

# 2024 AVS Prairie Chapter Symposium



ALMA MATER

TO THY HAPPY CHILDREN  
OF THE FUTURE  
THOSE OF THE PAST  
SEND GREETINGS

**I** ILLINOIS

Materials Research Laboratory

GRAINGER COLLEGE OF ENGINEERING

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**AVS Prairie Chapter**

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## Special Acknowledgements

Kristen Flatt (moderator), *University of Illinois at Urbana-Champaign*  
Mary Kraft (moderator), *University of Illinois at Urbana-Champaign*  
Mauro Sardela (moderator), *University of Illinois at Urbana-Champaign*  
Timothy Spila (moderator), *University of Illinois at Urbana-Champaign*

# Welcome

On behalf of the AVS Prairie Chapter, we welcome you to the 2024 AVS Prairie Chapter Symposium.

This year's symposium is a multi-topic conference, intending to instigate an exchange of ideas that goes beyond our usual collaboration circles. We have put together a very exciting program with 4 outstanding plenary talks, 10 contributed oral presentations and 34 posters on the many subjects of interest to the AVS.

We are presenting the 2024 AVS Prairie Chapter Outstanding Research Award and the 2024 AVS Prairie Chapter Early Career Award. We are fortunate to have both of this year's awardees presenting plenary talks. Dr. Seth Darling, from Argonne National Laboratory, will present the results of his studies about the mechanisms involved in transport of solutes through nanofabricated, defect-free isoporous membranes, showing promise for unprecedented membrane selectivity through judicious process design and tight pore-size control. Dr. Yi Li, also from the Argonne National Laboratory, will present his research about on-chip hybrid magnonic systems for quantum information science.

We are also honored and excited to have, completing our set of truly science cutting-edge research presentations, plenaries by two highly distinguished investigators. Prof. Elizabeth Goldschmidt, from the University of Illinois at Urbana-Champaign, who will share with us some of her group's studies on quantum light-matter interactions using rare earth materials, to understand quantum photonic physics in her talk "Quantum photonics with rare earth materials" and Dr. Elena Shevchenko from the Argonne National Laboratory, presenting how recent advances in the design and application of nanoscale materials are paving the way for groundbreaking solutions to some of the world's most pressing challenges, from energy production and storage to environmental sustainability.

We also have 4 companies, which will be presenting their newest technologies at our Scientific Equipment Exhibition, supporting the symposium. We encourage you to talk to their representatives and scientists about your instrumentation questions.

One of the highlights this year is our first Best Oral Presentation Award for the best oral presentation by a student or post-doctoral researcher. This award is sponsored by UC Components.

Thank you for your participation and contribution to the 2024 AVS Prairie Chapter Symposium, and thanks to all who contributed to enable this outstanding program.

2024 AVS Prairie Chapter Symposium program committee

## Awards ceremony and reception

Please join us at 5:45, after the last oral presentation, for a closing ceremony where we will present and celebrate this year's recipients of our Best Student Poster Presentation Award and a special Best Oral Presentation Award, sponsored by UC Components, this year.

**6:00 p.m.**

Exhibition hall



## Equipment Exhibition

We have four scientific equipment companies represented in our equipment exhibition this year. Several companies have brought some of their newest products, which could include the next tool you need to complete, extend, or enrich your current project, or even start a completely new one. They have experts who can answer most questions about the equipment and many of their applications. Make sure to take some time to talk to them during the coffee breaks.

Our exhibitors are the main sponsors of the AVS Prairie Chapter Symposia. Please make a point of thanking them for their support.

# Exhibitors

Equipment exhibition opens at 10:45 and closes at 4:15

The exhibition hall is located on the second floor



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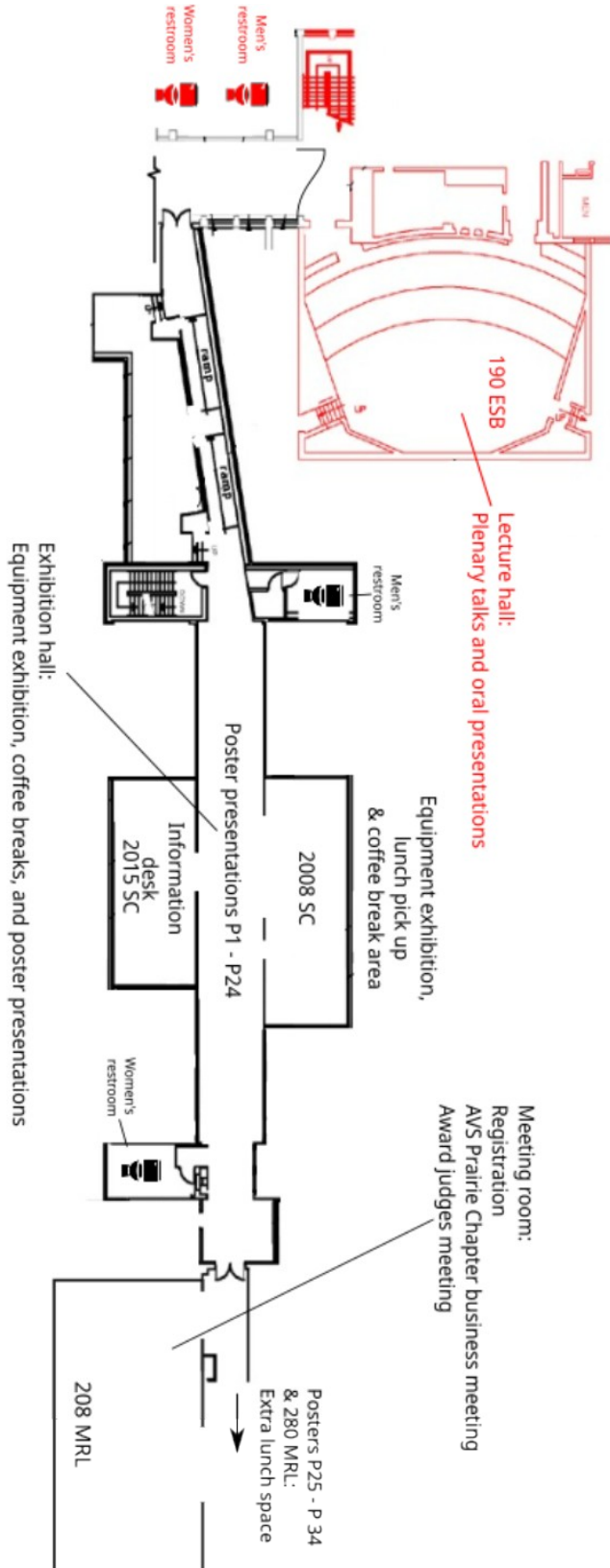
# Site map



— Metered Parking

➔ Materials Research Laboratory

# Conference rooms



Second floor areas indicated in black  
First floor areas indicated in red



# Schedule summary

Time	September 5, 2024
8:30	Registration
	<i>Session A (Lecture hall) – Moderator:</i>
8:45	<b>Welcome remarks</b>
8:55	<b>Plenary talk</b> AVS Prairie Chapter Early Career Research Award <u>Li Yi</u> , Argonne National Laboratory - <b>On-chip hybrid magnonic systems for quantum information science</b>
9:45	<u>Jack D'Amelio</u> , UIUC - <b>Optical characterization of single-crystal stoichiometric europium materials for quantum memory applications</b>
10:05	<u>Hanyu Hou</u> , UIUC/ANL - <b>High-resolution STEM cathodoluminescence of quantum emitters at the twist interface in 2D-exfoliated hBN</b>
10:25	<u>Joshua Wagner</u> , University of Chicago - <b>Coverage dependent diffusivity and binding of atomic oxygen on Moiré patterned graphene</b>
10:45	Coffee break and poster presentations (Exhibition hall)
	<i>Session B (Lecture hall) – Moderator: Mauro Sardela</i>
11:05	AVS Prairie Chapter Outstanding Research Award presentation
11:10	<b>Plenary talk</b> AVS Prairie Chapter Outstanding Research Award <u>Seth B. Darling</u> , Argonne National Laboratory - <b>Pushing the limits of membrane selectivity</b>
12:00	<u>Abdeliah Asserghine</u> , UIUC - <b>In situ detection of reactive oxygen species spontaneously generated on lead acid battery anodes: a pathway for degradation and self-discharge at open circuit</b>
	Lunch (Exhibition hall and Meeting room)
12:20	Lunch and AVS Prairie Chapter business meeting (open to all)
1:10	Poster presentations (Exhibition hall)
	<i>Session C (Lecture hall) – Moderator: Kristen Flatt</i>
1:50	<u>Grace McKnight</u> , UIUC - <b>Interstitial cluster families in semiconducting oxides: effects on post-synthesis defect engineering and purification using submerged surfaces</b>
2:10	<b>Plenary talk</b> <u>Elizabeth Goldschmidt</u> , University of Illinois at Urbana-Champaign - <b>Quantum photonics with rare-earth materials</b>
3:00	<b>Plenary talk</b> <u>Elena Shevchenko</u> , Argonne National Laboratory - <b>Design of nanoscale materials</b>
3:50	Coffee break and poster presentations (Exhibition hall)
	<i>Session D (Lecture hall) – Moderator: Timothy Spila</i>
4:15	<u>Xierong Qian</u> , UIUC - <b>Experimental efforts in water-ethanol-dimethylformamide ternary solvent to optimize advanced Pourbaix diagrams</b>
4:35	<u>Dairong Liu</u> , UIC - <b>Nanoscale chemical probing of metal-supported ultrathin ferrous oxide</b>
4:55	<u>Benjamin Heiner</u> , University of Notre Dame - <b>Scanning tunneling microscopy of ferrocenecarboxylic acid assemblies on Ag(111): a Comparison to Au(111)</b>
5:15	<u>Myoung-Woo Yoo</u> , UIUC - <b>Thermal contribution to current-driven antiferromagnetic-order switching in Mn<sub>3</sub>Sn</b>
5:35	<u>Michael van Duinen</u> , University of Chicago - <b>High-temperature diffraction and surface electron-phonon coupling of the unreconstructed metallic and (3x1)-o reconstructed nb(100) surfaces by helium atom scattering</b>
6:00	Closing reception and awards ceremony

# List of events

- 8:00 – Poster and vendor exhibit setup starts (Exhibition hall)
- 8:30 – Registration opens (Exhibition hall)
- 8:45 – Conference talks start (Lecture hall)
- 10:45 – Equipment Exhibition and poster area opens  
(Exhibition hall)
- 10:45 – Coffee break at the Equipment Exhibition  
(Exhibition hall)
- 10:45 – Poster presentations and judging - round 1  
(Exhibition hall)
- 11:05 – Conference talks resume (Lecture hall)
- 12:20 – Lunch served (Meeting room)
- 12:20 – AVS Prairie Chapter business meeting – open to all  
(Meeting room)
- 1:10 – Poster presentations and judging - round 2  
(Exhibition hall)
- 1:50 – Conference talks resume (Lecture hall)
- 3:50 – Coffee break at the Equipment Exhibition  
(Exhibition hall)
- 3:50 – Poster presentations and judging - round 3  
(Exhibition hall)
- 4:15 – Conference talks resume (Lecture hall)
- 4:15 – Equipment Exhibition closes
- 5:55 – Awards judges meeting (meeting room) – closed to the public
- 6:00 – Closing reception and awards ceremony  
(Exhibition hall)

Exhibition hall – 2008 SC and 2<sup>nd</sup> floor lobby SC

Lecture hall – 190 ESB

Meeting room – 208 MRL

# Plenary talks

9:15

*On-chip hybrid magnonic systems for quantum information science*



**Li Yi**

**Assistant Scientist in the Superconductivity and Magnetism Group**  
Argonne National Laboratory  
*2024 AVS Prairie Chapter Early Career Award*

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11:05

*Pushing the limits of membrane selectivity*



**Seth B. Darling**

**Chief Science & Technology Officer for the Advanced Energy Technologies Directorate**  
Argonne National Laboratory  
*2024 AVS Prairie Chapter Outstanding Researcher Award*

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2:15

Quantum photonics with rare-earth materials



**Elizabeth Goldschmidt**

**Assistant Professor, Physics**  
University of Illinois at Urbana-Champaign

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3:05

Design of nanoscale materials



**Elena Shevchenko**

**Scientist, Nanoscience**  
Argonne National Laboratory

# Oral presentations

## Lecture hall

### Session A Moderator: Mary Kraft, University of Illinois

- 8:55 – **Plenary Talk** AVS Prairie Chapter Early Career Research Award  
Li Yi - *On-chip hybrid magnonic systems for quantum information science*
- 9:45 – Jack A. D'Amelio, Amy Tram, Zach W. Riedel, Selvin Tobar, Donny Pearson, Elizabeth Goldschmidt, Daniel P. Shoemaker - *Optical characterization of single-crystal stoichiometric europium materials for quantum memory applications*
- 10:05 – Hanyu Hou, Muchuan Hua, Thomas E. Gage, Benjamin T. Diroll, Jian-Min Zuo, Jianguo Wen –*High-resolution STEM cathodoluminescence of quantum emitters at the twist interface in 2D-exfoliated hBN*
- 10:05 – Joshua Wagner, Steven J. Sibener - *Coverage dependent diffusivity and binding of atomic oxygen on moiré patterned graphene*

### Session B Moderator: Mauro Sardela, University of Illinois

- 11:10 – **Plenary Talk** AVS Prairie Chapter Outstanding Research Award  
Seth Darling - *Pushing the limits of membrane selectivity*
- 12:00 – Abdelilah Asserghine, Aravind Baby, Huimin Zhao, Joaquín Rodríguez-López - *In situ detection of reactive oxygen species spontaneously generated on lead acid battery anodes: a pathway for degradation and self-discharge at open circuit*

### Session C Moderator: Kristen Flatt, University of Illinois

- 1:50 – Grace McKnight, Heonjae Jeong, Elif Ertekin, Edmund Seebauer - *Interstitial cluster families in semiconducting oxides: effects on post-synthesis defect engineering and purification using submerged surfaces*
- 2:10 – **Plenary Talk**  
Elizabeth Goldschmidt - *Quantum photonics with rare-earth materials*
- 3:00 – **Plenary Talk**  
Elena Shevchenko - *Design of nanoscale materials*

### Session D Moderator: Timothy Spila, University of Illinois

- 4:15 – Xierong Qian, Joonsoo Kim, Jiadong Chen, Toby Woods, Wenhao Sun, and Daniel Shoemaker - *Experimental efforts in water-ethanol-dimethylformamide ternary solvent to optimize advanced Pourbaix d*
- 4:35 – Dairong Liu, Linfei Li, Nan Jiang - *Nanoscale chemical probing of metal-supported ultrathin ferrous oxide*
- 4:55 – Benjamin R. Heiner, Kaitlyn M. Handy, Alex L. Walter, Jacob P. Petersen, S. Alex Kandel - *Scanning tunneling microscopy of ferrocenecarboxylic acid assemblies on Ag(111): a comparison to Au(111)*
- 5:15 – Myoung-Woo Yoo, Virginia Lorenz, David Cahill, Axel Hoffmann - *Thermal contribution to current-driven antiferromagnetic-order switching in Mn<sub>3</sub>Sn*
- 5:35 – Michael F. Van Duinen, Caleb J. Thompson, Michelle M. Kelley, Cristobal Mendez, Sarah A. Willson, Van Do, Tomas A. Arias, S. J. Sibener - *High-temperature diffraction and surface electron-phonon coupling of the unreconstructed metallic and (3x1)-O reconstructed Nb(100) surfaces by helium atom scattering*

# Poster Presentations

Exhibition hall – round 1 - 10:45 a.m. to 11:05 a.m.

round 2 – 1:10 p.m. to 1:50 p.m.

round 3 - 3:50 p.m. to 4:15 p.m.

