Light Sources Enabled Science Mini-Symposium
Room 121 - Session LS-MoM

Light Sources Enabled Science Mini-Symposium

Moderators: Slavomir Nemsak, Advanced Light Source, Lawrence Berkeley National Laboratory, **Jessica McChesney**, Argonne National Laboratory

8:15am LS-MoM-1 Microsecond Dynamics of Surface Reactions Studied by the Time-resolved Ambient Pressure XPS with Chemical Perturbations, *C. Eads, W. Wang,* Max IV Laboratory, Sweden*; U. Kust, J. Prumbs,* Lund University, Sweden*; R. Temperton,* max iv Laboratory, Sweden*; M. Scardamaglia,* max iv laboratory, Sweden*; J. Knudsen,* Lund University, Sweden*; Andrey Shavorskiy,* Max IV Laboratory, Sweden **INVITED**
Recently,a new time-resolved Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) method based on chemical perturbations has been developed for studying dynamic processes with microsecond time resolution. The method uses the rapid change in the gas pressure/composition as a perturbation that drives the system away from equilibrium [1,2]. In the experiment, a sharp and strong gradient in chemical potential is created by modulating the gas composition over the catalyst via a fast valve. Such gas pulse has internal pressure in the mbar range and a rising edge of a few hundred microseconds. A time-sensitive delayline detector is synchronized with the valve operation to measure X-ray photoemission spectra with nano- to microsecond time resolution. We will present several experiments characterizing the setup's performance, including the CO oxidation reaction over Pt (111) to demonstrate the capability of the setup to correlate the gas phase composition with that of the surface during the transient supply of CO gas into an O2 stream [3]. These experiments demonstrate that under CO pressure modulation conditions, the system remains active (i.e. producing CO2) at temperatures below the CO lift-off temperature under the flow conditions. We will also demonstrate that little chemisorbed oxygen is observed during the active phase of the catalytic cycle when the Pt(111) surface is saturated with the oxide. This points out a much higher activity of the O_chemisorbed towards CO oxidation than O_oxide, resolving the ongoing debate about the role of the Platnum surface oxide in the reaction.

[1] J. Knudsen *et al. Nat Commun* **12**, 6117 (2021). doi:10.1038/s41467-021-26372-y

[2] A. Shavorskiy et al. *ACS APPLIED MATERIALS & INTERFACES* **13**, 47629 (2021). doi: 10.1021/acsami.1c13590

[3] C. Eads et al. *in preparation*

8:45am LS-MoM-3 HAXPES at PETRA III and IV: Electronic Structure, Operando Devices and In-situ Catalysis, *Christoph Schlueter,* Desy, Deutsches Elektronen-Synchrotron, Germany
The P22 beamline at PETRA III is a cutting-edge facility dedicated to hard X-ray photoelectron spectroscopy (HAXPES) techniques, featuring four specialized experimental end stations for high-resolution studies of electronic and chemical structures in various complex materials, device-like structures, and catalytic interfaces.

1. HAXPES Hemisphere: Known as the "workhorse" instrument, this setup offers extensive opportunities for operando device characterization, depth profiling, and chemical analysis.
1. POLARIS (Ambient Pressure XPS System): This system is tailored for investigating the catalytic properties of surfaces under industrially relevant conditions, making it crucial for practical catalysis research.
1. HarMoMic (Hard X-ray Momentum Microscope): This novel microscope explores electronic and atomic structures through wide-field imaging of band dispersions and electron diffraction patterns.
1. HAXPEEM (Hard X-ray Photoemission Electron Microscopy): Dedicated to studying laterally resolved chemical and elemental structures.

These instruments are fully operational and used in close collaboration with external user groups, reflecting the wide range of scientific fields engaged by the P22 beamline community. The P22 beamline first received light in November 2017 and conducted its first user experiments in June 2018. Since then, it has contributed to over 100 publications.

In this contribution, I will briefly present the experimental capabilities of the P22 beamline, provide an overview of the most prominent scientific results, and present an outlook towards HAXPES at PETRA IV.

9:00am LS-MoM-4 Hard X-Ray Photoelectron Spectroscopy and Its Application to the Bonding and Electronic Structure of Metal Dihydrides, *Anna Regoutz,* University College London, UK
Metal hydrides hold significant promise in various hydrogen-related technologies, encompassing energy storage, hydrogen compression, and hydrogen sensing. Although metal hydrides appear simple compared to many other energy materials, understanding the electronic structure and chemical environment of hydrogen within them remains a key challenge. This work presents a new analytical pathway to explore these aspects in technologically relevant systems using Hard X-ray Photoelectron Spectroscopy (HAXPES) on thin films of two prototypical metal dihydrides: YH2−δ and TiH2−δ.[1,2] By taking advantage of the tunability of synchrotron radiation, a non-destructive depth profile of the chemical states is obtained using core-level spectra. Combining experimental valence band spectra collected at varying photon energies with theoretical insights from density functional theory (DFT) calculations, a description of the bonding nature and the role of d versus sp contributions to states near the Fermi energy are provided. Moreover, a reliable determination of the enthalpy of formation is proposed by using experimental values of the energy position of metal s band features close to the Fermi energy in the HAXPES valence band spectra.

[1] C. Kalha, L. E. Ratcliff, G. Colombi, C. Schlueter, B. Dam, A. Gloskovskii, T.-L. Lee, P. K. Thakur, P. Bhatt, Y. Zhu, J. Osterwalder, F. Offi, G. Panaccione, A. Regoutz, "Revealing the Bonding Nature and Electronic Structure of Early-Transition-Metal Dihydrides", PRX Energy, 3, 013003, 2024, https://doi.org/10.1103/PRXEnergy.3.013003.

[2] C. Kalha, N. K. Fernando, P. Bhatt, F. O. L. Johansson, A. Lindblad, H. Rensmo, L. Zendejas Medina, R. Lindblad, S. Siol, L. P. H. Jeurgens, C. Cancellieri, K. Rossnagel, K. Medjanik, G. Schönhense, M. Simon, A. X. Gray, S. Nemšák, P. Lömker, C. Schlueter, and A. Regoutz, "Hard X-ray Photoelectron Spectroscopy – A Snapshot of the State-of-the-Art in 2020", J. Phys. Condens. Matter, 33, 233001, 2021, https://doi.org/10.1088/1361-648X/abeacd.

9:15am LS-MoM-5 The Electric Double Layer at Ultra-Thin Film Electrodes and How to Experimentally Assess It, *Maximilian Jaugstetter,* LBNL*; L. Falling,* Technical University Munich, Germany*; S. Nemsak, M. Salmeron,* LBNL
Understanding the structure of the electric double layer (EDL) is fundamental for the development of improved heterogeneous catalysts, batteries, and membranes for the sustainable accumulation of key materials and, generally, any process that involves a solid-liquid interface.Due to their hidden nature, the difficulty of spectroscopic detection, and the difficulty of formulating holistic molecular dynamics simulations, knowledge of the properties of these interfaces is sparse and focuses on a few example systems.

In order to obtain a better understanding of the effects of solvated ions on the interfacial water structure, local pH, and reactant adsorption, we employ soft X-ray techniques to spectroscopically investigate the atomic composition of the first few nanometers behind an X-ray transmissive electrode. For these experiments, we utilize interface-sensitive techniques such as X-ray absorption spectroscopy/total electron yield (XAS/TEY) and X-ray photoelectron spectroscopy (XPS) in combination with nano-electrochemistry as well as nanofabrication of ultra-thin free-standing films of graphene and graphene-like 2D materials.

With these methods, we are able to demonstrate the huge implications of different electrolytes and electrode materials on the structure of the EDL as well as the contributions of individual species to its formation. A quantification of dissolved species at the interface by XPS allows us to directly relate their presence to EDL properties.

By understanding the dependence of these properties, we are one step closer to fine-tuning them to support favorable transition states in electrocatalysis or decrease inhomogeneous growth processes in energy storage.

10:30am **LS-MoM-10 In situ Synchrotron Characterization of Materials Synthesis and Electrochemical Interfaces**, *Katherine Harmon,* Stanford University; *F. Heremans, S. Hruszkewycz, M. Highland,* Argonne National Laboratory **INVITED**

Advanced X-ray characterization tools exploiting the high coherent flux of 4th generation synchrotrons (e.g., the upgraded Advanced Photon Source) and X-ray free electron lasers promise to revolutionize our understanding of material synthesis, catalysis, and many other physiochemical processes. I will present our recent work investigating the synthesis of silicon carbide, a quintessential "polytypic" material. SiC is a versatile wide bandgap semiconductor host of optically active point defects (color centers) that may be exploited for quantum sensing and communications. SiC has also been reported to occur in over 200 polytypes, with mixed polytype inclusions being common in nominally single-polytype materials. Color centers are extremely sensitive to such heteropolytypic inclusions. Yet, the thermodynamic and kinetic drivers of polytype transformations during growth remain speculative due to a lack of characterization tools able to probe the growth process in real time. We developed a hard X-ray compatible chemical vapor deposition (CVD) reactor for the characterization of silicon carbide (SiC) polytype transformations during synthesis. Preliminary *in situ* crystal truncation rod measurements obtained using our new reactor at the Advanced Photon Source (APS) demonstrate the sensitivity to different polytypes in SiC. Notably, these measurements were carried out prior to the APS upgrade (APS-U) and did not exploit the coherent flux of the beam, which was not sufficiently high at the photon energies required to penetrate the CVD reactor walls (E > 24 keV). The APS-U will provide a two order of magnitude increase in the coherent flux of the beam across the energy spectrum, enabling advanced coherent X-ray measurements, namely, X-ray photon correlation spectroscopy (XPCS), at the requisite X-ray photon energies for SiC synthesis characterization. I will outline the principles of XPCS and discuss the upcoming opportunities at the APS-U not only for characterizing and controlling polytype transformations in SiC but also more broadly for understanding material processing in cases requiring complex sample environments that were previously inaccessible.

