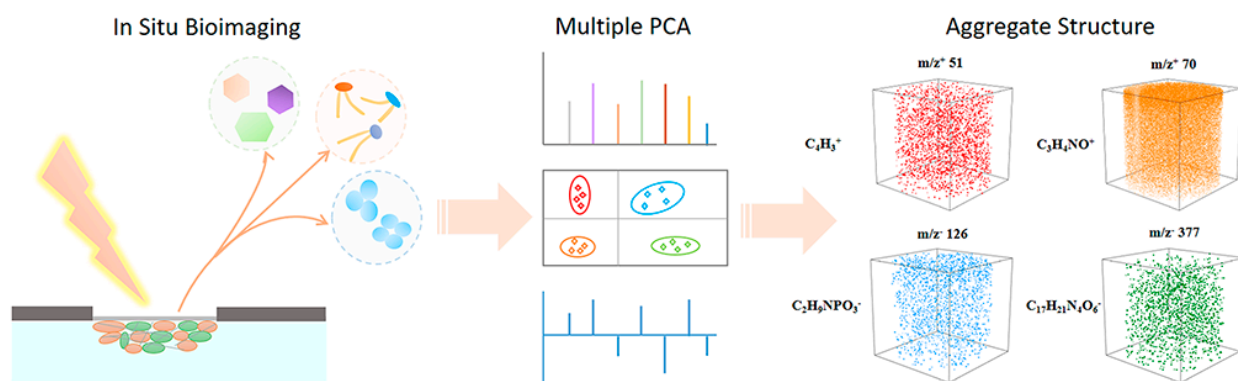


Figure 1 In vivo ToF-SIMS molecular bioimaging reveals the *Geobacter* aggregate structure.

References:

[1] W. Wei, A. Plymale, Z. Zhu, X. Ma, F. Liu, and X.-Y. Yu,* Molecular insights into communications of *Geobacter* syntrophic communities, *Anal. Chem.*, 2020, online ASAP published in July, 2020. Doi: 10.1021/acs.analchem.0c00653F.

September 25, 2020 (Friday) 11:40-11:55

Detection and identification of PFASs using ToF-SIMS and principal component analysis

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Per and polyfluoroalkyl substances (PFASs) have drawn considerable attention due to their ubiquitous existence in the environment as a result of extensive use in a variety of industries and commercial products. Direct detection of PFASs and its mixtures is challenging yet beneficial for environmental mitigation and restoration. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a highly sensitive chemical analytical technique with ppm-level detection, providing

molecular identification and direct observation of contaminants. We will present static ToF-SIMS results of molecular detection of five PFASs and their mixtures, respectively, in this work [1]. The mass spectral comparison shows chemical signatures of each PFAS compound, illustrating SIMS power of molecular identification. The application of principal component analysis (PCA) facilitates the identification of peak patterns; thus it is useful in differentiating PFASs in a mixture. A customer-developed software tool using R enables fast PCA processing of SIMS spectral data, allowing effective identification of the PFASs and their mixtures. Our results combining with the PCA tool demonstrate that ToF-SIMS, as a sensitive mass spectral imaging technique, provides a new and promising method of PFASs analysis in the future.

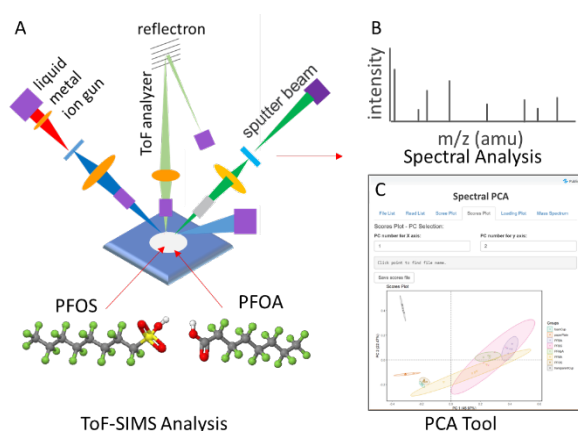


Figure 1 (a) The schematic of ToF-SIMS analysis of PFASs on a Si chip, (b) a representative SIMS spectrum, and (c) the spectral principal component analysis (PCA) tool developed for peak analysis.

References:

[1] Yang C., J. Yao, X-Y. Yu, *Environmental Chemistry Letters*. Paper in review. 2020.

September 25, 2020 (Friday) 11:55-12:30

Break

September 25, 2020 (Friday) Afternoon

Plenary Session (II); Chair: Mark Engelhard

September 25, 2020 (Friday) 12:30-13:10

Astronomy's Future is LOUD: LIGO+Virgo Observations of the Universe to-Date (Plenary)

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1.Laser Interferometer Gravitational-Wave Observatory

The LIGO and Virgo gravitational wave detector network has found 67 events in the last five calendar years of observing the universe. 55 of these events have been found in the most recent

observing period which took place between April 2019 and March 2020, quintupling the amount previous two runs combined. In this talk, I discuss how these detectors work and their recent history, highlight the astrophysical implications from a few of the ground breaking event details most recently published, and talk through the next five years which promise a very loud future for this new field of astronomy.

September 25, 2020 (Friday) 13:10-14:10

Award ceremony and closing remarks