- P1.** Mohammad Rahat Hossain, Michael Trenary - *Selective hydrogenation of 1,3-butadiene on a Pd/Cu (111) single-atom-alloy*
- P2.** Ayoyele Ologun, Michael Trenary - *Homoepitaxial growth of ZrB<sub>2</sub> on a ZrB<sub>2</sub>(0001) surface*
- P3.** Bidipta Ghosh, Cheng Zhang, Stefanie Frick, En Ju Cho, Toby Woods, Yujie Yang, Nicola H. Perry, Andreas Klein, Hong Yang - *Active site defect engineering in pyrochlore electrocatalysts for oxygen evolution through targeted composition and band tuning*
- P4.** Sonji Lamichhane, Mary L. Kraft - *A new tool for visualizing protein distribution in the marine diatom, *Phaeodactylum tricornutum**
- P5.** Adnan Mohammad and Jeffrey W. Elam - *Investigating the emissive properties of Ba-containing thin films synthesized via thermal atomic layer deposition*
- P6.** B. Kamiyama, M. A. Eslamisaray, E. Gillmore, A. Tomita, R. M. Sankaran - *Correlating process conditions to product distributions for nitrogen fixation by plasma electrolysis*
- P7.** Yoav Malka, Chi Thang Nguyen, Jeffrey W. Elam - *Fabrication of Ru:Al<sub>2</sub>O<sub>3</sub> resistive layer for microchannel plates using atomic layer deposition*
- P8.** Shuchen Li, Niu Chang, Axel Hoffmann, and Peide Ye - *Spin polarizations in chiral tellurium*
- P9.** Alexis Gonzalez, Elizabeth Jamka, Maxwell Gillum, Elizabeth Serna-Sanchez, Alisson Kerr, Dan Killelea - *Investigation of carbon monoxide (CO) oxidation on Rh(111) with reflectance absorbance infrared spectroscopy (RAIRS) and temperature program desorption (TPD)*
- P10.** Amit K. Datta, Nikhila C. Paranamana, Andreas Werbrouck, Patrick J. Kinlen, Matthias J. Young - *Synthesis of disulfide polymer by oxidative molecular layer deposition (oMLD)*
- P11.** Zhixin Zhang, Axel Hoffmann - *FeGaB alloys for magnetoelastic coupling at microwave frequencies*
- P12.** Musa O. Azeez, Andreas Werbrouck, Nikhila C. Paranamana, Matthew R. Maschmann, Matthias J. Young - *Examining UV-induced functional group formation on 2D nanomaterials for patterned ALD*
- P13.** Shima Mehregan, Mahya Mehregan, and Matthias J. Young - *Oxidative molecular layer deposition of polythiourea: unraveling its electrochemical and chemical characteristics*
- P14.** Maxwell Gillum, Arved Dorst, Alexis Gonzalez, Elizabeth Serna-Sanchez, Allison Kerr, Stephanie Danahey, Tim Schaefer, Daniel Killelea - *Characterization of oxygen species on Rh-based model catalysts*
- P15.** Jasper Brown and Steven J. Sibener - *Even-odd directed dehalogenation of bromine terminated alkane sams via atomic hydrogen*
- P16.** Elizabeth A Jamka, Francisco Lizano, & Steve J Sibener - *Sticking probabilities of carbon dioxide (CO<sub>2</sub>) isotopologues*
- P17.** Yufei Bai,<sup>1</sup> David L. Wisman,<sup>1,2</sup> and Steven L. Tait<sup>1</sup> - *Using Single-layered COFs to Stabilize Single-atom Catalysts on Model Surfaces*

- P18.** Seth Putnam, Joaquin Rodriguez-Lopez - *Redox-Active Spin Traps for the In-Situ Investigation of Radical Species at Electrocatalytic Interfaces*
- P19.** Yong-Yun Hsiau, Bernadette Cladek, Liz Griffin, Roberto dos Reis, Gabriel Trindade dos Santos, Katharine Page, Vinayak P. Dravid, Nicola H. Perry - *Growth, structure, and kinetics of triple-conducting vertically aligned nanocomposites*
- P20.** Jongmin Lee, Haley B. Buckner, Nicola H. Perry - *Proton surface exchange coefficients of perovskite thin films for efficient steam electrodes in protonic ceramic electrolysis cells*
- P21.** Zirui Wang, Michael A. Pence, Joaquín Rodríguez-López - *An automated platform for high-throughput surface interrogation studies on electrochemical energy storage materials*
- P22.** Alexia Popescu, Supriyo Majumder, Michael Bedzyk, Nicola H. Perry - *Understanding the transitioning surface exchange behavior between pure proton conducting to triple conducting thin films for steam electrodes*
- P23.** Supriya (Riyo) Das, Joaquin Rodriguez Lopez - *Harnessing electrostatics for the conversion of biomass inside a microdroplet to generate value-added products (DROPLETS Project)*
- P24.** Effie Gong, Myoung-Woo Yoo, Axel Hoffmann - *Enhancing the Magneto-Optical Kerr Effect in Non-collinear Antiferromagnets via a Dielectric Layer*
- P25.** Van Do, Helena Lew-kiedrowska, Chi Wang, and Steven J. Sibener - *In-situ characterization of Au capping on superconducting Nb(100)*
- P26.** Aditi Prasad, Joaquin Rodriguez-Lopez - *In-situ detection of reactive oxygen species generated from aptamer-based electrochemical biosensors using SECM*
- P27.** Sipei Zhang, Zhengwu Fang, Miaofang Chi, Nicola H. Perry - *Influence of particle size on defect chemistry - transport - chemical strain coupling of mixed-conducting (Pr,Ce)O<sub>2-δ</sub> nanoparticles*
- P28.** Jiu Kang, Chi Thang Nguyen, and Jeffrey W. Elam - *3D Ruthenium Block Design Strategy Using Area Selective Deposition Combined with Subsequent Etching*
- P29.** Hrishikesh Tupkar, Jack Verich, Sila Alemdar, Jack McAlpine, Matthew A. Gebbie - *Enhancing Interfacial Capacitance Using Anionic Amphiphiles in Ionic Liquid Electrolyte Blends*
- P30.** Samuel Johnstone, Seth Anderson, Matthew Gebbie - *Elucidating the Impact of Interfacial Anions on Electrochemical Reduction Reactions*
- P31.** Shilpa Choyal, Buddhika S.A. Gedara, Michael Trenary, and Nan Jiang - *Probing metal nanocluster on graphene via scanning probe microscopy*
- P32.** Chamath Siribaddana, Nan Jiang - *Surface-catalyzed Ullmann coupling via activation of highly labile C-I for nanostructure synthesis*
- P33.** Sean M. Peyres, Hoang M. Nguyen, Chiedozie B. Ogueri, Necip B. Üner, David B. Go, and R. Mohan Sankaran - *Reaction and Diffusion of Plasma-Injected Solvated Electrons in Non-Aqueous Solvents*
- P34.** Alaina Humiston, Jeff Terry, Daniel Olive, Mui (Andy) Lau, Ming Long, Evan Restuccia, and Timothy Stack - *X-ray Photoelectron Spectroscopy Data Fitting Using A Genetic Algorithm*

# **ABSTRACTS**

# 2024 AVS Prairie Chapter Early Career Research Award



## On-chip hybrid magnonic systems for quantum information science

**Yi Li**

Assistant Scientist in the Superconductivity and Magnetism Group  
Argonne National Laboratory

Recently, hybrid dynamic systems based on magnetic materials have attracted increasing interests as a new branch in quantum information science. Magnetic excitations, or magnons, are collective excitation of magnetic moments with frequency in the range of GHz to THz. Due to diverse coupling mechanisms, magnons can be coupled to a wide variety of excitations such as microwave, optic light, phonons and spins. They are promising for coherent information transfer between distinct physical platforms, making them promising for exploring potentials in quantum sensing and quantum transduction.

In this talk, we develop a superconducting circuit platform for implementing on-chip hybrid magnonic system, where the magnon mode is strongly coupled to the photon mode. In the first example, we explore the use of permalloy ( $\text{Ni}_{80}\text{Fe}_{20}$ ) thin film devices, where permalloy is a classical metallic ferromagnet with well-known magnetic dynamic properties and is easy to grow and integrate into complex devices. In the second example, we incorporate chip-mounted single-crystal YIG spheres, where YIG exhibit the lowest damping in the known magnetic materials. In particular, we demonstrate microwave-mediated distant magnon-magnon interactions by coupling two remote YIG spheres to a superconducting resonator as a coherent data bus. In addition, we demonstrate time-domain magnon interference between the two remotely coupled YIG spheres. Our results provide a realistic platform for constructing hybrid magnonic quantum networks at cryogenic temperatures and that can be scaled-up and incorporated into integrated circuits.



# AVS Prairie Chapter Outstanding Research Award



## Pushing the limits of membrane selectivity

### Seth Darling

Chief Science & Technology Officer for the Advanced Energy Technologies Directorate Argonne National Laboratory

Transport of solutes through porous membranes underlies numerous separation processes critical to industries ranging from water treatment to biotechnology to resource recovery. However, a dearth of tunable model systems has limited predictive understanding and, therefore, progress in improvements of selective membrane transport. In this presentation, I will give examples of recent advances in developing such systems for both 1D- and 2D-confined transport.

Transport of a spherical solute through a cylindrical pore has been modeled for decades using well-established hindered transport theory, predicting solutes with a size smaller than the pore to be rejected nonetheless because of convective and diffusive hindrance; this rejection mechanism prevents extremely sharp solute separations by a membrane. While the model has been historically verified, solute transport through near-perfect isoporous membranes may finally overcome this limitation. Here, encouraging solute rejections are achieved using nanofabricated, defect-free silicon nitride isoporous membranes. The membrane is challenged by a recirculated feed to increase the opportunity for interactions between solutes and the pore array. Results show the membrane completely reject solutes with greater size than the pore size while effectively allowing smaller solutes to permeate through. With effectively increasing the number of interactions, we propose that a steeper size-selective rejection curve may be achieved. With this traditional hurdle overcome, there is new promise for unprecedented membrane separations through judicious process design and extremely tight pore-size distributions.

The interlayer galleries in membranes integrating two-dimensional (2D) materials drive separation and selectivity, with specific transport properties determined by the chemical and structural modifications. We report an approach to tuning interlayer spacing in membranes derived from clay materials with molecular cross-linkers to control the gallery height, enhance the membrane stability, and manipulate the chemical and electrostatic environment in the channels. The cross-linked 2D phyllosilicate membranes exhibit ion diffusivities tuned by the length and functionality of the selected cross-linking molecule. The 2D nanochannels in these stabilized membranes enable a systematic study of confined ionic transport.

# Plenary talk



## Quantum photonics with rare-earth materials

**Elizabeth Goldschmidt**

Assistant Professor, Physics  
University of Illinois at Urbana-Champaign

Optically active and highly coherent emitters in solids are a promising platform for building practical quantum networks. Rare-earth atoms, in addition to having record long coherence times, have the added benefit that they can be hosted in a wide range of solid-state materials. We can thus target particular materials (and choose particular rare-earth species and isotopes) that enable certain application-specific functionalities. I will present recent results from our lab on studying rare-earth atoms in different host materials and configurations. This includes characterizing new stoichiometric rare-earth crystals with narrow line widths and record high emitter densities, as well as photonic integration of rare-earth doped samples to make on-chip quantum photonic devices.

# Plenary talk



## Design of nanoscale materials

**Elena Shevchenko**

Scientist, Nanoscience  
Argonne National Laboratory

Recent advances in the design and application of nanoscale materials are paving the way for groundbreaking solutions to some of the world's most pressing challenges, from energy production and storage to environmental sustainability. In my talk, we will explore how we can synthesize functional materials to create more efficient photocatalysts, batteries, catalysts, optically active coatings and sensors. We will discuss different strategies to control over composition and function of nanomaterials. We will show how the properties of nanomaterials can be turned by the synthesis parameters. We will discuss the possibility to enhance the function of nanomaterials via direct synthesis, surface modification and polymer templated synthesis to inspire further research and development that will help us move towards a more sustainable future.

## **Oral presentations (abstracts)**

Oral presentation 1

## **Optical characterization of single-crystal stoichiometric europium materials for quantum memory applications**

Jack A. D'Amelio\*,<sup>1,2</sup> Amy Tram,<sup>2,3</sup> Zach W. Riedel<sup>2,4</sup>, Selvin Tobar<sup>2,5,6</sup>, Donny Pearson<sup>2,7</sup>,  
Elizabeth Goldschmidt<sup>2,7</sup>, Daniel P. Shoemaker<sup>2,4,7</sup>

<sup>1</sup>*Physical Chemistry, UIUC, 505 S Mathews Ave, Urbana, IL 61801*

<sup>2</sup>*Materials Research Laboratory, UIUC, 104 S Goodwin Ave MC-230, Urbana, IL 61801*

<sup>3</sup>*Chemistry, Lake Forest College, 555 N Sheridan Rd, Lake Forest, IL 60045*

<sup>4</sup>*Materials Science, UIUC, 1304 W Green St, Urbana, IL 61801*

<sup>5</sup>*Chemical Engineering, UIUC, 600 S Mathews Ave, Urbana, IL 61801*

<sup>6</sup>*Engineering Sciences, Wright College 4300 N Narragansett Ave, Chicago, IL 60634*

<sup>7</sup>*Physics, UIUC, 1110 W Green St Loomis Laboratory, Urbana, IL 61801*

\*Corresponding author's email address: [damelio2@illinois.edu](mailto:damelio2@illinois.edu)

Three phases of stoichiometric europium (III) iodate compounds are probed as candidates for photon-based quantum information storage. Hydrothermal synthesis procedures for growing macroscopic single crystals of plate-shaped  $\text{Eu}(\text{IO}_3)_3$  [P21/n], rectangular-block  $\text{Eu}(\text{IO}_3)_3$  [P21/a], prismatic rod  $\text{NaEu}(\text{IO}_3)_4$  [Cc] are presented, along with analysis of reaction conditions which promote each phase. High stoichiometries above 10:1 mmol  $\text{NaIO}_3$ :  $\text{Eu}(\text{IO}_3)_3$  preferentially react to create  $\text{NaEu}(\text{IO}_3)_4$  over the P21/n  $\text{Eu}(\text{IO}_3)_3$ . Lower mole ratios of  $\text{NaIO}_3$  under less acidic conditions favor the P21/a  $\text{Eu}(\text{IO}_3)_3$ . Room temperature 785 nm Raman, 532 nm photoluminescence mapping, optical profilometry and single crystal XRD are analyzed for each compound.