11:00am **LS-MoM-12 Direct Imaging of Local Orbitals in Quantum Materials**, *Martin Sundermann,* Max Planck Institute for Chemical Physics of Solids, Germany; *H. Yavas,* PETRA III, Deutsches Electron Synchrotron, DESY, Germany; *P. Dolmantas, C. Chang,* Max Planck Institute for Chemical Physics of Solids, Germany; *H. Gretarsson,* PETRA III, Deutsches Elektron Synchrotron, DESY, Germany; *A. Komarek,* Max Planck Institute for Chemical Physics of Solids, Germany; *A. Severing,* Universität zu Köln, Germany; *M. Haverkort,* Universität Heidelberg, Germany; *L. Tjeng,* Max Planck Institute for Chemical Physics of Solids, Germany

The search for new quantum materials with novel properties is often focused on materials containing transition-metal, rare-earth and/or actinide elements. The presence of the atomic-like *d* or *f* orbitals provides a fruitful playground to generate novel phenomena. The intricate interplay of band formation with the local electron correlation and atomic multiplet effects leads to phases that are nearly iso-energetic, making materials' properties highly tunable by doping, temperature, pressure or magnetic field. Understanding the behavior of the *d* and *f* electrons is essential for designing and controlling novel quantum materials. Therefore, identifying the *d* or *f* orbitals that actively participate in the formation of the ground state is crucial. So far, these orbitals have mostly been deduced from optical, X-ray and neutron spectroscopies in which spectra must be analyzed using theory or modelling. This, however, is also a challenge by itself, since *ab-initio* calculations hit their limits due to the many-body nature of the problem.

Here we developed a new experimental method that circumvents the need for involved analysis and instead provides the information as measured. With this technique, we can make a direct image of the active orbital and determine what the atomic-like object looks like in the real solid. The method, X-Ray Raman spectroscopy or non-resonant inelastic X-ray scattering using an s-core level (s-NIXS), relies on high momentum transfer in the inelastic scattering process, which is necessary for dipole-forbidden terms to gain spectral weight. To demonstrate the strength of the technique, we imaged the (text-book example) ground-state x^2-y^2/$3x^2$-r^2 hole orbital of the Ni^{2+} ion in NiO single crystal [1] We will present the basic principles of s-NIXS and details of its experimental implementation. We will show how we can apply this technique to unveil the active orbitals in a wide range of quantum materials [2,3], including those that undergo complex metal-insulator transitions.

[1] H. Yavaş, M. Sundermann, K. Chen, A. Amorese, A. Severing, H. Gretarsson, M.W. Haverkort, L.H. Tjeng, **Nature Physics** 15, 559 (2019)

[2] B. Leedahl, M. Sundermann, A. Amorese, A. Severing, H. Gretarsson, L. Zhang, A.C. Komarek, A. Maignan, M.W. Haverkort, and L.H. Tjeng, **Nature Commun.** 10, 5447 (2019).

[3] A. Amorese, B. Leedahl, M. Sundermann, H. Gretarsson, Z. Hu, H.-J. Lin, C.T. Chen, M. Schmidt, H. Borrmann, Yu. Grin, A. Severing, M.W. Haverkort, and L.H. Tjeng, **Phys. Rev. X** 11, 011002 (2021).

11:15am **LS-MoM-13 Bismuth-Trimer Adlayer and Thin Film Growth on In- and Sb-Terminated InSb(111) Surfaces**, *Rohit Yadav, S. Huang, S. Ritter, R. Timm,* Lund University, Sweden

Bismuth-semiconductor interfaces are important from both fundamental and application point of view. For example, a monolayer of bismuth on compound semiconductors like SiC and GaAs is predicted to be a 2D topological insulator with a quantum spin hall phase.[1,2] Similarly, Bi-induced trimers on Si(111) have been reported for giant Rashba splitting.[3] Here, we investigate Bi incorporation on InSb(111)A and B surfaces due to their large spin-orbit coupling and the small lattice mismatch.[4] Furthermore, individual Bi-based compounds like InBi and $Sb_{1-x}Bi_x$ have been predicted to induce non-trivial topological states.[5,6] We are focusing on the initial deposition, from less than a monolayer up to a few monolayers of Bi.

We have employed scanning tunneling microscopy/spectroscopy (STM/S) and synchrotron-based angle-resolved photoemission spectroscopy (ARPES) and XPS to investigate surface topography, electronic properties, and chemical composition. STM topography of oxide-free InSb(111)A shows (2X2) reconstructions with In-trimers. Upon Bi incorporation, Bi mainly forms a homogeneous periodic hexagonal bilayer, highlighting the formation of large-scale Bi-induced (2X2) reconstruction, along with some areas of $(2\sqrt{3}X2\sqrt{3})$–R30° reconstruction. A bias-dependent STM study shows that the Bi-film is decorated with Bi-trimers. STS on these trimers show metallic character and discrete surface states in the InSb bandgap, indicating possible band engineering upon Bi incorporation. Discrete Bi-induced surface states are further confirmed by ARPES measurement. However, Bi-incorporation into InSb(111)B results in mixed surface topography of Bi-trimers and Bi-monomer structures. Bi 5d core-level XPS for both InSb(111)A and B reveals that Bi-incorporation results in mainly Bi-Sb bonding and minor metallic Bi-Bi bonds. Interestingly, the Bi-Sb layer thickness remains self-limiting in the case of Bi/InSb(111)B, when deposited at elevated temperature. Thus, the amount of Bi-Sb remains unchanged, regardless of the number of deposition cycles.

Here, we discuss Bi-induced electronic band engineering and the formation of several 2D structures on InSb. This research highlights the metallic behaviour of decorated Bi-trimers and self-limiting BiSb film thickness in InSb(111)A and B substrates, respectively, which is highly versatile from an application point of view

References:

[1] F. Reis et al., Science 357, 287–290 (2017)

[2] Y. Liu et al., ACS Nano 17, 5047−5058 (2023)

[3] I. Gierz et al., PRL 103, 046803 (2009)

[4] H .S. Inbar et al., arXiv:2302.00803 (2023)

[5] D. Hsieh et al., Nature 452, 970 (2008)

[6] H. Huang et al., Phys. Rev. B 90, 195105 (2014)

11:30am **LS-MoM-14 Innovative High Energy X-Ray Characterization of Interfaces for Quantum Application**, *Andrea Sartori, J. Drnec,* ESRF, France

Small layered junctions, integral to quantum applications, typically comprise thin films, often conductors or superconductors, separated by thin oxide layers. These junctions play critical roles in various quantum devices, including Josephson junctions, thermionic devices and parametric amplifiers. However, characterizing these structures poses significant challenges due to their small dimensions and complex compositions. Traditional techniques like cross-sectional SEM and TEM offer limited insights and may be destructive. While X-ray Reflectivity (XRR) provides valuable out-of-plane electron density profile information for these junctions, it lacks the in-plane spatial resolution required for detailed analysis. Here we introduce a novel approach utilizing High Energy XRR Tomography (HEXRR-Tomo). Unlike conventional XRR, HEXRR-Tomo enables spatial mapping of the entire surface, allowing for the potential reconstruction of a high-resolution 3D electron density map of the junction. This technique promises to offer easily accessible and non-destructive

insights into the thickness, density, and roughness of individual layers within the junction, thereby advancing our understanding of their structure and   properties.

In this contribution, we will present preliminary examples of the technique, demonstrating our ability to visualize the morphology and key features of various devices with specific applications. For instance, one example involves a thermoionic junction comprising complex layers of Si, SiO_2, Al, and V (Fig. 1), which is utilized as a cooling device for cryogenic temperatures. Another example features $NbAlAlO_xAlNb$ films and NbTiN structures on a Si wafer, which serve as Josephson junctions for quantum computing and as parametric amplifiers, respectively. Further analysis will provide information about the roughness and thickness of each individual layer.

Surface Science
Room 120 - Session SS+CA+LS-TuM

Electrochemical Transformations on Surfaces

Moderators: **Florencia C. Calaza**, Instituto de Desarrollo Tecnológico para la Industria Química, **Zhuanghe Ren**, University of Central Florida

8:00am **SS+CA+LS-TuM-1 Beyond Static Models: Chemical Dynamics in Energy Conversion Electrocatalysts**, *Beatriz Roldan Cuenya,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany   **INVITED**
Environmentally friendly technologies for green energy generation and storage in the form of chemical bonds are being urgently sought in order to minimize the future consequences of climate change. The latter includes developing more efficient and durable materials for green H_2 production from water splitting as well as for the re-utilization of CO_2 via its electrocatalytic reduction into value-added chemicals and fuels. Nonetheless, in order to tailor the performance of such energy conversion catalysts, fundamental insight must be gained on their evolving structure and surface composition under reaction conditions.