## High-resolution STEM cathodoluminescence of quantum emitters at the twist interface in 2D-exfoliated hBN

Hanyu Hou,<sup>1,2</sup> Muchuan Hua,<sup>2</sup> Thomas E. Gage,<sup>2</sup> Benjamin T. Diroll,<sup>2</sup> Jian-Min Zuo,<sup>1</sup>  
Jianguo Wen<sup>2\*</sup>

<sup>1</sup>Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL,  
United States of America

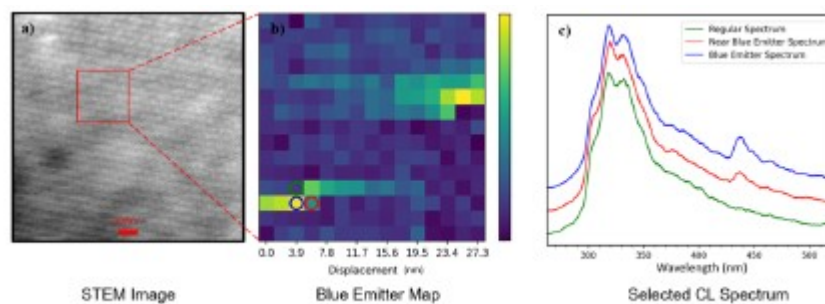
<sup>2</sup>Center for Nanoscale Materials, Argonne National Laboratory, Lemont, IL, United States of  
America

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Two-dimensional (2D) exfoliated materials with Van der Waal's interlayer bonding have attracted significant attention in recent years for their potential as quantum emitters that are critical towards quantum information science. Hexagonal boron nitrite (hBN) has a layered structure and a bandgap near 6 eV. Because of these attractive properties, the hBN materials have been engineered extensively to create quantum emitters.

Cathodoluminescence (CL) collects emitted photons induced by an electron beam. It is widely implemented in scanning electron microscopes (SEM). However, the spatial resolution is about tens of nanometers, which makes it difficult to resolve individual emitters. Here, we report an implementation of the aberration-corrected scanning transmission electron microscopy (STEM) based CL and its use to characterize color centers embedded in ultra-thin 2D exfoliated hBN materials. We show a significant improvement in the CL resolution at the twisted interface of hBN.

Figure 1 shows the results that we obtained with STEM CL on a carbon implanted hBN. Isolated blue emitters have been numerous found on the sample. The CL mapping was carried out using a nano probe by scanning the region of interest at 15 steps. This drastically improves the spatial resolution and provides the possibility to trace the corresponding deterministic defect structure. In addition to the probe size, the CL spatial resolution is determined by plasmon wave and charge carrier diffusion length. When CL resolution is narrowed down to several nanometers, we can accurately locate the spatial position of the defect. As shown in Fig. 1c, the selected CL spectrum on defect region shows carbon-related emission at 440 nm, and the color center can be defined within 2-3nm as shown in Fig. 1a and b. The results show that we can probe the blue and ultraviolet light emitter in a thin hBN (20 nm thick) with sufficient intensity and high spatial resolution.



**Fig. 1.** a) STEM image of twisted interface with Morrie pattern. b) Blue emitter intensity map of red box shown in a) after background subtraction, 2 emitters exist in the area. c) Selected spectrums of the circled positions with corresponding color. Blue emitter ZPL locates at 440nm.

Oral presentation 3  
**Coverage dependent diffusivity and binding of atomic oxygen on moiré patterned graphene**

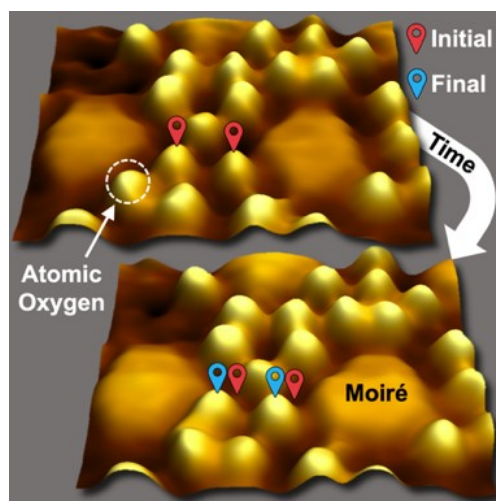
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The intrinsic moiré pattern of epitaxial graphene on Ru(0001) provides a wide palette of potential binding sites for atomic oxygen and a rich testbed for surface science. STM images show the site-specificity of O(<sup>3</sup>P) adsorption/binding on the moiré-patterned graphene is coverage dependent.<sup>1</sup> Multiparticle interactions lead to changes in site-specificity of oxygen binding across the moiré pattern and alter the diffusivity of oxygen on the surface. Local environment is also shown to be more important for oxygen diffusivity than global oxygen coverages. Side-by-side comparison of monolayer and bilayer graphene on Ru(0001) illustrates the importance of spin-forbidden reaction dynamics in the adsorption of ground state atomic oxygen onto graphitic surfaces.<sup>2</sup> Overall, results provide insights to the synthesis and stability of moiré-templated two-dimensional materials which are promising platforms for next-generation quantum materials and catalysts.



**Figure 1.** STM visualization of O atoms diffusing on moiré-patterned graphene on Ru(0001) is shown here.

- [1] Wagner, J.; Sibener, S. J. "Coverage-Dependent Site-Specific Placement and Correlated Diffusion of Atomic Oxygen on Moiré-Patterned Graphene on Ru(0001)" *J. Phys. Chem. Letters*, 15, 2936-2943 (2024)
- [2] Wagner, J.; Edel, R.; Grabnic, T.; Wiggins, B.; Sibener, S. J. "On-Surface Chemical Dynamics of Monolayer, Bilayer, and Many-Layered Graphene Surfaces Probed with Supersonic Beam Scattering and STM Imaging" *Faraday Discussion on New Directions in Molecular Scattering* (2024)

Oral presentation 4

## **In situ detection of reactive oxygen species spontaneously generated on lead acid battery anodes: a pathway for degradation and self-discharge at open circuit**

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Lead-acid batteries (LABs) represent 70% of the global secondary battery market due to their safety, performance, and cost-effectiveness.<sup>1</sup> They are extensively used in applications such as microgrids, photovoltaics, and mobility. However, LABs suffer from a relatively short cycle life (~300 cycles),<sup>1</sup> leading to high replacement costs and environmental issues. In 2014 alone, LABs generated 2.46 million tons of waste, including hazardous lead. The primary failure mode of LABs is hard sulfation, known by the formation of large, irreversible PbSO<sub>4</sub> crystals on the Pb negative electrode. This crystallization increases resistance and reduces capacity,<sup>2,3</sup> making it crucial to understand the underlying causes of PbSO<sub>4</sub> formation to extend LAB lifespan.

In my presentation, I will delve into how the oxygen reduction reaction (ORR) accelerates the sulfation of Pb-C anodes extracted from commercial LABs, as demonstrated through scanning electron microscopy and X-ray diffraction analyses. Additionally, I will demonstrate how electron spin resonance (ESR) and *operando* scanning electrochemical microscopy (SECM) have been applied for the real-time detection and quantification of reactive oxygen species (ROS), such as hydroxyl radicals (OH<sup>•</sup>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).<sup>4</sup> These ROS are generated at open circuit potential on Pb-C electrodes as products of the ORR. The ROS detection methods we have developed using SECM at open circuit potential offer valuable insights into the mechanistic aspects of battery electrode corrosion, highlighting the critical role of oxygen, whether introduced intentionally or unintentionally, in influencing the performance and lifespan of batteries, including but not limited to LABs.<sup>4</sup>

[1] Cano, Z. P., Banham, D., Ye, S., Hintennach, A., Lu, J., Fowler, M., & Chen, Z. (2018). Batteries and fuel cells for emerging electric vehicle markets. *Nat. Energy*, 3(4), 279-289.

[2] Lu, J., Baby, A., Asserghine, A., Rodríguez-López, J., & Zhao, H. (2024). Amino acid based ionic liquids for revitalization of sulfated lead anodes. *J. Power Sources*, 591, 233824.

[3] Asserghine, A., Baby, A., Gao, E., Zhao, H., & Rodríguez-López, J. (2023). Inducing and real-time monitoring of lead (de)sulfation processes using scanning electrochemical microscopy for applications in the refurbishment of lead-acid batteries. *Electrochimica Acta*, 143620.

[4] Asserghine, A., Baby, A., Putnam, S. T., Qian, P., Gao, E., Zhao, H., & Rodríguez-López, J. (2023). In situ detection of reactive oxygen species spontaneously generated on lead acid battery anodes: A pathway for degradation and self-discharge at open circuit. *Chem. Sci.*, 14(43), 12292-12298.



## **Interstitial cluster families in semiconducting oxides: effects on post-synthesis defect engineering and purification using submerged surfaces**

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Injection of interstitial atoms into semiconducting oxides by specially prepared surfaces submerged in liquid water near room temperature offers an attractive approach for post-synthesis engineering of atomic-scale defects and for isotopic purification.<sup>1</sup> For defect engineering, this approach avoids the high temperatures characterizing standard methods, which can generate undesirable defects, induce phase changes, and degrade nanostructures. Injection of oxygen interstitials ( $O_i$ ) effectively annihilates O vacancies that degrade carrier lifetime in photodevices and neutralizes unintentional electron donors such as adventitious hydrogen.<sup>2</sup> For isotopic purification, efficient injection generates steep  $O_i$  gradients, which in conjunction with statistical differences in the effective diffusivities of minority  $^{18}O$  and majority  $^{16}O$ , purify the near-surface region of  $^{18}O$ . Isotopically pure semiconductors are vital for quantum computing and sensing and enhance thermal conduction in conventional electronic devices for efficient heat removal. However, injected interstitials can undergo trapping reactions to form small interstitial clusters that restrict the penetration depth and affect the near-surface interstitial gradient. The possible cluster compositions and dissociation barriers remain unknown in most oxides. The present work begins to fill this knowledge gap by measuring the dissociation energies of  $O_i$  clusters that form in rutile  $TiO_2$  and wurtzite  $ZnO$  after immersion in liquid water. Isotopic self-diffusion measurements using  $^{18}O$ , combined with similar measurements during staged annealing at progressively increasing temperatures, suggest that the primary traps for  $O_i$  are interstitial clusters with dissociation energies ranging from 1.3 to 1.9 eV. Preliminary simulations by density functional theory suggest these traps involve a family of small interstitial clusters comprising O and H atoms in various numbers, compositions, and geometries. These defect families may increase the number of injected interstitials required to achieve trap saturation, necessitate an additional warming step to prevent material property drift, and complicate use of photostimulation for promoting cluster dissociation.

[1] ACS Applied Material Interfaces 2022, 14, 29, 34059–34068

[2] Journal of Materials Research 2012, 27, 2190–2198

Oral presentation 6

## **Experimental efforts in water-ethanol-dimethylformamide ternary solvent to optimize advanced Pourbaix diagrams**

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Solvothermal synthesis is a versatile method for producing functionalized framework materials and nanomaterials. The success of solvothermal synthesis is highly dependent on proper reagents, temperature, pressure, and, notably, solvents. However, the solvent selection was majorly conducted without thermodynamic guidance, which makes the selection process unpredictable. Therefore, we turned to advanced Pourbaix diagrams, which can reveal the phases with the lowest energy under a given reaction condition, to predict the synthetic results. Inspired by our previous work on synthesizing metastable phase  $\text{Cu}_4\text{O}_3$ , we first picked the water-ethanol-dimethylformamide (DMF) ternary solvent system to investigate. By dissolving  $\text{CuCl}_2$  into this ternary solvent, we explored the products under different solvent proportions. We find that some of the crystallized phases are new and unreported, so they are not predictable by the Pourbaix framework. We must solve their crystal structures to consider them as possible phases. We can then compare our experimental results with the plotted Pourbaix diagram to optimize the parameters.

## Nanoscale chemical probing of metal-supported ultrathin ferrous oxide

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Over the last few decades, extensive research on ultrathin ferrous oxide (FeO) islands and films has significantly contributed to understanding their structural and catalytic properties. One crucial aspect is the interfacial properties of ultrathin FeO islands in catalytic reactions, such as CO oxidation. Despite this, the ability to chemically probe the highly localized interfacial properties to establish structure-property relationships remains limited. Here, we utilized scanning tunneling microscopy (STM) and tip-enhanced Raman spectroscopy (TERS) to investigate FeO films grown on Au(111). For comparative analysis, single-crystal Au(111) and Au(100) substrates are used to tune the interfacial properties of FeO. Although STM images show distinctly different moiré superstructures on FeO nanoislands on Au(111) and Au(100), TERS demonstrates the same chemical nature of FeO by comparable vibrational features. In addition, combined TERS and STM measurements identify a unique wrinkled FeO structure on Au(100), which is correlated to the reassembly of the intrinsic Au(100) surface reconstruction due to FeO deposition. Beyond revealing the morphologies of ultrathin FeO on Au substrates, our study provides a thorough understanding of the local interfacial properties and interactions of FeO on Au, which could shed light on the rational design of metal-supported FeO catalysts. Furthermore, this work demonstrates the promising utility of combined TERS and STM in chemically probing the structural properties of metal-supported ultrathin oxides on the nanoscale.<sup>1</sup>

[1] Liu, D.; Li, L.; Jiang, N., Nanoscale Chemical Probing of Metal-Supported Ultrathin Ferrous Oxide via Tip-Enhanced Raman Spectroscopy and Scanning Tunneling Microscopy. *Chemical & Biomedical Imaging* 2024, 2 (5), 345-351.

## Scanning tunneling microscopy of ferrocenecarboxylic acid assemblies on Ag(111): a comparison to Au(111)

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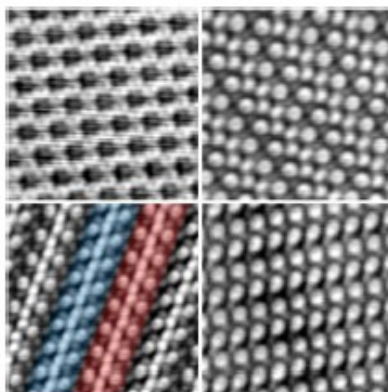
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Using scanning tunneling microscopy (STM), we can investigate the intermolecular interactions that drive the self-assembly of molecules onto the surface of a substrate. Au(111) is often chosen as a substrate because it is flat and inert. In studies of molecular assembly on Au(111), the influence of the gold surface on molecular organization is often ignored. In the specific case of ferrocenecarboxylic acid deposited on Au(111), a variety of structures form, including two-dimensional quasicrystals, dimers, pentamers, and hexamers—all of which can be explained solely by molecule-molecule interactions.<sup>1,2</sup>

To test the assumption that surface-molecule interactions are negligible in the formation of these structures, we conducted an experiment under identical conditions but replaced the substrate with Ag(111), another flat and inert surface. A completely different set of structures emerged, including a honeycomb packing and multiple striping phases (Fig. 1). In this presentation, I will discuss the interpretation of the STM images and present our proposed model for the molecular interactions responsible for these formations. Our findings suggest that, at least in the case of ferrocenecarboxylic acid, surface-molecule interactions play a role in self-assembly on inert substrates and warrant further investigation.



**Figure 1.** *The four assemblies of ferrocenecarboxylic acid when deposited on Ag(111) instead of Au(111).*

[1] Nature, 2014, 507, 86–89

[2] Chem. Commun., 2014, 50, 10229-10232

## **Thermal contribution to current-driven antiferromagnetic-order switching in $Mn_3Sn$**

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Non-collinear antiferromagnets, such as  $Mn_3X$  ( $X = Sn, Ge, \text{etc.}$ ), are non-trivial antiferromagnets that substantially interact with currents and light due to their band topology, making them promising materials for the next-generation spintronic devices.<sup>1,2</sup> Magnetic octupoles, the collective magnetic orders of non-collinear antiferromagnets, change the band structure and they can be controlled by electric currents.<sup>3</sup> Recently, Joule heating has also been thought to be crucial for the octupole switching,<sup>4</sup> but the self-heating temperature has not been studied quantitatively.

Here we study the temperature excursion due to Joule heating during the octupole switching process in  $Mn_3Sn$ . The threshold current density for the switching depends on the thickness of  $SiO_2$  layer of a  $Si/SiO_2$  substrate, while the switching temperature is almost constant at  $\sim 460$  K which is above the Néel temperature. The current density required to reach the Néel temperature is calculated analytically, and it quantitatively describes the dependence of the threshold current density on the substrate choice. This result shows that the current-driven switching is accompanied by demagnetization and reformation of the octupoles above and below the Néel temperature, respectively. This work demonstrates that temperature plays a decisive role in the octupole switching and a general guideline to calculate the Joule-heating temperature in micro-electronic devices. This work is supported by the NSF through the Illinois MRSEC (DMR-1720633).

- [1] T. Chen, et al., Anomalous transport due to Weyl fermions in the chiral antiferromagnets  $Mn_3X$ ,  $X = Sn, Ge$ , Nat. Commun. **12**, 572 (2021).
- [2] S. Nakatsuji, et al., Large anomalous Hall effect in a non-collinear antiferromagnet at room temperature, Nature **527**, 212 (2015).
- [3] H. Tsai, et al., Electrical manipulation of a topological antiferromagnetic state, Nature **580**, 608 (2020).
- [4] G. K. Krishnaswamy, et al., Time-Dependent Multistate Switching of Topological Antiferromagnetic Order in  $Mn_3Sn$ , Phys. Rev. Appl. **18**, 024064 (2022).

## High-temperature diffraction and surface electron-phonon coupling of the unreconstructed metallic and (3x1)-O reconstructed Nb(100) surfaces by helium atom scattering

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Superconducting radio frequency (SRF) cavities are the fundamental accelerating components of linear particle accelerators. Niobium is the material of choice for SRF cavities due to its high malleability, thermal conductivity, and superconducting critical temperature ( $T_C$ ). The improvement of Nb SRF cavities and the lowering of operating costs has been focused primarily on the development of new materials on the Nb surface. One of the primary limitations to both Nb SRF cavities and the new materials under study is the presence of a thermally stable and robust oxide. Understanding the formation, stability, and dynamics of the oxide and its effects on the operation of Nb SRF cavities requires study both of material superconducting properties and atomic-scale surface material chemistry. The studies contained in this work utilize helium atom scattering to determine atomic-scale surface structure through diffraction and an electron-phonon coupling (EPC) constant ( $\lambda$ ) through Debye-Waller measurements for the Nb(100) metallic and (3x1)-O oxidized surfaces ( $\lambda_s$ ). Higher  $\lambda_s$  is theoretically expected to correlate with stronger superconducting performance. We find a  $\lambda_s$  of  $0.50 \pm 0.08$  for the metallic Nb(100) versus a bulk  $\lambda$  of  $\sim 1$ , demonstrating that the superconducting state is significantly modified at the surface. We also find a  $\lambda_s$  of  $0.20 \pm 0.06$  for the Nb(100) (3x1)-O reconstruction. Lower  $\lambda_s$  corresponds to lower superconducting critical temperature  $T_C$  and overall poorer superconducting performance. Therefore, our studies strongly corroborate a strong body of previous literature that has hypothesized that the oxide diminishes superconducting performance for both bare Nb and new materials built atop it. From this fundamental starting point, we can further demonstrate the effect that doping, alloying, and thin-film material growth on the Nb surface have on its superconducting performance.

[1] C. J. Thompson, M. F. Van Duinen, M. M. Kelley, T. A. Arias, S. J. Sibener. *J. Phys. Chem. C* **128** (14), 6149-6157 (2024).

[2] C. J. Thompson, M. F. Van Duinen, C. Mendez, S. A. Willson, V. Do, T. A. Arias, S. J. Sibener. *J. Phys. Chem. C* **128** (25), 10714-10722 (2024).

## **Poster presentations (abstracts)**

## Selective hydrogenation of 1,3-butadiene on a Pd/Cu (111) single-atom-alloy

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Selective hydrogenation of 1,3-butadiene (BD) to 1-butene (1-B) is critical in refining alkene streams for high-quality polymer production. Typically, Pd and Pt are employed in hydrogenation reactions due to their nearly negligible barrier for H<sub>2</sub> activation. However, these catalysts are prone to coking and their high activity often reduces selectivity. Single-atom alloy (SAAs) catalysts are being developed to achieve high selectivity while retaining high activity. In an SAA, small amounts of an active metal, such as Pd or Pt, are doped into a less active host metal such as Cu. Previous work has shown that a Pd (111) surface exhibits superior selectivity for BD hydrogenation to 1-B compared to Pt (111) [1-4], suggesting that Pd/Cu (111) could be a suitable SAA model catalyst for this reaction. In this study, we investigated the adsorption and hydrogenation of 1,3-butadiene (BD) to 1-butene (1-B) over a Pd/Cu (111) SAA under ultrahigh vacuum (UHV) and ambient pressure conditions using reflection absorption infrared spectroscopy (RAIRS). Temperature programmed reaction spectroscopy (TPRS) in UHV showed that monolayer BD desorb at 217 K, while 2nd-layer and multilayer BD desorb between 112 to 180 K. RAIRS detected gas-phase 1-B formation and BD consumption. In ambient pressure conditions, this reaction was found to be first-order ( $1.12 \pm 0.03$ ) in H<sub>2</sub> and zero-order ( $-0.12 \pm 0.01$ ) in BD, correlating to a turnover frequency of  $36 \text{ s}^{-1}$  at 380 K. The activation energy was calculated to be  $63.2 \pm 2.8 \text{ kJ/mol}$  from an Arrhenius plot of the temperature dependence of the rate constant. Complete conversion of BD was found with 84% selectivity towards 1-B, without butane production. No surface species were detected during the reaction. Post-reaction analysis using Auger electron spectroscopy (AES) revealed carbon deposition, indicating some dissociation during hydrogenation.

[1] C.-M. Pradier, E. Margot, Y. Berthier and J. Oudar, *Appl. Catal.* 43 (1), 177-192 (1988).

[2] G. Tourillon, A. Cassuto, Y. Jugnet, J. Massardier and J. Bertolini, *J. Chem. Soc., Faraday Trans.* 92 (23), 4835-4841 (1996).

[3] T. Ouchaib, *J. Catal.* 119 (2) (1989).

[4] J. Massardier, J. Bertolini, P. Ruiz and P. Delichere, *J. Catal.* 112 (1), 21-33 (1988).



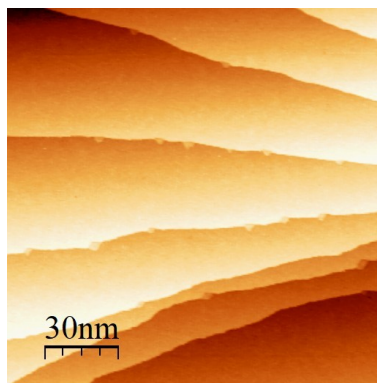
## Homoepitaxial growth of $\text{ZrB}_2$ on a $\text{ZrB}_2(0001)$ surface

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Transition metal diborides are known to either have a metal-terminated or boron-terminated surface. While group-V  $\text{MB}_2$  has boron-terminated surfaces, group-IV  $\text{MB}_2$  has metal-terminated surfaces.  $\text{ZrB}_2$ , a group-IV metal-terminated diboride, is an extremely hard material with a high melting point of 3246 °C. Thin films of  $\text{ZrB}_2$  can be grown conformally via chemical vapor deposition (CVD) using zirconium borohydride,  $\text{Zr}(\text{BH}_4)_4$ , as a precursor. Using reflection absorption infrared spectroscopy (RAIRS), the adsorption and surface chemistry of  $\text{Zr}(\text{BH}_4)_4$  on  $\text{ZrB}_2(0001)$  was characterized. Using low-energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS), we demonstrated that  $\text{ZrB}_2$  can have a boron-terminated surface under boron-rich conditions. Decomposition of  $\text{Zr}(\text{BH}_4)_4$  on  $\text{ZrB}_2(0001)$  surface at 1473 K revealed a  $\sqrt{3}\times\sqrt{3}$  boron-terminated surface, with a stoichiometry of  $\text{ZrB}_{2.60}$ . In contrast to the zirconium-terminated surface, the boron-terminated surface is resistant to oxidation. Using ultrahigh vacuum scanning tunneling microscopy (STM), we investigated the atomic-scale structure of  $\text{ZrB}_2(0001)$  and the homoepitaxial growth of  $\text{ZrB}_2$  on this surface. After relatively low exposures of  $\text{Zr}(\text{BH}_4)_4$  to  $\text{ZrB}_2(0001)$  at 1473 K and immediately cooling to room temperature, Zr-terminated bilayer islands of  $\text{ZrB}_2$  were observed. Coalescence of the  $\text{ZrB}_2$  islands was observed when the substrate was left for 60 mins at the deposition temperature before imaging at room temperature.



**Figure 1.** Clean  $\text{ZrB}_2(0001)$  surface showing monolayer step edges and terraces.

## Active site defect engineering in pyrochlore electrocatalysts for oxygen evolution through targeted composition and band tuning

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Oxygen evolution reaction (OER) is vital for energy conversion and storage in electrochemical devices. While factors such as oxygen vacancies, electronic structure, oxidation state and hydroxyl groups are known to influence OER activity, their individual contributions are not well understood. This study introduces a strategy to demonstrate the structure-property relationship in OER electrocatalysts by employing B-site defect engineering in pyrochlore-structured electrocatalysts. Initially, we developed a  $Y_2MnRuO_7$  catalyst that exhibited 14-fold increase in turnover frequency (TOF) compared to  $RuO_2$ . X-ray photoelectron spectroscopy (XPS) revealed that this catalyst has a slightly higher Ru oxidation state than  $Y_2Ru_2O_7$ , with Mn substitution at the B-site leading to a broadened and lowered Ru 4d band. The results suggest that the Ru oxidation state plays a crucial role in enhancing OER performance, outweighing the impact of surface hydroxyl group density. Building on these insights, we further investigated the effects of lower-valence cation substitution on the active metal site, focusing on site-mixed  $Y_2(Y_xRu_{1-x})_2O_{7-\delta}$  pyrochlore. By partially replacing B-site  $Ru^{4+}$  with A-site  $Y^{3+}$ , we observed a shift in the Ru oxidation state from 4+ to 5+, confirmed by XPS and electron paramagnetic resonance (EPR) spectroscopy. However, thermogravimetric analysis (TGA) indicated that this substitution did not lead to a continuous increase in oxygen vacancy concentration, suggesting that the acceptor dopant is electronically rather than ionically compensated. XPS analysis further determined the optimal valence band center to be approximately 1.27 eV below the Fermi level, a critical factor for achieving high catalytic activity. Our studies across both systems confirm that the oxidation state of Ru is more influential on OER performance than surface hydroxyl group concentration or oxygen vacancies. In conclusion, defect engineering proves to be an effective approach to optimizing the oxidation state and electronic band structure, significantly enhancing the catalytic performance of complex oxide electrocatalysts for OER.

**A new tool for visualizing protein distribution in the marine diatom,  
*Phaeodactylum tricornutum***

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The function of algal ecosystem is influenced by microbial attachment, which can affect the algal cell viability and their ability to convert solar energy and CO<sub>2</sub> into useful organic molecules. We hypothesize that changes in the organization of proteins and lipids in algal cell membrane are indicative of the nature of the bacterial interaction with algae (i.e., parasitic or beneficial). The Kraft lab is developing tools that enable visualizing the distributions of specific proteins and specific lipid species in the membranes of algal cells using a new Cameca NanoSIMS instrument, which enables mapping elemental and isotopic labels with as good as 10 nm lateral resolution. This will aid in imaging the response of algae to bacteria at the cell membrane scale and provide a direct readout of the nature of the interaction. My goal is to develop a microalgae line that expresses the bicarbonate (HCO<sub>3</sub><sup>-</sup>) transporter protein, SLC4-2, fused to a self-labeling protein, such as SNAP-tag or HaloTag. This enzymatic tag will allow us to label the protein it is fused to with a substrate that may be detected with NanoSIMS or any other imaging modality. Though both the SNAP-tag and HaloTag technologies has been extensively used in mammalian systems, there is only one demonstration of SNAP-tag usage in plant cells and usage of either tag in microalgae has not been reported. To create vectors for expressing each fusion protein construct in the model microalgae species, *Phaeodactylum tricornutum*, the linker and stop codon's placement was optimized using PCR and Gibson assembly to maintain the enzyme's catalytic activity. Then new episomal vectors for the expression of SLC4-2-SNAP-tag and SLC4-2-HaloTag fusion proteins in *P. tricornutum* were synthesized, purified, and amplified. To enable assessing whether SNAP-tag and HaloTag may be expressed in *P. tricornutum*, and whether they retain their enzymatic activities, new episomal vectors that enable the expression of just the SNAP-tag protein and only the HaloTag protein in *P. tricornutum* were also synthesized and amplified. These episomal plasmids were transferred into *P. tricornutum* via conjugation with *E. coli*, the transformed *P. tricornutum* cells were selected based on antibiotic resistance and expanded. By labeling in vivo with fluorescent SNAP-tag and HaloTag substrates, I demonstrated the SNAP-tag and HaloTag proteins were expressed by *P. tricornutum*, and they retained their catalytic activity, even when fused to the SLC4-2 membrane protein. The successful expression of catalytically active SNAP-tag and HaloTag proteins fused to SLC4-2 in *P. tricornutum* will enable us to test the hypothesis that membrane protein organization within the algal cell envelope changes in response to bacterial attachment. Moreover, this research broadens the fluorophores that may be selectively attached to a protein-of-interest in algae, thus opening new avenues of algal research.

## Investigating the emissive properties of Ba-containing thin films synthesized via thermal atomic layer deposition

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Microchannel plate (MCP) electron amplifiers are an integral component of large area photodetectors used in astronomy, high energy physics, and medical imaging. Thin film coatings with a high secondary electron yield (SEY) can improve the gain and performance of MCPs. Barium oxide (BaO) has a high SEY value and is a promising candidate for MCPs. Atomic layer deposition (ALD) is gaining popularity as a thin film processing method due to its low temperature, uniform, pinhole free deposition, and atomic scale thickness control. There are very few studies on BaO ALD in the literature and no reports applying ALD BaO in MCPs.

In this study, we report the thermal ALD of barium oxide (BaO) and barium hydroxide (Ba(OH)<sub>2</sub>) using bis(tri(isopropyl)cyclopentadienyl)barium, Ba(iPr<sub>3</sub>cp)<sub>2</sub>, as the barium precursor and ozone and water co-reactants. The Ba(iPr<sub>3</sub>cp)<sub>2</sub> was heated to 175 °C, the hot-wall reactor growth temperature was 250 °C, and the pressure ~1.2 Torr. We performed saturation experiments to optimize the precursor temperature, precursor dose time, purge time, and co-reactant exposure time. We used *in-situ* spectroscopic ellipsometry measurements to record the real-time instant thin film growth process, which is beneficial to perform the saturation studies with short cycles and amount of time. The *in-situ* spectroscopic ellipsometry also provided notable insights about the surface reactions that occur during the ALD unit cycle via *in-situ* ellipsometry. The growth per cycle (GPC) found with ozone is ~0.7 Å/cycle and saturated at 3 s of Ba(iPr<sub>3</sub>cp)<sub>2</sub>. On the other hand, using water we noticed an increasing trend of GPC till 7 s of Ba(iPr<sub>3</sub>cp)<sub>2</sub>. Further experimentations will be performed to explore and determine the ALD type growth window for water-based barium compound recipe.