This talk will illustrate how morphologically and chemically well-defined pre-catalysts experience drastic modifications under operation. Examples for the electrocatalytic reduction of CO_2 as well as the oxygen evolution reaction in water splitting will be given. The model pre-catalysts studied range from size and shape-controlled nanoparticles (Co_3O_4, Fe/Co_3O_4, Fe/NiO, Cu_2O, ZnO/Cu_2O, Au/Cu_2O), thin films (NiO_x, $CoFe_2O_4$, Co_3O_4, Fe_3O_4) to single crystals (differently-oriented Cu surfaces). The need of a synergistic multi-technique *operando* microscopy, spectroscopy and diffraction approach will be evidenced in order to follow the active state formation of complex catalytic materials. Correlations between the dynamically evolving structure and composition of the catalysts and their activity, selectivity and durability will be featured.

8:30am **SS+CA+LS-TuM-3 Sulfur-Doped Carbon Support Boosts CO2RR Activity of Ag Electrocatalysts**, *Xingyi Deng,* D. Alfonso, T. Nguyen-Phan, D. Kauffman, National Energy Technology Laboratory
In this work, we show that the activity of Ag electrocatalysts for electrochemical CO_2 to CO conversion is improved when supported on sulfur-doped (S-doped) carbon materials. S-doped carbon support was created by treating the heavily sputtered, highly oriented pyrolytic graphite (HOPG) in H_2S at elevated temperatures, as confirmed by the S 2p X-ray photoelectron spectroscopy (XPS) peak. Scanning tunneling microscopy (STM) images indicated that Ag nanoparticles supported on S-doped HOPG had similar size distributions as those supported on sulfur-free (S-free) HOPG. While both catalysts reached > 90% CO Faradaic efficiency (FE_{CO}) at E = -1.3 V vs. the reversible hydrogen electrode (RHE) in the CO_2 reduction reaction (CO_2RR), Ag catalysts supported on S-doped HOPG demonstrated 70% higher CO turnover frequency (TOF_{CO} = 3.4 CO/atom$_{Ag}$/s) than those supported on S-free HOPG (TOF_{CO} = 2.0 CO/atom$_{Ag}$/s). Preliminary calculations based on density functional theory (DFT) indicated a more favorable energetic pathway of CO_2-to-CO at the C-S-Ag interface, tentatively consistent with experiments. These results hint at a new approach to design active and selective electrocatalysts for CO_2 conversion.

8:45am **SS+CA+LS-TuM-4 Non-Metal Cations for Enhancing CO₂ Electroreduction on Bismuth Electrode**, *Theodoros Panagiotakopoulos,* K. Shi, D. Le, X. Feng, University of Central Florida; T. Rahman, University of Central Florida
In exploring the effectiveness of non-metal cations in CO_2 electroreduction, we have carried out a comparative examination of the mechanisms for CO_2 electroreduction to formate (HCOO–) and CO on the Bi(111) electrode in the presence of cations, Na+ and NH_4^+, using grand canonical density functional theory. Our results reveal that the reduction of CO2 to formate is driven by the direct hydrogenation of aqueous CO_2 with a hydrogen atom adsorbed on the electrode (H*), i.e., $CO_2(aq) + H^* \rightarrow HCOO^-$. The activation barrier for this process is found to be small, less than 100 meV, in the presence of both cations. Furthermore, our results show that the adsorbed intermediate COOH* is formed via a proton shuttling process, i.e., H* moves from the Bi(111) electrode to a H_2O molecule and one of its H atoms is then transferred to a CO_2^*. The activation energy barrier for this step was determined to be 0.77 eV and 0.75 eV in the presence of Na+ and NH_4^+, respectively. CO is formed via the dissociation of COOH* species with an activation energy barrier of 0.62 eV and 0.01 eV in the presence of Na+ and NH_4^+, respectively. These findings lead to two important conclusions: 1) the non-metal cation NH_4^+ can be equally effective as the alkali metal cation Na+

in promoting the CO_2 electroreduction to formate; 2) NH_4^+ is actually more effective than Na+ in promoting the CO_2 electroreduction to CO on the Bi(111) electrode, in excellent agreement with experimental observations [1].

[1] K. Shi, D. Le, T. Panagiotakopoulos, T. S. Rahman, and X. Feng, Effect of Quaternary Ammonium Cations on CO_2 Electroreduction (Submitted, 2024).

9:00am **SS+CA+LS-TuM-5 AVS Russell and Sigurd Varian Awardee Talk/SSD Morton S. Traum Award Finalist Talk: How do Cations Promote CO₂ Reduction at the Electrode-Electrolyte Interface**, *Kaige Shi[1][2], D. Le, T. Panagiotakopoulos, T. Rahman, X. Feng,* University of Central Florida
Electrochemical CO2 reduction reaction (CO2RR) can enable a promising path towards sustainable fuel production and closing the carbon cycle. Despite the reports of numerous electrocatalysts, the mechanism of CO2RR at the electrode-electrolyte interface remains to be elucidated, particularly on the role of electrolyte cations in the reaction. While most studies of CO2RR focused on alkali metal cations, we investigate CO2RR using quaternary ammonium cations, which provide unique tunability in size, shape, and charge distribution to elucidate the cation effect. For the CO2RR on a Bi catalyst that produces both CO and formate, we find that the cations are essential for both products. Furthermore, we observe a significant impact of the cation identity and concentration on CO production but a minor one on formate production. Our computational studies reveal that cations are required to stabilize adsorbed *CO2 on Bi surface via electrostatic interaction, and the quaternary ammonium cations have a more profound effect on the CO2 adsorption characteristics and CO2RR activity than metal cations. The adsorbed *CO2 is an essential step for CO production, but not necessary for formate production due to the pathway with direct reaction of aqueous CO2 with surface *H species. Based on the understanding, we employ the substitute ammonium cations to enhance CO2 electrolysis in a gas-diffusion-electrode (GDE) flow cell, which achieves multi-fold improvement of the activity for CO2RR to CO on Bi and other metal catalysts, as compared to that using alkali metal cations. Our work elucidates the critical effect of cations on the CO2RR at the electrode-electrolyte interface and demonstrates a strategy to enhance electrocatalysis by optimizing electrolyte composition.This work is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences Catalysis Science program under Award Number DE-SC0024083.

9:15am **SS+CA+LS-TuM-6 Atomistic Simulations on the Triple-Phase Boundary in Proton-Exchange Membrane Fuel Cells**, *J. Jimenez, G. Soldano, E. Francesichini,* Facultad de Ciencias Quimicas UNC, Argentina; *Marcelo Mariscal,* Universidad Nacional de Cordoba, Argentina   **INVITED**
In this work, we use molecular dynamics simulations and electrochemical experiments on a Nafion/Pt/C system. We perform a systematic analysis, at an atomistic level, to evaluate the effect of several fundamental factors and their intercorrelation in the ECSA (electrochemical surface area) of the catalysts. Besides, we evaluate the diffusion and structuring processes of water at different system interfaces. Overall, this investigation allows us to rationalize how the catalyst utilization is affected, which is an important step in establishing the relationship between the environment and the effectiveness and durability of the PEMFC system. It is important to consider that when experimentally analyzing the changes originating from the different experimental parameters in the operation of a fuel cell, only the average effect of the catalyst, flow field and membrane as a whole can be measured, and it is not possible to separate the corresponding contributions, even less from a region as complex as the TPB. Thus, computational studies provide the appropriate tools for studying each of the parameters separately and in sufficient detail to understand the effects found experimentally.

Proton Exchange Membrane Fuel Cells (PEMFCs), are a well-developed technology aimed at providing cleaner and more sustainable energy solutions. They offer a promising alternative to traditional fossil fuel systems that produce harmful emissions. However, the success of these cells depends greatly on the Three-Phase Boundary (TPB), a critial region composed by the ionomer (liquid, usually Nafion), catalyst (solid, usually platinum) and fuel (H_2 gaseous) interact and is the most important region in a fuel cell, as it is where the electrochemical reaction occurs with the adsorption of the fuel (or oxygen) on the catalyst surface, electron transfer

---

[1] **AVS National Student Awardee**
[2] **SSD Morton S. Traum Award Finalist**

to form H^+ and subsequent conduction of the generated ions to the ionomer for transport across the membrane. This is because experimentally only a few very general parameters, such as temperature, humidity or fuel flow rate, can be modified, and each of these parameters affects all components of the fuel cell and not just the three-phase region so it is impossible to separate the contributions corresponding to the three-phase boundary from the effects occurring, for example, in the membrane or from the kinetic effects in catalysis. Therefore, understanding, characterizing, and optimizing the variety of factors that affect the TPB content in fuel cells provide excellent opportunities for performance enhancement.