We characterized the Ba-containing thin films using X-ray photoelectron spectroscopy, X-ray diffraction, and atomic force microscopy to evaluate the composition, phase, and surface topography, respectively. We discovered that the films deposited using ozone consisted of BaO while the films deposited using water were Ba(OH)<sub>2</sub>. Finally, we deposited ALD BaO onto MCP substrates and measured the resistance, gain, and temporal stability to determine the SEY and evaluate the material as a candidate high SEY coating for MCPs.

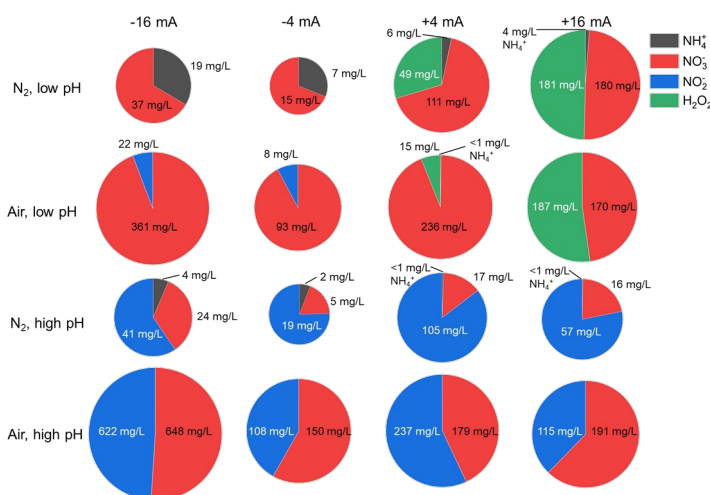
## Correlating process conditions to product distributions for nitrogen fixation by plasma electrolysis

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Nitrogen fixation is critical to our most basic need: Food production. Currently, almost all fixed forms of nitrogen substrates come from large-scale and fossil-fuel dependent industrial processes (e.g., Haber-Bosch, Ostwald processes), which have large physical and environmental footprints. The development of alternative methods that are sustainable and deployable at a small scale has emerged as one of our critical technological challenges. Among the different approaches being explored, plasma-based electrolytic reactors have shown great promise, capable of activating nitrogen in air or with water as a source of hydrogen at atmospheric pressure and near room temperature without any catalyst. However, a key challenge is that these processes generate a wide range of nitrogen products, including ammonium ions ( $\text{NH}_4^+$ ), nitrates ( $\text{NO}_3^-$ ), and nitrites ( $\text{NO}_2^-$ ), as well as other products such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). In this work, we performed a parametric study of a direct-current plasma in contact with an electrolyte solution and systematically varied several important process conditions including the gas feed, electrode configuration, electrolyte pH, and system current. The major products were quantitatively characterized including  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{H}_2\text{O}_2$ . We found important correlations between the process conditions and the product distributions. Electrolyte pH and molecular oxygen had a strong effect on  $\text{NH}_4^+$  vs.  $\text{NO}_x$ . These results provided important insight into the reaction mechanisms and can be used to selectively synthesize nitrogen products for different applications.



**Figure 1.** Effects of plasma reactor process conditions on the product yield and selectivity. Note: Diameter  $\propto$  log(total product mass concentration)  
[1]. *Science Advances* 5.1 (2019): eaat5778.

## Fabrication of Ru:Al<sub>2</sub>O<sub>3</sub> resistive layer for microchannel plates using atomic layer deposition

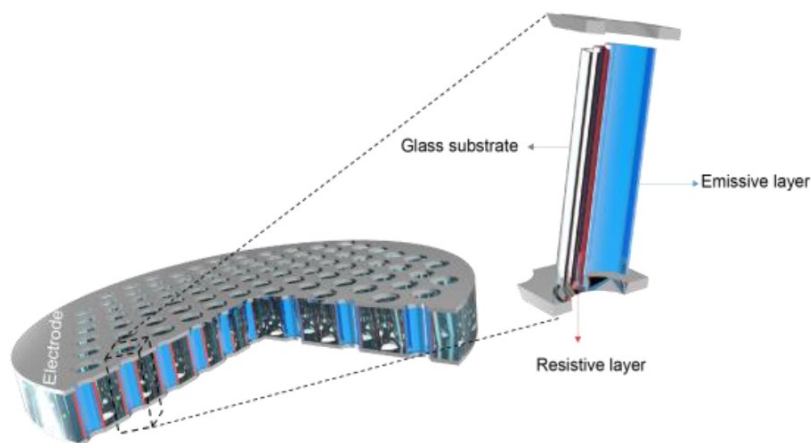
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Microchannel plates (MCPs) are high gain electron amplifiers utilized for applications such as night vision, electron microscopy, and mass spectrometry. MCPs can be fabricated starting from capillary glass array templates which are coated with resistive and emissive layers. This strategy allows one to independently tune the secondary electron emission and electrical conductivity. The resistive layers can be synthesized by blending metal dopants into an insulating host matrix. Controlling the metal dopant concentration can tune the electrical resistivities of MCPs. In this work, we used atomic layer deposition (ALD) to produce highly conformal Ru:Al<sub>2</sub>O<sub>3</sub> hybrid films with varying Ruthenium (Ru) metal dopant concentrations. We studied a new Ru ALD precursor, TRuST, which has a high vapor pressure making it a promising precursor for mass production on high aspect ratio geometries. Density functional theory (DFT) calculations and quadrupole mass spectrometry (QMS) measurements were used to investigate the chemisorption of TruST. The Ru to Al<sub>2</sub>O<sub>3</sub> ALD cycle ratio was varied to tune the resistivity across a wide range. As a result, the resistivities of Ru:Al<sub>2</sub>O<sub>3</sub> films show applicability as resistive layer, ranging from ~1013–107 Ω.cm, as the Ru sub-cycle % increased from 10% to 33%. Additionally, the change in resistivity post thermal annealing was investigated from 300 to 400°C. We believe that Ru:Al<sub>2</sub>O<sub>3</sub> shows excellent potential not only for MCPs but also for various applications, including microelectronics.



**Figure 1.** Schematic of the emissive and resistive layers coated on capillary glass arrays

## Spin polarizations in chiral tellurium

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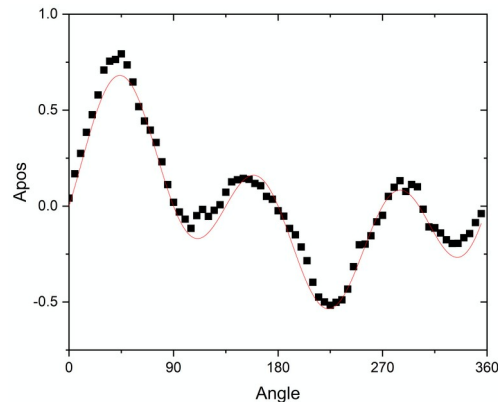
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Tellurium has a chiral helical structure. This chirality in tellurium breaks the inversion symmetry and results in a momentum-dependent radial spin texture at the Fermi level. With a charge current applied along the chirality direction, the Fermi level will be shifted and spins of electrons will be polarized either parallel or anti-parallel to the current (or chirality) direction depending on the handedness of the Te chirality [1]. This effect is similar to the Rashba-Edelstein effect. We are studying this chirality-induced spin polarizations by using spin-torque ferromagnetic resonance (ST-FMR) to observe the spin-orbit torques generated from single-crystalline Te flakes. In order to integrate exfoliated Te samples into devices, we first deposited a 10-nm Permalloy (Py; Ni<sub>80</sub>Fe<sub>20</sub>) layer and used ion-milling and lithography to integrate Te/Py heterostructure into a coplanar waveguide for radio frequency (rf) measurements. We applied GHz rf currents through Te/Py devices and collect a dc mixing voltage ( $V_{\text{mix}}$ ) due to the mixing of anisotropic magnetoresistance of Py and rf current [2]. The characteristics of spin-orbit torque components generated by Te flakes can be obtained by studying the dependence of  $V_{\text{mix}}$  as a function of applied magnetic field direction. As shown in Fig.1, the antisymmetric component of  $V_{\text{mix}}$  from our measurements shows spin torques ( $\tau_x$ ) due to x spins, which are collinear with the current direction, in addition to the Oersted torques generated from the rf current, indicating chirality-induced spin polarizations from Te.



**Figure 1.** Antisymmetric angular dependencies, showing the extracted antisymmetric component at each angle between the rotating magnetic field and the rf current.

[1] T. Furukawa, et al., Observation of current-induced bulk magnetization in elemental tellurium Nature Communications 8, 954 (2017)

[2] L.Liu, et al., Spin-Torque Ferromagnetic Resonance Induced by the Spin Hall Effect, Phys. Rev. Lett. 106, 036601 (2011)

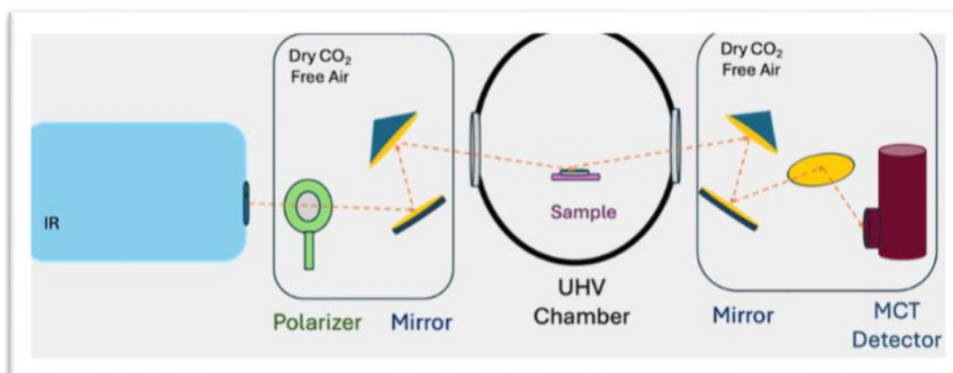
## Investigation of carbon monoxide (CO) oxidation on Rh(111) with reflectance absorbance infrared spectroscopy (RAIRS) and temperature program desorption (TPD)

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To create accurate models of catalysis, the energies and kinetics of catalytic systems must first be experimentally derived. In previous studies, we have proven that Rh-based catalysts provide an ideal model system to study oxidation reactions due to the reliability with which we can produce a limited number of oxygen species on the surface. This allows better control of the variables of the system. By probing the reactivity of these various surface species, such as adsorbed surface oxygen and subsurface oxygen, using the CO oxidation reaction we will be able to better ascertain the influence of various oxygen species on these catalytic systems. Herein, we present preliminary data on how the integration of reflectance absorbance infrared spectroscopy (RAIRS) into our ultra-high vacuum (UHV) setup greatly increases the amount of data we collect from our experiments. IR and TPD spectra indicated that there was more carbon dioxide production on the Rh(111) surface prepared with molecular oxygen than the surface prepared with atomic oxygen[1]. This contradicts what is expected due to the larger availability of reactants from higher oxygen concentrations on the surface prepared with atomic oxygen. Using IR spectroscopy concurrent with our temperature programmed desorption (TPD) experiments allows us to collect real time information about what is going on at the surface of the crystal as the CO oxidation reaction is occurring.



**Figure 1.** The beam path of the infrared beam through the UHV chamber is illustrated with a dashed red line depicting the beam's trajectory.

[1] Jamka, E. A.; Gillum, M. Z.; Grytsyshyn-Giger, C. N.; Lewis, F. J.; Killelea, D. R. Temperature-resolved surface infrared spectroscopy of CO on Rh(111) and (2 × 1)-O/Rh(111). *Journal of Vacuum Science & Technology A* 2022, 40 (4). DOI: 10.1116/6.0001932 (accessed 7/30/2024).



## Synthesis of disulfide polymer by oxidative molecular layer deposition (oMLD)

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Poly-2,5-dimercapto-1,3,4-thiadiazole (pDMCT) is a redox-active polymer consisting of heterocyclic monomer units connected by disulfide bonds. pDMCT has been used as a battery material, biocide, and corrosion inhibitor. Upon electrochemical reduction, the disulfide bonds in pDMCT break to form thiolate anions that readily coordinate with cations, providing lithium ion conductivity for battery applications and allowing for capture of heavy metal cations. In this work, our goal is to study the vapor-phase formation of thin films of pDMCT using oxidative molecular layer deposition (oMLD) for use as a protective coating in solid state lithium-ion batteries. We employ alternating vapor exposures of the 2,5-dimercapto-1,3,4-thiadiazole (DMCT) monomer and a molybdenum pentachloride (MoCl<sub>5</sub>) chemical oxidant to perform oMLD growth in a custom viscous-flow reactor at 150 °C and ~1 Torr. We employ *in situ* quartz crystal microbalance (QCM) studies during growth to understand the film growth chemistry, as well as *ex situ* spectroscopic and electrochemical characterization to confirm formation of pDMCT. QCM studies and *ex situ* thickness measurements indicate controlled linear growth. The controlled growth of ultrathin films of pDMCT shows promise for the application of this chemistry as a protective coating for lithium-ion battery applications and for passive uptake of heavy metal ions. More broadly, these studies establish that oMLD can be used to create polymers connected by disulfide linkages, opening a new class of polymers accessible by oMLD synthesis.

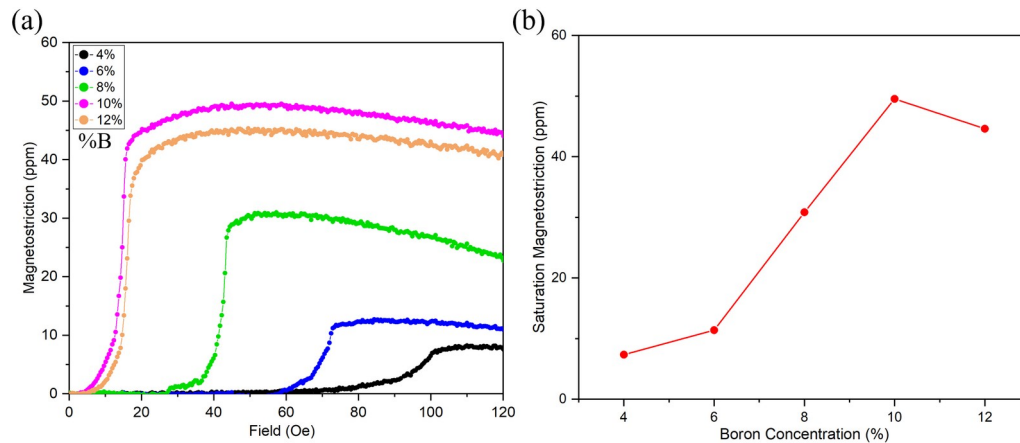
## FeGaB alloys for magnetoelastic coupling at microwave frequencies

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Due to their short wavelengths and long propagation distances, surface acoustic waves are promising candidates for miniaturizing microwave devices such as isolators and circulators, which rely on large nonreciprocity and low propagation loss facilitated by low damping and large magnetoelastic coupling.  $\text{Fe}_{80}\text{Ga}_{20}$  is a popular choice for the magnetoelastic layer due to its high magnetoelastic response in the disordered A2 phase. In this work, we stabilized this disordered phase by boron doping. Subsequently we studied the influence of boron concentration on magnetoelastic coupling and temperature dependent damping.  $(\text{Fe}_{80}\text{Ga}_{20})_{1-x}\text{B}_x$  films with boron content from 2% to 16% were synthesized by co-sputtering. Structural characterization by x-ray diffraction reveals a reduction in the Fe (100) Bragg peak when increasing B from 2% to 8%, and a vanishing of the peak at 10% B, indicating gradually stabilized disorder. The magnetostriction was measured by cantilever deflection in a rotating magnetic field, as shown in Fig. 1(a). Fig. 1(b) shows that the saturation magnetostriction increases with B concentration until reaching a peak at 10% B. Boron doping effect on the magnetic damping was studied by field modulation ferromagnetic resonance (FMR). The damping decreases with B concentration with the lowest damping of  $5.8 \times 10^{-3}$  achieved at 12% B. Additionally, temperature dependent FMR was performed on 6% and 10% B doped  $\text{Fe}_{80}\text{Ga}_{20}$  to analyze the damping as a function of temperature. Both samples show a damping peak upon cooling down to 50 K. The damping peak for 10% B sample represents 61.38% increase relative to room temperature damping, while the increase in the 6% sample is mitigated to 26.67%. This suggests that the damping peak at around 50 K may have a large contribution from magnetoelastic coupling.