9:45am **SS+CA+LS-TuM-8 Mechanism of Activity Decrease in Orr on Nitrogen-Doped Carbon Catalysts Based on Acid-Base Equilibrium**, *Kenji Hayashida, R. Shimizu,* Tsukuba University, Japan*; J. Nakamura, M. Isegawa,* Kyushu University, Japan*; K. Takeyasu,* Hokkaido University, Japan

Fuel cells, which use the energy carrier hydrogen directly as a fuel, are important devices for achieving carbon neutrality. However, current fuel cell catalysts use a large amount of platinum, therefore a fuel cell catalyst that can replace platinum in the future is essential. A plausible candidate is nitrogen-doped carbon catalysts, which are durable and abundantly available. However, their activity is very low in acidic media, a practical condition, and this is the biggest challenge to overcome. In this study, we focused on the acid-base equilibrium of pyridinic nitrogen (pyri-N), the active site of nitrogen-doped carbon-based catalysts, to elucidate the reaction mechanism and clarify the mechanism of reduced activity in acidic media. Using a model catalyst with pyri-N-containing molecules adsorbed on a carbon support, we observed the change in electronic state upon immersion in electrolyte and application of potential, and analyzed the kinetics of the activities. It was found that the pyri-N, which is the active site, becomes protonated and hydration-stabilized in the acidic electrolyte, resulting in a decrease in activity. In particular, kinetic analysis showed that the 2 or 2+2 electron pathway via H_2O_2 proceeds independently of the acid-base equilibrium. X-ray photoelectron spectroscopy revealed that the potential for the formation of pyri-NH, associated with oxygen adsorption, an important reaction intermediate, is 0.4 V lower in acidic than in basic conditions. This is due to the formation of pyri-NH^+, in which pyri-N is protonated by acid-base equilibrium and its stabilization by hydration lowers the pyri-NH formation potential, resulting in lower activity in acidic conditions. Therefore, to improve catalytic activity in acidic conditions, it is important to increase the redox potential of this pyri-NH formation. A possible guideline is to decrease the pK_a and impart hydrophobicity.

11:00am **SS+CA+LS-TuM-13 Particle Size Effect of Ru Nanocatalyst for Nitrate Electroreduction**, *Zhen Meng, K. Shi, Z. Ren, X. Feng,* University of Central Florida

Electrochemical nitrate reduction reaction (NO_3RR) shows great promise for the recycling of nitrate from wastewater sources for the denitrification of wastewater and sustainable NH_3 production. Among various catalytic materials, Ru shows a high activity and selectivity for the NO_3RR to NH_3, while the effect of Ru atomic structure and active sites on the NO_3RR activity and selectivity remains ambiguous. Here, we prepare size-controlled Ru nanoparticles ranging from 2.2 to 7.1 nm and investigate the dependence of the NO_3RR on the Ru particle size. The activity (current density) decreases along with the increase of Ru particle size, mainly due to the more Ru surface area for the smaller particles, given the same Ru loading. In contrast, the specific (Ru-surface-area-normalized) activity for the NO_3RR exhibits a volcano-shaped dependence on the particle size, with 4.9-nm Ru nanoparticles showing the highest activity, which should reflect their intrinsic activity and active sites. On the other hand, the specific activity for the competing hydrogen evolution reaction (HER) increases with the particle size, so that an optimal selectivity for NO_3RR to NH_3 is also reached on the 4.9-nm Ru nanoparticles. Looking into the size-dependent ratio of Ru surface sites, we find that the superior activity of 4.9-nm Ru nanoparticles correlates with the surface population of the D_5 step site, which favors the adsorption of NO_3RR reaction intermediate as compared to other surface sites. This work is supported by the National Science Foundation (NSF) Chemical Catalysis Program under Grant No. 1943732.

11:15am **SS+CA+LS-TuM-14 Probing Solvation with Liquid Jet Photoelectron Spectroscopy**, *Jared Bruce, S. Faussett, R. Woods,* University of Nevada, Las Vegas*; K. Zhang,* MIT*; A. Haines, F. Furche,* University of California Irvine*; R. Seidel,* Helmholtz Zentrum Berlin, Germany*; B. Winter,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*; J. Hemminger,* University of California Irvine

The local chemical structure around solutes in aqueous solution is challenging to characterize on a molecular scale given the amount of hydrogen bonding interactions that occur in solution. Liquid jet photoelectron spectroscopy (LJ-XPS) can be a critical tool providing valuable chemical information both near the surface and in the bulk of the solution.

In this talk I will discuss how a combination of liquid jet photoelectron spectroscopy and electronic structure calculations were used to investigate the local chemical solvation of two systems – Fe^{2+} and acetic acid aqueous solutions. Each system has specific interfacial behavior that was investigated with liquid jet photoelectron spectroscopy. Fe showed coordination events with small anions like Cl^- alter the relative concentration of both species near the interface, whereas acetic acid shows alterations to its local solvation environment as a function of both the proximity to the interface and the pH of the bulk solution. Each will be discussed in detail and recent work from the lab at UNLV will be highlighted.

Tuesday Afternoon, November 5, 2024

2D Materials

Room 122 - Session 2D+LS+NS+SS-TuA

Electronics Properties

Moderators: Masa Ishigami, University of Central Florida, **Slavomir Nemsak**, Advanced Light Source, Lawrence Berkeley National Laboratory

2:15pm 2D+LS+NS+SS-TuA-1 NanoARPES for the Study of 2D Materials, *Aaron Bostwick*, Advanced Light Source, Lawrence Berkeley National Laboratory **INVITED**

Angle-resolved photoemission spectroscopy (ARPES) is the premier technique for the determination of the electronic bandstructure of solids, and has found wide application for manyclasses of materials, such as oxides, semiconductors, metals, and low-dimensional materials and surfaces. Among the important topics it addresses are the underlying many-body interactions that determine the ground and excited state functionalities of all materials. Recently the development of nanoARPES using microfocused x-ray beams has opened ARPES to a wider class of samples and enabled the measurement of 2D devices *in-situ* with applied electric fields, currents, strain and femtosecond laser pulses to the samples. In this talk I will give an introduction to the ARPES technique, the MAESTRO facility and share some our recent work on the bandstructure and many-body interactions in 2D heterostructuresof chalcogenides, graphene, and boron nitride and light induced metastable phases in 1T-TaS$_2$.

2:45pm 2D+LS+NS+SS-TuA-3 Observation of Interlayer Plasmon Polaron in Graphene/WS$_2$ Heterostructures, *S. Ulstrup*, Aarhus University, Denmark; *Y. Veld*, Radboud University, Netherlands; *J. Miwa, A. ones*, Aarhus University, Denmark; *K. McCreary, J. Robinson, B. Jonker*, Naval Research Laboratory; *S. Singh*, Carnegie Mellon University, USA; *R. Koch, E. Rotenberg, A. Bostwick, C. Jozwiak*, Advanced Light Source, Lawrence Berkeley National Laboratory; *M. Rosner*, Radboud University, Netherlands; *Jyoti Katoch*, Carnegie Mellon University, USA

Van der Waals heterostructures offer us exciting opportunity to create materials with novel properties and exotic phenomena such as superconductivity, bound quasiparticles, topological states as well as magnetic phases. In this talk, I will present our work on directly visualizing the electronic structure of graphene/WS$_2$/hBN heterostructure using micro-focused angle-resolved photoemission spectroscopy (microARPES). Upon electron doping via potassium deposition, we observe the formation of quasiparticle interlayer plasmon polarons in graphene/WS$_2$ heterostructure due to many-body interactions. I will discuss that such low-energy quasiparticle excitation is important to consider as they can have huge implications on the electronic and optical properties of heterostructures based on 2D transition metal dichalcogenides.

3:00pm 2D+LS+NS+SS-TuA-4 Harnessing the Synergy of X-ray Photoelectron Spectroscopy (XPS) and Argon Cluster Etching for Profound Analysis of MoS$_2$ and Graphene, *Jonathan Counsell*, Kratos Analytical Limited, UK; *C. Moffitt, D. Surman*, Kratos Analytical Inc.; *L. Soomary, K. Zahra*, Kratos Analytical Limited, UK

Understanding the intricate properties of two-dimensional (2D) materials such as MoS2 and graphene is pivotal for advancing their applications across diverse fields. However, achieving comprehensive characterization at the nanoscale requires advanced analytical techniques. This study explores the synergistic potential of X-ray Photoelectron Spectroscopy (XPS) coupled with Gas Cluster Ion Source (GCIS) etching and depth profiling to delve deeper into the structural and electronic intricacies of MoS2 and graphene.

By integrating XPS with GCIS etching, we not only discern the elemental composition, chemical bonding, and electronic states of these materials with exceptional precision but also unravel their depth-dependent characteristics. The incorporation of GCIS etching facilitates controlled removal of surface layers, enabling depth profiling to uncover buried interfaces, defects, and contamination effects that influence spectral results.

The combined approach allows for the characterization of MoS2-graphene heterostructures, providing insights into interfacial interactions and electronic coupling mechanisms. Through systematic analysis, we demonstrate the complementary advantages of XPS and GCIS etching in elucidating the structural and electronic complexities of 2D materials.

The integration of GCIS etching with XPS not only enhances the depth resolution and sensitivity of the analysis but also offers a deeper understanding of the nanoscale landscape of MoS2, graphene, and their heterostructures. This multidimensional approach accelerates the development of tailored devices and applications based on 2D materials, propelling advancements in nanotechnology and beyond.

3:15pm 2D+LS+NS+SS-TuA-5 Monark Quantum Foundry: Advancing 2d Quantum Materials Through Automated Pipelines, *Amirhossein Hasani, N. Borys*, Montana State University, USA; *H. Churchill*, University of Arkansas

At the MonArk Quantum Foundry, located at Montana State University and the University of Arkansas, we are advancing the field of 2D quantum materials through the development of 2D Quantum Materials Pipelines (2D-QMaPs). These pipelines automate and streamline the critical stages of 2D quantum material sample preparation and device fabrication.

Robotic Exfoliation and Flake Hunting: Our process begins with an automated robotic exfoliator designed to produce up to 50 chips per hour, each measuring 1 cm by 1 cm. This machine carefully peels off thin layers from bulk materials, allowing precise control over factors such as temperature, pressure, and applied force, which is crucial for producing high-quality thin flakes, including single-layered crystals. After exfoliation, an automated optical cataloger identifies and catalogs the thin flakes. This system scans the entire chip, locates these flakes, and stores their information in a database. The cataloger uses advanced machine learning and AI algorithms for quick and accurate detection and features a motorized stage with photoluminescence and Raman spectroscopy capabilities, completing a full scan at 20x magnification in approximately 5 minutes.

Device Fabrication and Packaging: The identified flakes are then transferred to a specialized environment for device fabrication and packaging. This stage employs high-resolution thermal scanning probe lithography, laser writing systems, and electron beam evaporators to create devices. The entire process is conducted in an inert atmosphere (glove box), preserving the material's integrity by preventing exposure to air and moisture.

Characterization: The final stage integrates quantum device characterization tools, including photoluminescence (PL), Raman spectroscopy, magneto-optical probes, nano-optical spectroscopy, bulk and nanoscale cryogenic magnetometry, and magneto-transport measurements. These tools provide a comprehensive analysis of material and device properties, including mobilities, transition temperatures, photon autocorrelations, coherence times, and more.

Through the development of the 2D-QMaPs, the MonArk Quantum Foundry is revolutionizing the study of 2D quantum materials, paving the way for significant advancements in quantum computing, sensing, and other technologies.

4:00pm 2D+LS+NS+SS-TuA-8 Manipulation of Chiral Interface States in a Moiré Quantum Anomalous Hall Insulator, *Tiancong Zhu*, Purdue University **INVITED**

Quantum anomalous Hall (QAH) effect reflects the interplay between magnetism and non-trivial topology characterized by integer Chern numbers, which is expressed by chiral edge states that carry dissipationless current along sample boundaries. The recent discovery of QAH effect in van der Waals moiré heterostructures provides new opportunities in studying this exotic two-dimensional state of matter. Specifically, magnetism in these moiré QAH systems is induced by orbital motion of electrons, which allows full electrical control of the magnetic and the corresponding topological state. In this talk, I will discuss our recent scanning tunneling microscopy and spectroscopy (STM/STS) measurements on twisted monolayer-bilayer graphene (tMBLG), where QAH effect with gate-switchable Chern numbers have been observed previously in transport measurement. First I will discuss local scanning tunneling spectroscopy measurements on the correlated insulating states at v = 2and v = 3electrons per moiré unit cell, where the v = 3state shows a total Chern number of ±2. Under a small magnetic field, the sign of Chern number at the v = 3states can be switched by changing the local carrier concentration with gating, which is a result of competition between bulk and edge orbital magnetization of the QAH state.[1] The observation of a gate-switchable Chern number provides us an opportunity to directly visualize the chiral edge state in a moiré QAH insulator for the first time, which I will show through gate-dependent STS measurement and dI/dV mappings.[2] I will also demonstrate the capability to manipulate the spatial location and chirality of the QAH edge state through controlling the local carrier concentration with the STM tip.

[1] C. Zhang, T. Zhu et al,. Nature Communications, 14, 3595 (2023)

[2] C. Zhang, T. Zhu et al., Nature Physics (2024)

4:30pm 2D+LS+NS+SS-TuA-10 Scanning Tunneling Microscopy and Spectroscopy of Single Layer NiTe₂ on Au, *Stephanie Lough,* University of Central Florida*; M. Ishigami,* University of Central Florida

Previous angle-resolved photoemission studies [1, 2] have shown that $NiTe_2$ is a type II Dirac material that possesses a Dirac point very close to the Fermi level. In addition, the material has a topological surface state which can be valley spin-polarized.A recent study [3] has shown that this state can be exploited to develop Josephson diodes with potential applications as memory devices which can be coupled to qubits. There has been a significant interest [3-5] in studying properties of single layer $NiTe_2$ due to its strong interlayer coupling in bulk via Te Pz orbitals.

In this talk, we will discuss the properties of single layer $NiTe_2$ on Au generated by gold-assisted exfoliation measured using low temperature scanning tunneling microscopy and spectroscopy. We find that this interface possesses rectangular lattice with periodicities that are different from bulk $NiTe_2$ or Au (111) by over 30%.Tunneling spectra reveals strong coupling between $NiTe_2$ and Au (111).We compare these results recent theoretical calculations [6] on strained $NiTe_2$ and its impact on topological surface states.

1.Ghosh, S., et al., *Observation of bulk states and spin-polarized topological surface states in transition metal dichalcogenide Dirac semimetal candidate NiTe2.* Physical Review B, 2019. **100**.

2.Mukherjee, S., et al., *Fermi-crossing Type-II Dirac fermions and topological surface states in NiTe.* Scientific Reports, 2020. **10**(1).

3.Pal, B., et al., *Josephson diode effect from Cooper pair momentum in a topological semimetal.* Nature Physics, 2022. **18**(10): p. 1228-+.

4.Zhao, B., et al., *Synthetic Control of Two-Dimensional NiTeSingle Crystals with Highly Uniform Thickness Distributions.* Journal of the American Chemical Society, 2018. **140**(43): p. 14217-14223.

5.Zheng, F.P., et al., *Emergent superconductivity in two-dimensional NiTe crystals.* Physical Review B, 2020. **101**(10).

6.Ferreira, P.P., et al., *Strain engineering the topological type-II Dirac semimetal NiTe.* Physical Review B, 2021. **103**(12).

4:45pm 2D+LS+NS+SS-TuA-11 Nanoscale heterogeneities at Transition Metal Dichalcogenide-Au Interfaces, *Taisuke Ohta,* A. Boehm, A. Kim, C. Spataru, K. Thuermer, J. Sugar, Sandia National Laboratories*; J. Fonseca Vega, J. Robinson,* Naval Research Laboratory

Two-dimensional geometry renders unique screening properties in transition metal dichalcogenides (TMDs). Consequently, the electronic properties of TMDs are susceptible to extrinsic factors (*e.g.*, substrate, strains, and charge transfer), and display spatial nonuniformities. Thus, material combinations (*i.e.*, TMD, dielectrics, and metals) and their nuanced interactions need to be considered when designing TMD-based devices. Of particular importance are the interfaces with metallic contacts. Uncovering the origin of heterogeneities at TMD-metal interfaces and establishing strategies to control TMD-metal interfaces could enable engineering pathways for future applications. We show that the electronic structures of exfoliated WS₂-Au interfaces exhibit pronounced heterogeneity arising from the microstructure of the supporting metal. These electronic structure variations indicate spatially nonuniform doping levels and Schottky barrier height across the junction. Through examination using photoelectron emission microscopy, we reveal key differences in the work function and occupied states. With *ab initio* calculation, electron backscatter diffraction, and scanning tunneling microscopy, our measurements show distinct variations in excess of 100meV due to the crystal facets of Au. Additionally, when multilayer WS₂ and Au(111) facets are azimuthally aligned, strong interactions induce mechanical slippage of the interfacing WS₂ layer, with respect to the rest of the WS₂ layers, resulting in local stacking variations with an occupied state energy shift of 20-50meV. Finally, we employed oxygen plasma treatment of Au to fabricate homogenous TMD-Au interfaces while also tuning the electronic properties of the TMDs. Our findings illustrate that the electronic properties of TMDs are greatly impacted by the interface interactions at energy and length scales pertinent to electronics and optoelectronics.

The work at Sandia National Laboratories (SNL) was supported by LDRD program and the US Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences and Engineering (BES 20-017574). The work at the US Naval Research Laboratory was funded by the Office of Naval Research. SNL is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly-owned subsidiary of Honeywell International, Inc., for the US DOE's National Nuclear Security Administration under contract DE-NA0003525.

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the US DOE or the US Government.

5:00pm 2D+LS+NS+SS-TuA-12 Xenon Trapping in Silica Nanocages Supported on Metal Powder, *Laiba Bilal,* SBU*; A. Boscoboinik,* Brookhaven National Laboratory

Trapping of Xenon gas atoms in silica nanocages supported on metal powders (Ru and Co) is investigated by lab-based ambient pressure X-ray photoelectron spectroscopy (AP-XPS).Xenon, being a noble gas, has very low reactivity[1]. This makes it useful for applications where chemical reactions are unwanted. The first use for Xenon was in flash lamps used in photography[2], and it is still used for this purpose today. It has wide applications, from its use in the cells of plasma television as a propellant in spacecraft that use ion propulsion[3] to its various applications in the medical industry[4].