**Figure 1.** (a) Magnetostriction as a function of field for  $\text{Fe}_{80}\text{Ga}_{20}$  with different B doping; (b) Saturation magnetostriction as a function of B concentration.

## **Examining UV-induced functional group formation on 2D nanomaterials for patterned ALD**

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In our previous work, we employed a focused electron beam (e-beam) within an environmental scanning electron microscope (eSEM) to break down water vapor, allowing for the precise creation of hydroxylated patterns on highly oriented pyrolytic graphite (HOPG) surfaces. These patterns facilitated subsequent atomic layer deposition (ALD) in patterned areas, offering exceptional control over spatial resolution (exceeding 42 nm), and surface selectivity (ranging from 69.9% to 99.7%). However, despite its precision, the use of an e-beam is time-consuming and lacks industrial scalability due to the limited functionalization area on the substrate. In this study, we aim to explore the feasibility of patterning large areas of 2D material using UV irradiation in the presence of water vapor. Specifically, we seek to understand the impact of the direct UV ionization of water vs. ionization of water from secondary emitted electrons. Our experimental setup utilizes a custom-built hot-walled viscous-flow ALD reactor equipped with a vacuum ultraviolet (VUV) source unit with a peak emitted wavelength of 160 nm. This UV source incorporates a compact deuterium lamp with a MgF<sub>2</sub> window and UV photons are focused onto the sample using a convex MgF<sub>2</sub> lens to enhance photon flux density. We posit that the UV irradiation induces the formation of hydroxyl defects on the MoS<sub>2</sub> and HOPG surface. To verify this, we employ spectroscopy including Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy (RS), assessing the formation of functional groups on 2D material surfaces. We also examine the impact of UV-functionalization on ALD nucleation and growth onto 2D materials. Our studies inform the applicability of this method for patterned thin-film deposition for semiconductor manufacturing.

## **Oxidative molecular layer deposition of polythiourea: unraveling its electrochemical and chemical characteristics**

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Polythiourea exhibits versatile applications, extending beyond fuel cells and batteries to include its potential use in sensors. The polymer's ion-conductive properties, attributed to the unique characteristics of its thiourea groups, make it a candidate for sensor applications where ion detection is crucial. By leveraging its ability to interact with ions, polythiourea could enhance the sensitivity and performance of various sensors. Whether incorporated into methanol fuel cells, batteries, or sensor devices, the chemistry results revolve around understanding the specific interactions between poly thiourea and relevant ions, ensuring stability under diverse operational conditions, and optimizing the functionality of each application. Researchers exploring poly thiourea in these fields aim to unlock its multifaceted potential for improving electrochemical performance and sensing capabilities. This polymer can be synthesized through different techniques like radical polymerization, ionic polymerization, polycondensation, and oxidative molecular deposition which for the first time has been done in this research. The oxidative molecular layer deposition (OMLD) technique for the synthesis of polymers, such as poly thiourea, shows many benefits such as controlled polymerization, uniform film formation, mild reaction conditions, and reduced byproduct formation as a result this method has gained popularity in certain applications. The presentation will be about experimental techniques, the mechanism of polymerization, and characterization techniques to investigate more about the chemical properties of the deposited thin film. In addition, the poster will present the potential applications of the synthesized poly thiourea, focusing on its use in different fields of study like as, sensors, and electrochemical devices.

Loscutoff, Paul W., Han-Bo-Ram Lee, and Stacey F. Bent. "Deposition of ultrathin polythiourea films by molecular layer deposition." *Chemistry of Materials* 22.19 (2010): 5563-5569.

Li, Ai-Fang, et al. "Anion complexation and sensing using modified urea and thiourea-based receptors." *Chemical Society Reviews* 39.10 (2010): 3729-3745.

Wyatt, Quinton K., et al. "Mechanistic Insights into Oxidative Molecular Layer Deposition of Conjugated Polymers." *Chemistry of Materials* 35.1 (2022): 154

## Characterization of oxygen species on Rh-based model catalysts

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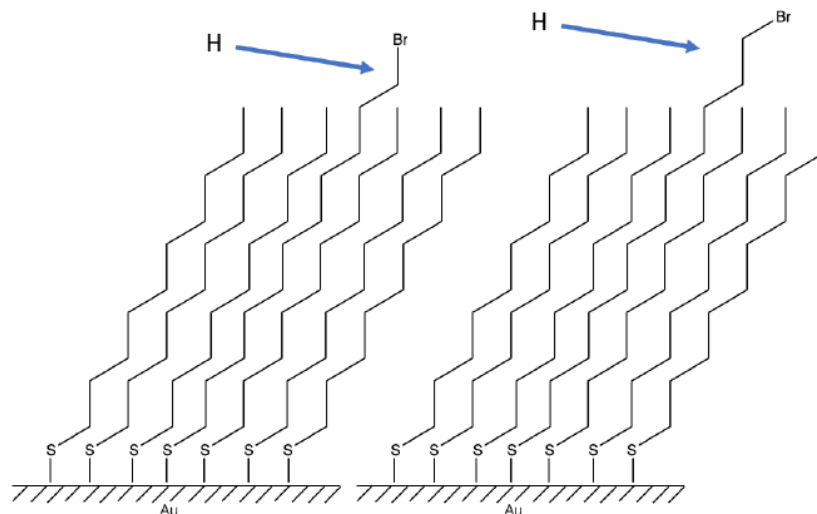
The studies presented investigate the influence that surface and defect geometry have on the kinetics and reactivity of oxygen on various Rh-based model catalysts. The experiments herein focus on gaining structural information about the oxygen species present on the surface under various oxidative conditions utilizing scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). These techniques are used in unison with temperature programmed desorption (TPD) and Meitner-auger electron spectroscopy (MAES) to identify optimal conditions for further study. The most optimal surfaces will then be prepared for velocity and ion map imaging experiments conducted at Georg-August University in *Göttingen, Germany*.

## Even-odd directed dehalogenation of bromine terminated alkane sams via atomic hydrogen

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Self-assembled monolayers (SAMs) present a unique system for the chemical control and passivation of surfaces. In their most dense phase, referred to as highly close-packed (HCP) or “standing-up”, SAMs of pure composition present a rigid and regular surface. By creating a SAM of mixed composition wherein a minority of the composition is several atoms longer than the majority, these extended terminations protrude from the monolayer at angles defined by the parity of the chain length. Herein, mixed SAMs of 95% decanethiol (10c) and 5% 11-bromoundecanethiol (11-Br) or 12-bromododecanethiol (12-Br) are formed on Au(111). The protrusions of 11-Br and 12-Br from the 10c SAM are imaged *via* ultra-high vacuum scanning tunneling microscopy (STM). The SAMs are exposed to atomic hydrogen formed in a thermal gas cracker oriented 50° from the surface normal with a flux of approximately  $10^{12}$  atoms per square centimeter per second, and dehalogenation rates are directly monitored by using the surface coverage observed in STM images. STM data are supported by X-ray photoelectron spectra of pure brominated films subject to the same hydrogen doses. Insights into the reaction mechanisms of debromination are revealed.



**Figure 1.** A schematic depicting the two experimental systems. Samples contain isolated and small clusters of brominated thiols contained within the decanethiol matrix. The hydrogen atoms approach the films from the same angle relative to the surface normal meaning the direction of the terminal bond controls the collisional angle.

## Sticking probabilities of carbon dioxide (CO<sub>2</sub>) isotopologues

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Gas absorption on interstellar ices are important processes in many astrophysical events. Specifically, one of the most common adsorption events involve carbon dioxide (CO<sub>2</sub>) and isotopes adsorption, thus, it is significant to understand how the mass changes affect molecular sticking. Past research has shown that isotopes of methane, CH<sub>4</sub> and CD<sub>4</sub>, affected the sticking probabilities on ice surfaces made of the same compound [1]. This study investigates the different sticking behaviors between CO<sub>2</sub> isotopes of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> at various velocities and energies using *in situ* reflection absorption infrared spectroscopy (RAIRS) to monitor on surface growth and King and Wells mass spectrometry techniques to determining sticking probability.

- [1] M. R. Brann, X. Ma, and S. J. Sibener, *J. Phys. Chem. C*, 127, 27, 13286-13294 (2023)  
DOI: [10.1021/acs.jpcc.3c02386](https://doi.org/10.1021/acs.jpcc.3c02386)

## Using Single-layered COFs to Stabilize Single-atom Catalysts on Model Surfaces

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Single-atom catalysts (SACs) combine the advantages of homogeneous and heterogeneous catalysts by limiting the reaction sites to isolated single metal atoms with well-defined chemical properties. A metal-ligand coordination method to stabilize SACs has been developed by our group, in which 1,10-phenanthroline-5,6-dione (PDO) or another ligand is used to coordinate with single metal atoms, including Pt, Fe, Pd, Cr, and other metals. To further improve the stability of SACs and increase the metal loading, we have synthesized single-layered covalent organic frameworks (sCOFs) on model surfaces under ultra-high vacuum (UHV) conditions or under ambient conditions. These networks with high porosity and stability were used to confine single Pt atoms coordinated with ligands into sCOF pores. Under UHV conditions, the successful formation of sCOF with hexagonal pores on the Au(111) surface was achieved by surface-mediated Ullmann radical coupling of 1,3,5-tris-(4-bromophenyl)benzene (TBB). Further sequential deposition of PDO ligand and Pt on the TBB-sCOF surface allowed the formation of single-site Pt catalysts by coordination interaction. The scanning tunneling microscopy (STM) images show the confinement of PDO in the sCOF pores, while X-ray photoelectron spectroscopy (XPS) has proven the existence of oxidation state of Pt, which is an indication of the single atom character. Under ambient conditions, an imine-linked sCOF was formed on the highly oriented pyrolytic graphite (HOPG) surface by a solid-vapor interface mechanism which allows the formation of high quality sCOF with long-range order. STM characterization has shown that sCOF networks with hexagonal symmetry and few defects were formed on the HOPG surface. This sCOF is facile to prepare and can be stored stably under ambient conditions for several weeks. These systems which combine the COF and metal-ligand coordination strategy to stabilize SACs offer the possibility to achieve higher stability and greater loading in SACs.



## Redox-Active Spin Traps for the In-Situ Investigation of Radical Species at Electrocatalytic Interfaces

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The oxygen reduction reaction (ORR) is a kinetically slow reaction involved in a variety of electrochemical energy conversion and storage devices such as fuel cells and metal-air batteries. However, despite decades of intensive study, the mechanism of ORR is still poorly understood for many industrially relevant materials for this complex, multistep reaction. Computational studies generally suggest that the stabilization of various adsorbed radical intermediates such as hydroxyl (OH<sup>•</sup>), hydroperoxyl (OOH<sup>•</sup>), or oxygen atoms (O<sup>•</sup>) is key to enhancing the kinetics of ORR.<sup>1</sup> Despite a clear computational picture of the importance of these species, their direct experimental detection and quantification (particularly under reaction conditions) remain rare in the literature.

In my work, we have used redox-active spin traps as a method to identify and quantify these reactive oxygen intermediates *in situ*.<sup>2,3,4</sup> Typically, spin traps molecules to trap and stabilize short-lived radical species for detection *ex situ* using electron spin resonance (ESR). However, the use of a redox active spin trap allows for the application of electrochemical methods to investigate these processes. Within electrochemistry, scanning electrochemical microscopy (SECM) is an ideal technique because it allows for the sensitive local detection and quantification of dilute quantities of species in real-time. This allows for the design of *in situ* experiments that can measure and quantify with high spatial and temporal resolution.

We have applied this technique over materials such as boron-doped diamond that are well known to produce significant quantities of hydroxyl radicals at anodic potentials,<sup>2</sup> as well as in the corrosion of lead-acid battery cathodes<sup>3</sup> and by the oxygen reduction reaction at Fe-N-C electrocatalysts.<sup>4</sup> Currently, ongoing work is being done to expand our methodologies to determine the thermodynamics and kinetics of adsorbed radical species involved in the oxygen reduction reaction.

[1] J. Phys. Chem. B 2004, 108, 46, 17886–17892

[2] J. Am. Chem. Soc. 2022, 144, 41, 18896–18907

[3] Chem. Sci., 2023, 14, 12292-12298

[4] Chem. Sci., 2024, 15, 10036-10045

## **Growth, structure, and kinetics of triple-conducting vertically aligned nanocomposites**

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This research focuses on the correlation between the processing conditions and the structure of vertically aligned nanocomposite (VAN) thin films, as well as the proton transport and surface exchange kinetics, targeting protonic ceramic electrochemical cells (PCECs). The VAN films are composed of a proton conductor ( $\text{BaZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-6}$ , BZY) as one phase and a mixed p-type/oxide-ion conductor ( $\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2-6}$ , PCO) as the other. With these two phases, BZY-PCO VANs can task-share the proton incorporation and redox ORR/OER processes needed to potentially achieve rapid proton surface exchange at the solid-gas interface and transport along the solid-solid heterointerfaces.

These VAN thin films were deposited on MgO (100) substrates with pulsed laser deposition (PLD). Due to the immiscible crystal structures of perovskite BZY and fluorite PCO and the small lattice mismatch between MgO and BZY, this combination can likely result in vertically aligned phase-separated nanostructures. To optimize the PLD recipe to obtain high-quality VAN thin films, various PLD conditions were tested, including different temperatures, repetition rates, and oxygen processing pressures. The films were characterized by a variety of techniques. The crystallinity and phases were confirmed by grazing-incidence X-ray diffraction (GI-XRD). Structural analysis and elemental mapping were analyzed through scanning/transmission electron microscopy (S/TEM), with energy-dispersive X-ray spectroscopy (EDS), and electron energy-loss spectroscopy (EELS). Additional characterization of strain and structural order as a function of depth was achieved using angle-dependent synchrotron X-ray pair distribution function (PDF) analysis. Furthermore, electrical conductivity relaxation (ECR) and optical transmission relaxation (OTR) measurements were used to study the proton surface exchange kinetics.

This study sheds light on the impact of processing conditions on mesostructure ordering within VANs as well as the complex chemistry at heterointerfaces. Moreover, it delves into the kinetics of proton surface exchange, providing a pathway to task-sharing triple-conducting VANs.