Xenon occurs in slight traces within Earth, 1 part in 10 million by volume of dry air[2]. Like several other noble gases, xenon is present in meteorites and manufactured on a small scale by the fractional distillation of liquid air. However, Xe's concentration in the earth's crust and the atmosphere are much lower than predicted, which is also known as the "missing Xenon paradox"[5].

The Discovery of an effective way to trap and separate Xenon from other gases can have significant advantages. The presence of Xenon in nuclear fuel rods was partially responsible for the Chernobyl accident[6]. Consequently, the nuclear energy industry is also trying to imprint a way to control the release of Xe, produced during the nuclear fission of uranium. Characteristics of chemical interactions between Xe and metal surfaces have been observed and explained, also several low-energy electron diffraction studies at cryogenic temperatures have experimentally demonstrated an on-top site adsorption preference for Xe adatoms on metal surfaces[7].

Prior studies on 2D silicate bilayers grown on metal supports at Brookhaven National Lab showed that these structures could irreversibly trap all noble gases larger than Ne[8] at room temperature. The noble gas atoms were trapped within hexagonal prism-shaped silicate nanocages-like structures and could then be released by heating the materials to different temperatures, i.e., Ar: 348 K, Kr: 498 K, Xe: 673 K, Rn: 775 K[8,9]. Figure 1A illustrates the potential energy diagram for a noble gas atom getting trapped in a silica nanocage. It can be seen that the activated physisorption mechanism that traps noble gas atoms has a high desorption energy barrier (E_{des}).

Figure 1B shows a silicate bilayer structure (side and top views), while Figure 1C shows a hexagonal prism nanocage, the building block of the bilayer structure.[8]. Since synthesizing such silicate bilayers is very expensive and time-consuming[10] for practical purposes, my project focuses on developing and testing scalable silicate nanocage[9] materials to trap noble gases, with especial focus on Xenon.

Surface Science
Room 120 - Session SS+CA+LS-TuA

Electrochemistry and Photocatalysis

Moderators: Jared Bruce, University of Nevada Las Vegas, **Taku Suzuki,** NIMS (National Institute for Materials Science), Japan

2:15pm SS+CA+LS-TuA-1 Surface Sensitive Studies of the Electrolyte-Electrode Interface, *Edvin Lundgren,* Lund University, Sweden   **INVITED**
The electrified electrode electrolyte interface is notoriously difficult to study during electrochemical (EC) reactions. Most traditional surface science techniques are disqualified due to the use of electrons, on the other hand, several new in-situ experimental methods have been developed recently. Examples are Electro Chemical X-ray Photoelectron Spectroscopy (ECXPS), Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), High Energy Surface X-Ray Diffraction (HESXRD) [4] and EC-IRAS [5].

In the first part of the talk, the corrosion of an industrial Ni base Ni-Cr-Mo alloy will be addressed. A comprehensive investigation combining several synchrotron-based techniques are used to study the surface region of a Ni-Cr-Mo alloy in NaCl solutions in situ during electrochemical polarization. X-Ray Reflectivity (XRR) and ECXPS were used to investigate the thickness and chemistry of the passive film. Grazing Incidence X-ray Diffraction (GIXRD) was used to determine the change in the metal lattice underneath the

passive film. X-Ray Fluorescence (XRF) was used to quantify the dissolution of alloying elements. X-ray Absorption Near Edge Structure (XANES) was used to determine the chemical state of the dissolved species in the electrolyte. Combining these techniques allowed us to study the corrosion process, detect the passivity breakdown in situ, and correlate it to the onset of the Oxygen Evolution Reaction (OER) [6].

In the second part, an alternative approach to study the development of a model electro catalyst surface is presented. By using a combination of Grazing Incidence X-ray Absorption Spectroscopy (GIXAS) [7], 2D Surface Optical Reflectance (2D-SOR) [8] and Cyclic Voltammetry (CV) and a Au(111) electrode model surface, direct surface information during real-time CV can be obtained.

[1] S. Axnanda et al, Sci. Rep. **5** (2016) 9788.

[2] A. A. Gewirth, B. K. Niece, Chem. Rev. **97** (1997) 1129.

[3] K. Itaya, Prog. Surf. Sci. **58** (1998) 121.

[4] M. Ruge et al, J. Electrochem. Soc. **164** (2017) 608.

[5] T. Iwasita, F. C. Nart, Prog. Surf. Sci. **55** (1997) 271.

[6] A. Larsson et al, Adv. Mat. (2023) 230462.

[7] H. Abe, Y. Niwa, M. A. Kimura, Phys. Chem. Chem. Phys. **22** (2020) 24974.

[8] S. Pfaff et al, ACS Appl. Mater. Interfaces **13** (2021) 19530.

2:45pm SS+CA+LS-TuA-3 Operando Studies of CO2, CO and N2 Catalytic Hydrogenation Reactions investigated with Ambient Pressure XPS, *P. Amann,* Scienta Omicron, Germany*; Andrew Yost,* Scienta Omicron, USA
Some of the most essential catalytic reactions for our energy society is to reduce CO_2 to hydrocarbons and alcohols to be used as fuels and base chemical for the chemical industry. Furthermore, the catalytic reduction of N_2 to ammonia has been considered as one of the most important discoveries during the 20th century to produce fertilizers for a growing population. Despite an enormous effort in studying these catalytic reactions we are still lacking experimental information about the chemical state of the catalytic surface and the adsorbates existing as the reaction is turning over. X-ray photoelectron spectroscopy (XPS) is a powerful surface sensitive technique that can provide almost all essential chemical information and it has been developed to operate also in a few mbar of pressure with great success for probing oxidation catalytic reactions. Unfortunately, this pressure regime is too low for the hydrogenation reactions to turn over. Here we will present how Fischer-Tropsch, methanol and ammonia synthesis reactions on single crystal metal surfaces have been probed during operando conditions in the pressure range 100 mbar-1 bar using a specially engineered XPS system built at Stockholm University (1) and permanently located at the PETRA III synchrotron in Hamburg. The instrument is commercially available at Scienta Omicron (BAR XPS) and can vary the incidence angle of the X-rays allowing it to be either surface or bulk sensitive. Examples will be presented about the chemical state of Zn in Cu-Zn methanol (2) and of Fe in Fischer-Tropsch (3,4) and ammonia synthesis reactions (5) as well as the various adsorbates at different pressures and temperatures.

(1) P. Amann et al. Rev. Sci. Instrum. **90**, 103102 (2019)

(2) P. Amann et al. Science 376, 603-608 (2022)

(3) D. Degerman et al. J. Phys. Chem. C 128, 13, 5542–5552 (2024)

(4) M. Shipilin et al. ACS Catalysis 12, 7609-7621 (2022)

(5) C.M. Goodwin et al. Nature, 625, 282-286 (2024)

3:00pm SS+CA+LS-TuA-4 Understanding the Intrinsic Activity and Selectivity of Cu for Ammonia Electrosynthesis from Nitrate, *Zhuanghe Ren, K. Shi, Z. Meng, X. Feng,* University of Central Florida
Electrocatalysis play a central role in the development of renewable energy technologies towards a sustainable future, such as the recycling of nitrate from wastewater sources. The concentration of nitrate (NO_3^-) in ground water, rivers, and lakes has been increasing due to the excessive use of agricultural fertilizers and the discharge of industrial wastewater, which has caused severe environmental problems such as eutrophication. Electrochemical reduction of nitrate to ammonia has emerged as a promising route for the recycling of nitrate from wastewater and sustainable ammonia production when powered by renewable electricity. Here I present our recent study of Cu catalyst for nitrate electroreduction, with a focus on its intrinsic activity and selectivity. Using polycrystalline Cu foils for benchmarking, we elucidated the impact of often overlooked factors on nitrate reduction, including Cu facet exposure, nitrate concentration, and electrode surface area. We find that an electropolished Cu foil exhibits a higher activity and selectivity for nitrate reduction to ammonia than a wet-etched Cu foil, benefiting from a greater exposure of Cu(100) facets that are more favorable for the reaction. While the NH_3 selectivity shows no apparent dependence on the nitrate concentration, it increases with Cu electrode area, which is attributed to a promoted conversion of intermediately produced NO_2^- to NH_3 on a larger electrode. Based on the understandings, we developed a modified Cu foil electrode with increased Cu(100) facets and surface area, which enhanced the NO_3RR activity by ~50% with a NH_3 Faradaic efficiency of 91% at −0.2 V vs RHE.

This work is supported by the National Science Foundation (NSF) Chemical Catalysis Program under Grant No. 1943732.

References:

(1) Ren, Z.; Shi, K.; Feng, X. Elucidating the intrinsic activity and selectivity of Cu for nitrate electroreduction. *ACS Energy Lett.* **2023**, *8*, 3658−3665.

3:15pm SS+CA+LS-TuA-5 Insights Into Photocatalytic Reduction Activities of Different Well-Defined Single Bulk Crystal TiO₂ Surfaces in Liquid, *Olawale Ayoade, W. Lu, H. Zhu, Z. Zhang,* Baylor University
Understanding the activity of TiO_2 photocatalysts is crucial for designing and optimizing efficient photocatalysts, requiring a fundamental understanding of the photooxidation and photoreduction activities of different TiO_2 crystal facets. Although photoreduction activities on several TiO_2 crystal facets have been extensively studied in reactor or ultra-high vacuum environments, studies of well-defined TiO_2 crystal facets in a liquid environment are still lacking.In this study, the photocatalytic reduction activities of resazurin (RZ) were investigated using well-defined bulk single-crystal anatase (001), anatase (101), rutile (001), and rutile (110) facets. The experiment used a liquid cell containing RZ solution and TiO_2 crystal. A lab-built Raman microscope monitored the photoluminescence (PL) spectra of RZ under UV irradiation. We observed an increase in peak intensity at 583 nm and a decrease at 630 nm in the PL spectra of the solution on the TiO_2 crystal facets upon UV illumination, suggesting a conversion from RZ to its product, resorufin (RS). Given that both RZ and RS have distinctive peaks, we used their ratios to estimate their concentrations. This enabled us to assess the conversion rate and reaction rate of the crystals.Our results show that rutile had significantly higher conversion rates and faster reaction rates than anatase for RZ reduction. Rutile (110) had conversion rates about four times greater, and rutile (001) about three times greater than anatase. Rutile (110) reaction rates were about 1.5 times faster than rutile (001) and significantly faster than anatase (101) & (001). Further evaluation of the photoreactivity was conducted using pseudo-order kinetics to determine the rate constant. The significant difference observed in rates between the rutile and anatase phases highlights the successful migration of electrons to the surface of the rutile crystal compared to the anatase surface, emphasizing the importance of crystal structure. The difference observed between rutile (001) and rutile (110) (as well as anatase facets 001 and 101) shows the effect of surface structure on photocatalytic activity. To advance the development of effective TiO_2-based photoreduction materials, we explored plasmon-assisted photoreactions. We have studied the impact of Au nanoparticles on the reactivity of the aforementioned TiO_2 facets. This study will involve modulating hot electron generation and increasing electric fields to better understand their effects on photoreactivity.

4:00pm SS+CA+LS-TuA-8 Selectivity Control by Ionic Liquid Layers: From Surface Science to the Electrified Interface, *Joerg Libuda,* Friedrich-Alexander-Universitaet Erlangen-Nuernberg, Germany   **INVITED**
Recently, the concept of "Supported Catalysts with Ionic Liquid Layer" (SCILL) has attracted much attention in heterogeneous catalysis and electrocatalysis. In the SCILL concept, a heterogeneous catalyst is impregnated with a thin layer of ionic liquid (IL) that serves as a catalytic modifier. In this presentation, we will give an overview of selected surface science and electrochemical surface studies on the origin of this selectivity control.

In the surface science studies, we investigated the growth, wetting behavior, structure formation and thermal behavior of various ILs on a wide range of model catalysts (Pt, Pd and Au single crystal surfaces and supported nanoparticles) using scanning tunneling microscopy (STM), atomic force microscopy (AFM) and infrared reflection absorption spectroscopy (IRAS). We were able to show that most ILs form a strongly interacting wetting layer with a high degree of intrinsic structural flexibility. Depending on the conditions, 2D glassy or different crystalline wetting layers are formed, in which the molecular orientation is dynamic and allows

the embedding of reactants and thus the modification of the reaction environment.

In our electrochemical surface science studies, we investigated the interaction of selected imidazolium-based ILs with reactive and non-reactive single-crystal electrodes (Au, Pt). Using electrochemical IRAS (EC-IRRAS), we monitored the potential-dependent adsorption of IL ions on the electrode and used electrochemical STM (EC-STM) to investigate the effects of the ILs on the electrode structure. We used the selective oxidation and reduction of hydrocarbon oxygenates as test reactions. For the selective electrooxidation of 2,3-butanediol (a very structure-sensitive reaction at Pt electrodes), we were able to show that small additions of specific ILs (e.g. $[C_1C_2Im][OTf]$) have a large effect on selectivity (e.g. on C-C bond cleavage and selectivity towards the two partial oxidation products acetoin and diacetyl). We attribute these effects to the possible adsorption of the IL anions on the Pt surfaces.

Our results rationalize the origin of selectivity control by IL coatings in heterogeneous catalysis and demonstrate the potential of ILs for selectivity control in electrocatalysis.

[1] R. Eschenbacher et al.,. J. Chem. Phys. Lett. 12, 10079 (2021)
[2] T. Yang et al., Angew. Chem. Int. Ed. 61, e202202957 (2022)
[3] M. Kastenmeier et al., J. Phys. Chem. C 127, 22975 (2023)
[4] H. Bühlmeyer et al., Chem. Eur. J., in press (2024), DOI10.1002/chem.202301328
[5] Y. Yang at al., J. Phys. Chem. C, accepted for publication (2024)

4:30pm SS+CA+LS-TuA-10 Area Selective Atomic Layer Deposition for Spatial Control of Reaction Selectivity on Model Photocatalysts, *Wilson McNeary*, National Renewable Energy Laboratory; *W. Stinson*, Columbia University; *W. Zang, M. Waqar, X. Pan*, University of California Irvine; *D. Esposito*, Columbia University; *K. Hurst*, National Renewable Energy Laboratory

Photocatalytic water splitting holds great potential in the pursuit of the U.S. Department of Energy's Hydrogen Shot initiative to bring the cost of H_2 to \$1/kg by 2031. A key challenge in the development of photocatalysts is increasing their overall solar-to-hydrogen efficiency by enhancing charge separation yields and redox selectivity. In this work, we use area selective ALD of oxide films (e.g., TiO_2 and SiO_2) to develop tunable interphase layers for selective oxidation and reduction reactions on a single substrate. This presentation details initial synthesis and characterization of monometallic Pt- and Au-based planar thin film electrodes in which Au regions were deactivated towards ALD growth through self-assembled thiol monolayers. The efficacy of thiols in suppressing ALD growth was assessed through ellipsometry, X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry. A patterned planar sample comprised of interdigitated arrays of Au and Pt, used as a surrogate for a photocatalyst particle containing two different co-catalysts, was exposed to ALD growth and removal of the inhibitor species. Area selectivity of the ALD coatings on the patterned substrates was evaluated through cross-sectional scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-EDS). Scanning electrochemical microscopy (SECM) was then used to probe the local activity of different regions of the patterned surface towards the hydrogen evolution reaction (HER) and iron oxidation and correlated with the ionic and e⁻ blocking effects of the area selective ALD coating. We will also detail the application of these findings to the ongoing development of 3D, particle-based photocatalysts

4:45pm SS+CA+LS-TuA-11 Titanium-Based Catalysts for CO_2 Activation: Experimental Modelling of Hybride (Photo-)Catalysts, *N. Kruse, J. Klimek, C. Groothuis*, **Lars Mohrhusen**, University of Oldenburg, Germany

Conversion of greenhouse gases and especially CO_2 into useful hydrocarbons via a low-cost route is among the major challenges of the current energy transition. For this purpose, photocatalysis may be a relevant technology, as sunlight is a free and unlimited energy source, and photoreactions usually do not require high temperatures. Oxide-based photocatalysts usually consist of a semiconducting oxide support with nanostructured (noble) metal particles.[1] Unfortunately, these metals are often expensive and have limited lifetimes due to for example sintering, coking or poisoning with carbon monoxide. Thus, for several reasons, it is attractive to develop strategies to replace noble metal in such systems.[2]

Titanium is one of the few elements, that are attractive in terms of its natural availability and considering various economic and ecological aspects. Titanium dioxide (TiO_2) for example offers a broad platform, as e.g. defects such as Ti^{3+} interstitials can boost the photocatalytic activity towards oxygen containing molecules.[3,4] TiO_2 also readily forms hybrid systems with other oxides (e.g. WO_3 clusters)[4] or sulfides such as MoS_2.[5]

Thus, we investigate titanium-based hybrid photocatalytic systems using well-defined model catalysts under ultrahigh-vacuum conditions.

Herein, we present selected results from well-defined model catalysts en route to the desired Ti-based hybrid materials, for example, nanostructured combinations of TiS_2 and TiO_2. TiS_2 has a broad light absorbance throughout the visible range, is easily reduceable and widely inert to CO poisoning, rendering it an attractive material. Our multi-method approach involves combinations of spectroscopy (esp. photoelectron spectroscopy (XPS)), microscopy (scanning tunneling microscopy (STM)) and reactivity studies (temperature-programmed desorption (TPD)). As one example, nanoparticles of TiS_2 as a classic 2D TMDC can be fabricated and studied on various substrates to derive an atomic-level understanding of structure-reactivity relationships.

References

[1] Linsebigler, Lu, Yates: Chem. Rev. **95**, 735-758 (1995).

[2] Shen et al. Solar RRL **4**, 1900546 (2020).

[3] Mohrhusen, Al-Shamery Catal. Lett. **153**, 321-337 (2023).

[4] Mohrhusen, Kräuter, Al-Shamery PCCP **21**, 12148-12157 (2021).

[5] Kibsgaard et al., J. Catal. **263** 98-103 (2009).