## Proton surface exchange coefficients of perovskite thin films for efficient steam electrodes in protonic ceramic electrolysis cells

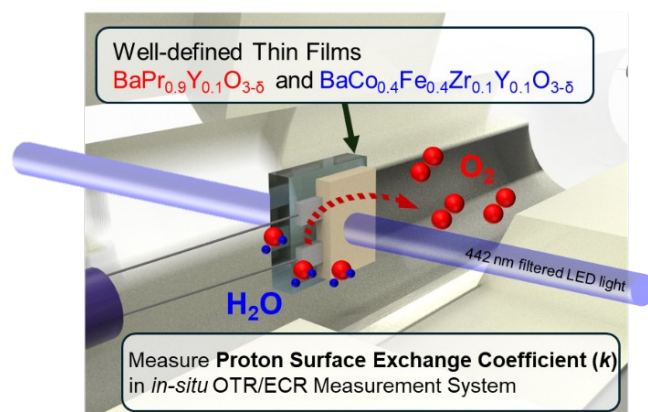
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Green hydrogen production technology has been advancing with high temperature steam electrolysis, which takes advantage of reduced electrical energy requirements by compensating with heat supply. Protonic ceramic electrolysis cells (PCECs) are a promising green hydrogen production technology because they have benefits of long-term stability and direct production of dry hydrogen gas at intermediate temperatures around 400-600 °C compared to solid oxide electrolysis cells, operating above 700 °C. However, sluggish steam-splitting kinetics and durability challenges at the oxygen electrode limit the current performance of PCECs. In this work, we evaluated the proton surface exchange coefficients ( $k$ ) of perovskite thin film oxygen electrode compositions ( $\text{BaPr}_{0.9}\text{Y}_{0.1}\text{O}_{3-d}$ , BPY vs.  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-d}$ , BCFZY) with a well-defined geometry through simultaneous optical transmission relaxation and electrical conductivity relaxation measurements at  $\sim 400$  °C. The BPY thin films exhibit more stable and higher  $k$  values over time compared to those of BCFZY thin films. Compositional analyses before and after steam relaxations reveal new design recommendations for efficient and durable perovskite oxygen electrodes in PCECs. [1]



**Figure 1.** Schematic of *in-situ* OTR/ECR setup for steam relaxation measurements in modified optical furnace. Proton surface exchange coefficient ( $k$ ) is extracted from OTR/ECR curves upon switching steam (0 to 2.3 %pH<sub>2</sub>O) at a temperature of  $\sim 400$  °C.

[1] Jongmin Lee, Haley B. Buckner, and Nicola H. Perry, *J. Mater. Chem. A*, 2024, **12**, 15412-15429 [DOI: 10.1039/d3ta07534f]

## An automated platform for high-throughput surface interrogation studies on electrochemical energy storage materials

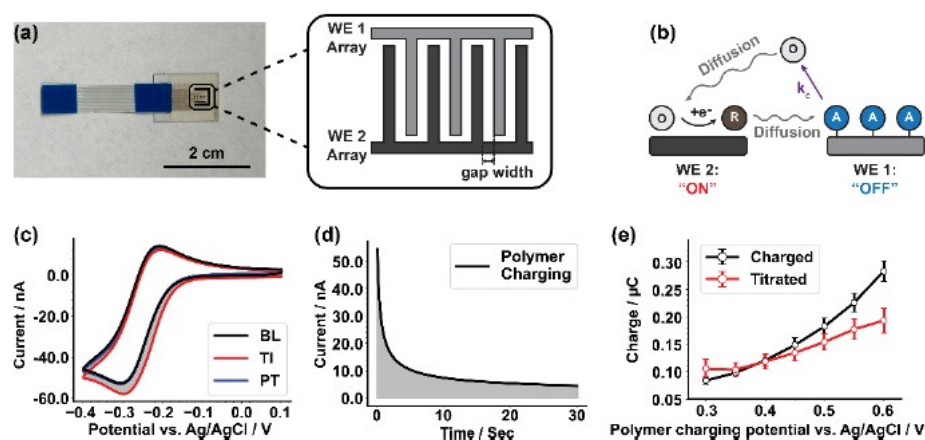
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Surface interrogation scanning electrochemical microscopy (SI-SECM) is a powerful electrochemical technique for the study of redox active surface species and thin-film materials with applications in catalysis, energy conversion, and energy storage.<sup>1</sup> However, its low-throughput and experimental difficulty prevents automated studies over a broad range of operational parameters. Here, we present a surface interrogation method based on microfabricated interdigitated electrode arrays (IDA) that enable high-throughput SI measurements. We used hardware and software developed by our group to control the IDA and commercial electrochemical instruments to perform SI measurements automatically.<sup>2,3</sup> We demonstrated the power of our new SI method by studying electrodeposited polypyrrole (PPy), a conductive polymer that has found use in energy storage applications. Here we performed SI measurements with different IDA geometries, charging potentials, voltametric scan rates, and two electrolyte concentrations. In total, we performed 504 automated measurements in less than 50 hours. The high-throughput, automated, and versatile nature of our platform will enable advanced studies of the redox behavior of thin-film and surface species across parameter spaces that would be otherwise intractably large to explore with other electrochemical techniques.



**Figure 1.** (a) A picture of IDA and its geometry (WE: working electrode). (b) Schematic of SI measurement with IDA. (c) Typical voltametric response (BL: baseline, TI: titration, PT: post-titration). (d) Typical PPy charging curve. (e) Comparison between interrogated charge and actual PPy charge at different charging potentials.

[1] Journal of the American Chemical Society **2008** 130 (50), 16985-16995, DOI: [10.1021/ja8050553](https://doi.org/10.1021/ja8050553)

[2] ACS Measurement Science Au **2023** 3 (1), 62-72, DOI: [10.1021/acsmesuresciau.2c00054](https://doi.org/10.1021/acsmesuresciau.2c00054)

[3] Analytical Chemistry **2023** 95 (11), 4840-4845, DOI: [10.1021/acs.analchem.2c04862](https://doi.org/10.1021/acs.analchem.2c04862)

## **Understanding the transitioning surface exchange behavior between pure proton conducting to triple conducting thin films for steam electrodes**

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Protonic ceramic cells (PCCs) in fuel and electrolysis modes are promising electrochemical devices for a clean energy economy. Compared to their solid oxide counterparts, PCCs run at lower temperatures, enabling improved stability and reduced costs. Oxide perovskite materials that are triple conductors of holes, oxygen vacancies and protons are some of the top candidates for the efficiency-limiting steam ( $\text{H}_2\text{O}_{(\text{gas})}$ ) electrode component. However, there is a lack of knowledge in understanding the mechanisms of the associated proton ( $\text{H}^+$ ) surface exchange reactions, especially regarding composition and defect chemistry. Theories have hypothesized that triple conductors such as Y-doped  $\text{BaFeO}_3$  and  $\text{BaPrO}_3$  are subject to a fundamentally different set of reactions than the traditional pure proton conductor, such as Y-doped  $\text{BaZrO}_3$ , used in electrolytes. This project investigates the proton surface exchange kinetics and oxidation state changes within the  $\text{Ba}(\text{Fe}, \text{Pr}, \text{Zr}, \text{Y})\text{O}_3$  thin film system. The speed of reactions is quantified with the proton surface exchange coefficient ( $k_{\text{H}^+}$ ), found upon steam introduction with optical transmission and electrical conduction relaxation methods (OTR/ECR). These leverage the relationship between defect concentration and optical absorption or electrical conductivity, respectively. The valency changes between dry and wet samples provide complementary evidence to OTR/ECR in elucidating hydrogen surface exchange reactions and are found through X-ray absorption near edge spectroscopy (XANES) of the Pr L3-edge and Fe, Zr, and Y K-edges. The findings of this work support the difference between the behavior of pure proton conductors and triple conductors, but also suggest additional complexity in comparing Fe- and Pr- based systems, as Fe-based systems show a different behavior from previously hypothesized reactions. The implication is that new reactions should be considered for different types of triple conductors which may require future experimental and computational work.

## Harnessing electrostatics for the conversion of biomass inside a microdroplet to generate value-added products (DROPLETS Project)

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Microdroplets provide a unique reaction environment that can be used to enhance the reaction rate dramatically, many orders of magnitude compared to the corresponding reaction in bulk. Microdroplets facilitate different chemistry to occur conveniently through the generation of various reactive species. We want to utilize these special characteristics of microdroplets to make use of lignin to generate value-added products, especially quinone-like frameworks. Lignin, a complex biopolymer derived from wood-pulp waste, is a perfect example of chemically diverse waste feedstock that can be upcycled using redox at microdroplets. It is one of the largest sources of natural aromatic compounds, making it an ideal material for oxygen functionalization. This will be pursued at bare microdroplets using some oxidizing agents to generate redox-active quinonoid systems for use in redox flow batteries (RFBs). These microdroplets are generated very easily using a water-oil biphasic system through sonication [1]. Lignin is mixed in 10% aq. HNO<sub>3</sub> solution and hexadecane (an inert alkane) is used as the oil phase to generate water microdroplets in oil through sonication [2]. Microdroplets serve as the special micro-reaction environment to break down the polymeric framework of lignin into smaller fragments. This procedure generates water-soluble smaller fragments of lignin which were extracted further and analyzed. Extensive analysis until now demonstrates that these molecules are capable of showing moderate to good redox activity and acid-base indicator-like properties, turning yellow to bright red once the pH is changed from acidic to basic. We are constantly putting our efforts into properly modifying the structure by changing the variables to obtain the perfect small molecule with proper redox activity and to make it useful to be utilized in Redox-Flow Batteries.



**Figure 1.** Schematic and visual representation of how lignin is transformed into other products through Emulsive microdroplets generated through sonication

[1] ACS Cent. Sci. **2022**, 8, 9, 1265–1271 <https://doi.org/10.1021/acscentsci.2c00694>

[2] Industrial Crops and Products **2021**, 170, 113757 <https://doi.org/10.1016/j.indcrop.2021.113757>

[3] Nat. Chem. **2021**, 13, 1118–1125 <https://doi.org/10.1038/s41557-021-00783-2>

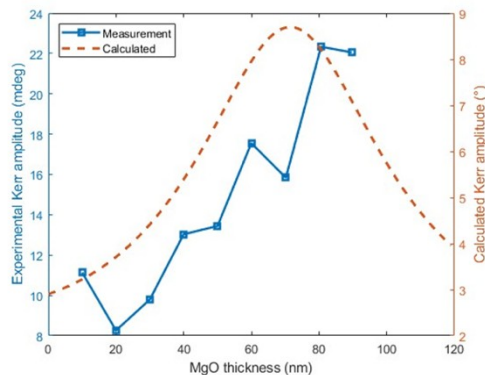
## Enhancing the magneto-optical Kerr effect in non-collinear antiferromagnets via a dielectric layer

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Non-collinear antiferromagnets, such as  $\text{Mn}_3\text{Sn}$  and  $\text{Mn}_3\text{Ge}$ , have unique magnetic properties, such as the anomalous Hall effect and the magneto-optical Kerr effect (MOKE) [1, 2], where their significant interactions with electric currents and light are determined by the orientation of magnetic octupole moments [3]. However, the lack of a net magnetization of the octupole moments poses challenges for magneto-optical observations. Here we demonstrate the enhancement of MOKE in  $\text{Mn}_3\text{Sn}$ , with specific thicknesses of a dielectric material, MgO, by creating constructive interference with the reflected light. We determined the complex refractive index by ellipsometry measurements, and performed subsequent numerical calculations to determine how the Kerr amplitude varies with different thicknesses of MgO [4]. The calculations show that the Kerr amplitude has a sinusoidal dependence on the MgO thickness and is maximized at the optimized thickness. Next, we measured the Kerr amplitude across a range of MgO layer thicknesses using a polar MOKE system. The measured data show a sinusoidal trend with a doubling of the Kerr amplitude at an optimized MgO thickness compared  $\text{Mn}_3\text{Sn}$  without MgO and agree qualitatively with our numerical calculations (Figure 1). This study will improve the detection of magnetic domains with high sensitivity and contrast, which is essential for exploring antiferromagnetic spintronics. This work was supported by the NSF through the Illinois MRSEC (DMR-1720633).



**Figure 1.** Measured Kerr amplitude as a function of MgO layer thickness (left y-axis), compared with the trend from numerical calculations (right y-axis).

- [1] Nakatsuji, S., Kiyohara, N. and Higo, T.. *Nature* **527**, 212–215 (2015).
- [2] Higo, T., Man, H., Gopman, D.B. *et al. Nat. Photon.* **12**, 73–78 (2018).
- [3] Chen, T., Tomita, T., Minami, S. *et al. Nat. Commun.* **12**, 572 (2021).
- [4] Kim, D., Oh, YW., Kim, J.U. *et al. Nat. Commun.* **11**, 5937 (2020).

## **In-situ characterization of Au capping on superconducting Nb(100)**

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Nb is the highest temperature elemental superconductor, however, its application in particle accelerators and quantum computers are limited by growth of surface native Nb oxides. Au capping layers have been shown to prevent deleterious Nb oxidation, however, Au adsorption, growth, and morphology on Nb has not been fully investigated. This work characterizes physical deposition and subsequent anneals of sub-monolayer to monolayer converges of Au on Nb(100) using Scanning Tunneling Microscopy, X-ray and UV Photoelectron Spectroscopy, and Auger Electron Spectroscopy.



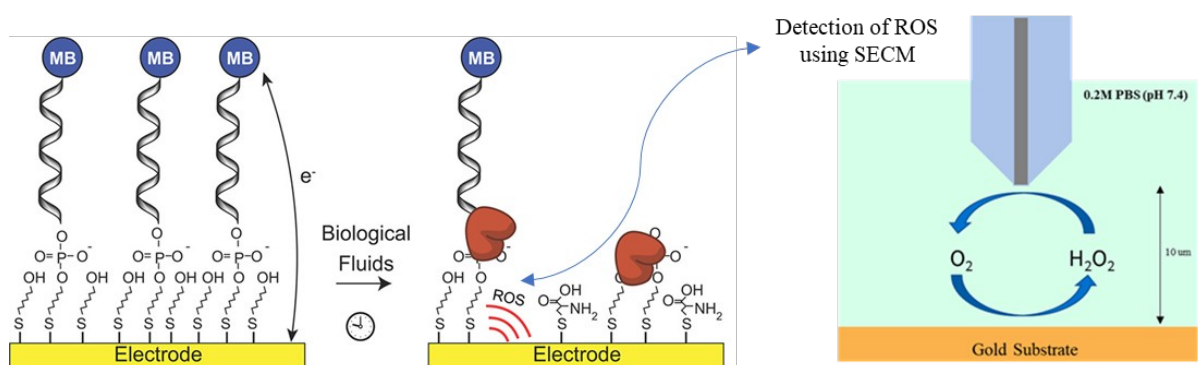
## In-situ detection of reactive oxygen species generated from aptamer-based electrochemical biosensors using SECM

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Nucleic acid-based electrochemical sensors (NBEs) technology is limited by the lability of the thiol-based monolayers employed for sensor fabrication. Voltage-induced desorption of monolayer elements is the main mechanism by which NBEs decay in phosphate-buffered saline. The applied voltage window during sensor interrogation is one of the most important driving forces for sensor signal decay. Monolayer loss is observed with time, even while operating in the stable potential window [1]. Production and accumulation of small amounts of reactive oxygen species (ROS) leads to the degradation of the monolayer. Real-time investigation of the stability of the monolayer under continuous electrochemical interrogation, therefore, becomes necessary. Here, we investigate the real-time production of ROS generated from different thiolate-based SAM coated gold substrates during the onset of ORR (oxygen Reduction Reaction) using in situ scanning electrochemical microscopy (SECM). SECM, in its generation-collection (SG/TC) mode, is capable of collecting the freshly generated ROS at the ultramicroelectrode tip biased at specific collecting potentials [2][3]. Apart from the detection of  $\text{H}_2\text{O}_2$ , the amount/flux of current response recorded at the tip for different SAM molecules under study also indicates the relative packing efficiency or surface coverage of these molecules under continuous voltammetric interrogation, further explaining their stability on the substrate.



**Figure 1.** Sensor decay due to ROS formation and its real-time detection via SECM in substrate generation tip collection (SG/TC) mode.

### References:

- [1] Analytical Chemistry, 2023, 95 (11), 4974-4983.
- [2] Chemical Science, 2023, 14 (43), 12292–12298.
- [3] Journal of the American Chemical Society, 2022, 144 (41), 18896–18907.

## **Influence of particle size on defect chemistry - transport - chemical strain coupling of mixed-conducting (Pr,Ce)O<sub>2-δ</sub> nanoparticles**

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Solid oxide fuel/electrolysis cells (SOFC/SOECs) draw great interest given their advantages including high efficiency, low emissions, and fuel flexibility. Nanostructuring of SOFC/SOEC electrodes enables improvement of the reaction kinetics and reduction of the operating temperature, because of their enlarged surface area, short diffusion lengths, and unique surface & interface chemistries. Chemo-mechanical coupling is an important metric for mixed ionic-electronic conductors (MIEC) that can undergo changes in oxygen stoichiometry with variations in the surrounding atmosphere/temperature. Chemical strains can cause cracking of monolithic parts during fabrication and delamination of electrodes from electrolytes in operation. However, the effect of nanostructuring on MIEC chemical strain, coupled with transport properties, has not yet been well investigated.

In this work, Pr<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2-δ</sub> (PCO20) was selected as a model system and prepared as nanoparticles by a surfactant-free, low temperature co-precipitation method. Prepared nanopowders were first *in-situ* sintered in the dilatometer at three different temperatures (600 °C, 725 °C, 850 °C) for microstructure evolution, giving 3 samples with various mean particle sizes (~20 – 50 nm). The chemical strain and electronic/ionic conductivity were then studied simultaneously on stable microstructures at 4 different isotherms (550 °C – 400 °C) with steps in pO<sub>2</sub> (1 atm – ~10<sup>-4</sup> atm O<sub>2</sub>). We found the chemical strains associated with losing oxygen monotonically decrease with the reduction of particle size. Correspondingly, samples with smaller particle size exhibit less pO<sub>2</sub> dependence of the conductivity, which implies a transition in the mixed ionic/electronic conduction behavior toward mainly ionic behavior as particle size decreases. The difference of chemical composition and valence states between particle surface and interior bulk were further investigated by S/TEM-EELS, to reveal the bulk vs. surface defect chemistry. Implications of the results and mechanism for size-dependent chemical strain and transport behavior will be further discussed.

## 3D Ruthenium block design strategy using area selective deposition combined with subsequent etching

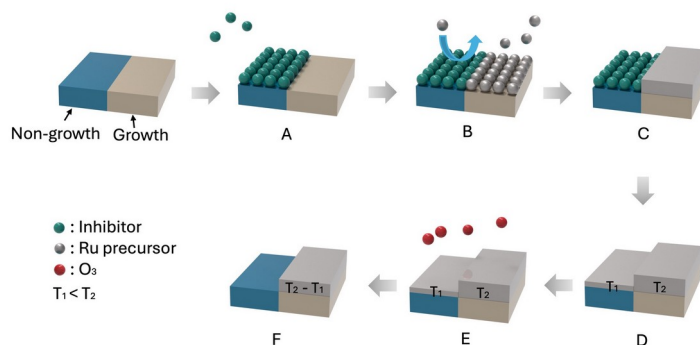
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Ruthenium (Ru) is a promising material in the microelectronic industry due to its excellent thermal and chemical stability, high conductivity, and high work function. As the size of electronic devices shrinks, the conversion of 2D structures to 3D architectures is required. Traditional 2D fabrication methods face many challenges in this transition. In this context, area selective deposition (ASD), a method based on atomic layer deposition (ALD), shows great potential for overcoming these challenges. By using an inhibitor, ASD can passivate a surface and control the thin film growth on desired areas. However, after certain subsequent ALD cycles, the inhibitor loses its blocking properties, leading to undesirable growth. Eliminating this undesirable growth is required. In this work, a novel Ru ALD process using tricarbonyl ( $\eta^4$ -2-methylene-1,3-propanediyl)Ruthenium(II) (TruST) and O<sub>2</sub> as co-reactant was investigated. A Si-source inhibitor was used to control the selective Ru growth. We observed complete blocking of Ru growth at 10 cycles with a selectivity  $\sim 96\%$ . However, the blocking effectiveness degraded over 30 cycles with selectivity dropping to  $\sim 48\%$  after 50 cycles of subsequent Ru ALD. To improve the selectivity, we used O<sub>3</sub> to etch the Ru film from the non-growth areas, restoring the original substrate surface and leaving a thicker film on the growth area as a 3D block.



**Figure 1:** Concept for fabricating 3D Ruthenium block using the ASD process and O<sub>3</sub> treatment. (A → C) The inhibitor (cyan balls) passivates the non-growth area (NGA), allowing selective Ru thin growth on the growth area. (D) After several cycles, undesired Ru growth occurs on the NGA, resulting in a thickness T<sub>1</sub>. (E, F) The samples are then treated with O<sub>3</sub> to eliminate the undesired Ru/ NGA, effectively removing the T<sub>1</sub> thickness.

## **Enhancing interfacial capacitance using anionic amphiphiles in ionic liquid electrolyte blends**

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The acceleration of climate change due to carbon emissions has generated an imminent need to transition towards renewable energy sources. However, the intermittent nature of renewable sources like wind or solar energy necessitates breakthroughs in energy storage devices that can rapidly charge and discharge. This demand creates a new role for high power density supercapacitors. While supercapacitors can quickly discharge electricity, they are limited by low energy densities. This limitation in energy density has generated research interest into charge storage mechanisms at interfaces and new types of supercapacitor electrolytes. An ideal supercapacitor electrolyte has a wide electrochemical stability window and high capacitance to maximize the energy density. Ionic liquids (ILs) show potential for this role with their wide electrochemical stability windows, nonflammability, and nonvolatility. Problematically, strong ion correlations present in ILs result in low capacitances. I will discuss our work aimed at tuning ionic correlations in binary IL blends to provide pathways towards higher energy density capacitive interfaces. We show how the addition of surface-active amphiphilic anions weakens these correlations increasing the interfacial charge density and capacitance of these IL blends. Notably, we find that mixing surface-active amphiphilic anions with nonamphiphilic ILs doubles the capacitance at negative surfaces. We hypothesize that polarity-dictated anion-anion van der Waals interactions serve to weaken IL cation-anion interactions and ultimately drive molecular assembly at negative surfaces, increasing capacitance. I will also present our complementary investigations of non-amphiphilic binary IL mixtures and provide spectroscopic insight into bulk ion correlations within these systems. Our study ultimately paves the path towards fundamental investigations into the chemical nature of additives in ionic liquid blends to boost performance within next-generation supercapacitors.

## Elucidating the impact of interfacial anions on electrochemical reduction reactions

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The properties of the electric double layer (EDL) that form at electrode-electrolyte interfaces play a defining role in the rates and selectivity of electrochemical reactions. For example, electroreduction reactions are characterized by EDLs enriched with positively charged cations, and various studies have demonstrated that these interfacial cations can alter reactivity via multiple mechanisms including intermediate stabilization, modulation of the water network, and even proton donation. However, the impact of anions in electroreduction reactions is less explored, especially in concentration regimes where ionic correlations are expected to increase the presence of interfacial anions at negatively charged interfaces. To elucidate the role anions play at reductive interfaces, we explored two model electroreduction reactions: the hydrogen evolution reaction (HER) in aqueous solution and the carbon dioxide reduction reaction (CO<sub>2</sub>RR) in non-aqueous solution. Using voltammetry and potentiometry, we found that the identity of the anion had a significant impact on the kinetics and steady state performance of both reactions, especially at high salt concentrations. In particular, we identified the tetrafluoroborate (BF<sub>4</sub><sup>-</sup>) anion as being especially capable of enhancing reactivity by acting as a Lewis base to stabilize hydroxide, a byproduct in both reactions. Through <sup>11</sup>B and <sup>19</sup>F NMR, we show that during HER an equilibrium develops between BF<sub>4</sub><sup>-</sup> and a fully hydrolyzed tetrahydroxyborate (B(OH)<sub>4</sub><sup>-</sup>) anion. We propose that this exchange enhances reactivity by “trapping” hydroxide generated at the interface and transporting it away from the reaction environment. Even in an acetonitrile solution with only ~1000 ppm of water, partially hydrolyzed versions of BF<sub>4</sub><sup>-</sup> develop and likely contribute to improved CO<sub>2</sub>RR rates. Overall, this study provides fundamental insight into how anions can play an important role in modulating reactions at negatively charged interfaces.

## Probing metal nanocluster on graphene via scanning probe microscopy

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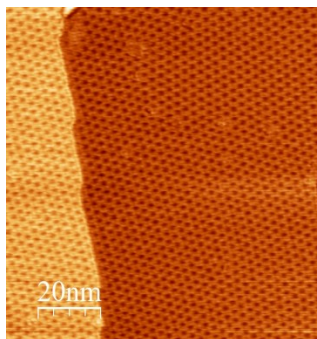
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Graphene, a two-dimensional (2D) carbon crystal with  $sp^2$  hybridization, has garnered significant attention due to its unique chemical, electrical, and mechanical properties, making it a versatile material for nanotechnology applications. This study investigates the formation of moiré patterns and their role in the nucleation of metal nanoclusters on a graphene monolayer synthesized on an Ir(111) single crystal. The graphene layer was prepared via pyrolytic cleavage of ethylene ( $C_2H_4$ ) on the Ir(111) surface.

Using scanning tunneling microscopy (STM), we observed a well-aligned, incommensurate moiré pattern characterized by alternating bright and dark regions due to the interaction between the graphene and Ir(111) lattices. The quality of the graphene was further verified through Low-Energy Electron Diffraction (LEED) analysis. These moiré patterns serve as nucleation sites for the growth of metal nanoclusters, where distinct regions—atop, face-centered cubic (fcc), and hexagonal close-packed (hcp)—are determined by the relative arrangement of carbon atoms to the underlying Ir surface.

Our ultra-high vacuum STM (UHV-STM) studies revealed that metal nanoclusters nucleate and grow differently depending on the metal type and deposition temperature. Specifically, palladium (Pd) forms triangular clusters, while platinum (Pt) forms spherical clusters. The shape and size of these nanoclusters are influenced by the cohesive energy of the metals and the nucleation temperature.

This research provides insights into the structural evolution of metal nanoclusters on graphene moiré patterns, which is critical for developing nanoscale materials and devices.



**Figure 1.** STM image of graphene on Ir(111) in a  $100 \times 100 \text{ nm}^2$  with moiré periodicity of  $2.5 \pm 0.2 \text{ nm}$ .

## Surface-catalyzed Ullmann coupling via activation of highly labile C-I for nanostructure synthesis

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On-surface synthesis is a widely used method to synthesize graphene nanostructures with desired functionalities. By selecting an organic molecule with a suitable symmetry, backbone, metalation, and functional groups as a building block graphene nanoarchitectures with nanoscale structural precision can be realized by a bottom-up synthetic method. It is important to study the on-surface reactions that allow us to synthesize 2D nanoarchitectures with sub-nanoscale spatial resolution to identify their local heterogeneities. Here, we have used Scanning tunneling microscopy (STM) to study surface-catalyzed aggressive Ullmann-coupling via activation of highly labile C-I and the synthesis of extended covalent organic frameworks through controlled on-surface reactions. Unexpectedly the C-I bonds do not dissociate upon deposition of the molecule on the Au(111) surface held at room temperature which is known to catalyze the C-I dissociation reaction under such conditions. Rather the molecules form self-assembled monolayers stabilized by halogen bonds on Au(111). Annealing this sample to 100° C or direct deposition of the molecules on a Au(111) substrate held at 100° C triggers partial C-I bond cleavage. Annealing to 200° C results in complete dehalogenation of the molecules and forming two types of COFs with triangle and cross-shaped connections with the dissociated Iodine atoms incorporated within the COF. The two kinds of COFs exhibit only short-range network order due to the irreversible nature of the C-C bond formation.

## **Reaction and Diffusion of Plasma-Injected Solvated Electrons in Non-Aqueous Solvents**

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Plasmas in contact with liquids are characterized by the generation of unique and powerful species. For example, plasma electrons can be injected into solution to produce solvated electrons, the most powerful chemical reducing species. Plasma-injected solvated electrons have been used directly or indirectly to carry out challenging chemistries such as destruction of organic contaminants and chemical transformation. However, many of the experiments to date have been limited to liquid water. Here, to expand the scope of plasma-liquid chemistry and its applications, we study plasmas in contact with non-aqueous solvents. A particular focus is the reaction and diffusion of solvated electrons that are generated at the plasma-liquid interface. First, we directly probe solvated electron in ethylene glycol by total-internal reflection absorption spectroscopy (TIRAS) supported by a simple reaction-diffusion model. Second, we indirectly characterize the reaction of solvated electrons by using chloroacetate as a model substrate. Experimental results are shown for water and ethylene glycol, with support using a film model [1] to describe the reaction and transport near the interface.

[1] S. M. Peyres, J. Wang, D. W. Hollyfield, N. H. Abuyazid, R. M. Sankaran, and N. B. Üner. *Under Review*. (2024)



## **X-ray Photoelectron Spectroscopy Data Fitting Using A Genetic Algorithm**

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The ever-growing problem in modern science is that data is being collected at a rate faster than analysis can be performed by characterization experts. The analysis that is done for many recently published x-ray photoelectron spectroscopy (XPS) data, is often incorrect/irreproducible and leads to a cycle of incorrect fits in this spectroscopy data. In this work, a genetic algorithm (GA) is being constructed to potentially minimize this human error. This GA code known as XPS Neo, is based on the Neo package which exists for EXAFS (EXAFS Neo) and Nanoindentation (Nano Neo) data. GAs are based on biological methods and depend on parameters such as populations size, number of generations, genes, crossover, and mutation. The GA takes in a certain population size and constructs individual vectors each with their own unique genes i.e the fitting parameters we are trying to optimize. It then performs crossover and mutation to these individual vectors to progress toward a lower global minimum. The difficulties in making this work for XPS data arise from complicated backgrounds due to many effects such as plasmon loss, Auger peaks, and satellite peaks. XPS data can also have many peaks that are difficult to distinguish from one another. Currently, the algorithm is only able to fit simplistic XPS spectra such C, O, N, and Si and is being worked on with the hopes of it becoming applicable for more difficult data. The goal is to make the algorithm applicable to all XPS data, with a greater focus given to the actinides, specifically for the use of fitting plutonium data as analysis of this spectra is highly sought after and difficult to fit. Through proper use of an informed GA, and collaboration with the XPS database website XPSOasis.org, theoretically correct fitting of this data is hoped to be achieved.