5:00pm SS+CA+LS-TuA-12 Tracking the Ultrafast Dynamics of a Photoinduced Reaction at the Surface of a Reactive Semiconductor: CH_3I Photoinduced Reaction on TiO_2 (110) Surface, *A. Gupta*, University of Central Florida; *T. Wang*, University of Washington; *K. Blackman, C. Smith*, University of Central Florida; *X. Li*, University of Washington; *Mihai E. Vaida*, University of Central Florida

The detection of intermediate species during surface photoinduced reactions and the correlation of their dynamics with the properties of the surface is crucial to fully understand and control heterogeneous reactions. In this study, a technique that combines time-of-flight mass spectrometry with laser spectroscopy and fast surface preparation with molecules is employed to investigate the mechanism of photoinduced CH_3I reactions on a TiO_2(110) surface through the direct detection of intermediate species and final products. On a freshly prepared TiO_2(110) surface, the photoinduced reaction dynamics of CH_3I follows similar trends observed on other metal oxide surfaces.[1,2] Specifically, the pump laser pulse at 266 nm excites the CH_3I molecule into the dissociative A-band, which leads to the formation of CH_3 and I intermediates that can further react to form I_2 and reform the CH_3I molecule. Subsequently, the probe laser pulse ionizes the intermediate and final products, which are detected by a mass spectrometer as a function of the pump-probe time delay. The minimum dissociation time of CH_3I obtained by monitoring the CH_3^+ fragment, which is 110 fs, and the fast rise of the CH_3^+ signal, indicates that CH_3I is adsorbed on pristine TiO_2(110) with I atom facing the surface. A fraction of the I atoms produced on a freshly prepared TiO_2(110) are trapped on the surface. On this TiO_2(110) surface decorated with I atoms, the CH_3 fragment can react with CH_3I to form CH_3ICH_3, which leads to a completely different dynamics at the surface due to a change into the pump-probe schema. The evolution dynamics of CH_3^+ and CH_3I^+ after the CH_3ICH_3 photoexcitation will be discussed and compared with results obtained for CH_3I dosed on a freshly prepared TiO_2(110) surface.

1. M. A. K. Pathan, A. Gupta and M. E. Vaida, *J. Phys. Chem. Lett.*, 2022, **13**, 9759-9765.
2. M. E. Vaida and T. M. Bernhardt, in *Ultrafast Phenomena in Molecular Sciences: Femtosecond Physics and Chemistry*, eds. R. de Nalda and L. Bañares, Springer International Publishing, Cham2014, pp. 231-261.

5:15pm SS+CA+LS-TuA-13 Kinetic Theory of Mixed-Potential-Driven Catalysis and the Experimental Proof, *M. Yan, N. Namari, R. Arsyad, H. Suzuki*, University of Tsukuba, Japan; *J. Nakamura*, Kyushu University, Japan; *Kotaro Takeyasu*, Hokkaido University, Japan

It has recently been suggested that thermal heterogeneous catalysis can also involve electrochemical processes, resulting in selectivity that is markedly different from that of conventional thermal catalysis. If the catalyst is conductive and a suitable electrolyte is present nearby, anodic and cathodic half-reactions may occur simultaneously on a single catalyst surface, forming a mixed potential. This reaction is characterized by the anode and cathode being exposed to the same reactant, unlike conventional fuel cells where different reactants are supplied to each electrode. Interestingly, mixed potentials have been reported to be involved in reactions with gas molecules, such as the formation of H_2O_2 and the oxidation of alcohol. These reports suggest that electrochemical processes

play a role in controlling catalytic activity and selectivity without external energy. Catalysts based on mixed potentials are a promising new category of catalysts for both basic research and industrial applications, but the principles that determine their activity and selectivity are not yet fully understood.

We first report the theoretical framework of mixed-potential-driven catalysis, including exchange currents, as a parameter of catalytic activity. The mixed potential and partitioning of the overpotential were determined from the exchange current by applying the Butler–Volmer equation at a steady state far from equilibrium [1].

To prove the theoretical framework,we measured the short-circuit current in a model reaction system without applying an external potential to demonstrate electron transfer for enzyme-like glucose oxidation. Specifically, glucose oxidation includes paired electrochemical anodic glucose oxidation and cathodic oxygen reduction, as evidenced by the consistency between the predicted and measured mixed potentials in identical reaction environments. Therefore, it can be categorized as a mixed-potential-driven catalysis. We further demonstrated that the Gibbs free energy drop, as the total driving force, was partitioned into overpotentials to promote each half-reaction in the mixed-potential-driven catalysis. This driving force partitioning, which is controlled by catalytic activity, is a powerful tool for guiding the design of mixed-potential-driven catalytic systems [2].

[1] M. Yan, N. A. P. Namari, J. Nakamura, K. Takeyasu, Commun. Chem. 7, 69 (2024).

[2] M. Yan, R. Arsyad, N. A. P. Namari, H. Suzuki, K. Takeyasu, ChemCatChem,accepted (2024).

Light Sources Enabled Science Mini-Symposium
Room Central Hall - Session LS-ThP

Light Sources Enabled Science Mini-Symposium Poster Session

LS-ThP-1 Near-Ambient Pressure XPS/Nexafs at Diamond Light Source, *Georg Held,* Harwell Science Campus, UK

The near-ambient-pressure beamline B07 (Versatile Soft X-ray beamline) at Diamond Light Source opened for users in July 2017. It features a design, where beamline and electron analyser meet in the same flange, such that experimental chambers and reaction cells can be exchanged relatively easily. The energy range 250 – 2800 eV allows accessing a wide range of core levels and is optimised for the electron kinetic energy range necessary to penetrate gas environments in the 10 mbar range. The differentially pumped beamline entrance and analyser enable measurements routinely up to 30 mbar. We will present the beamline design and performance and present results of experiments studying industrial and model catalysts in ambient-pressure conditions, demonstrating the research possibilities it offers.

Surface Science
Room 120 - Session SS+AMS+AS+CA+LS-FrM

Advanced Surface Characterization Techniques & Mort Traum Presentation

Moderator: Charles Sykes, Tufts University

8:15am SS+AMS+AS+CA+LS-FrM-1 Infrared Spectroscopy as a Surface Science Technique, *Michael Trenary*, University of Illinois - Chicago **INVITED**
Infrared spectroscopy is widely used to probe the vibrational properties of molecules in the gas, liquid, and solid phases. On the other hand, precise information on the structure and chemistry of solid surfaces, and of molecular adsorbates on solid surfaces, is best gained through use of surface science methods. These methods generally entail the use of single crystals, ultrahigh vacuum conditions, and surface sensitive techniques. Reflection absorption infrared spectroscopy (RAIRS) is a surface sensitive technique that can be used in ultrahigh vacuum to study molecular adsorption on well characterized metal single crystal samples. Unlike many other surface science methods, it can also be used under elevated gas pressures. The spectra obtained display features that are quite distinct from those of other phases of matter. For example, in the gas phase, rotational fine structure greatly complicates the appearance of the spectra but is absent in the spectra of adsorbed molecules. In the liquid phase, spectra are broadened by both static and dynamic effects often making it difficult to resolve vibrational peaks due to different chemical species. In polycrystalline molecular solids, molecules are randomly oriented relative to the electric field directions of the infrared radiation, limiting the value of the spectra as a structural probe. In contrast, when molecules adsorb on metal surfaces, they often adopt a definite orientation with respect to the surface normal. This orientation can be deduced through the surface dipole selection rule, which states that only normal modes with a component of the dynamic dipole moment oriented along the surface normal will be allowed. While IR spectroscopy in several forms has long been used to study molecular adsorption on supported transition metal catalysts, the high degree of heterogeneity of the catalyst surfaces leads to very broad peaks, with full width at half maxima (FWHM) of 10-50 cm^{-1}. In contrast, the FWHM of peaks measured with RAIRS on well-ordered metal surfaces can be quite narrow, in some cases even less than 1 cm^{-1}. When a polyatomic molecule exhibits sharp peaks throughout the mid-IR range, the advantages of performing RAIRS with a Fourier transform infrared spectrometer are most pronounced. This talk will cover the speaker's forty years of research using the technique of RAIRS to study molecular adsorbates on metal surfaces.

8:45am SS+AMS+AS+CA+LS-FrM-3 Modeling Pipeline Surface Chemistry: Reaction of Monochloramine on Iron Surfaces, *Kathryn Perrine*, S. Pandey, O. Agbelusi, Michigan Technological University
Monochloramine (NH_2Cl), a secondary disinfectant, is utilized to treat pathogens in the municipal water system, producing fewer halogenated disinfection by-products and lasting longer than free chlorine (hypochlorite). Although a weaker oxidant, NH_2Cl has the potential to corrode the surface of pipeline materials resulting in the dissolution of unwanted species. Copper and lead pipelines have been shown to corrode in chloramine solutions, however on iron materials the surface chemistry is unexplored. Complex chemistry occurs on the surface of pipelines at solution/metal interfaces, thus providing catalytic sites for dissociation, decomposition, and degradation. Iron comprises distribution pipelines and also exists as oxides in soils in the natural environment. Redox reactions occur on the surface of iron materials, thus initiating surface corrosion. Here, various active sites on iron are produced and known for high reactivity with nitrogen compounds. Our group employs a surface science approach to uncovering mechanisms at complex interfaces.

In this study, the reaction of monochloramine (NH_2Cl) was investigated on single crystal Fe(111) in ultra-high vacuum at the gas/solid interface using *in situ* infrared reflection absorption spectroscopy and Auger electron spectroscopy. At -160 °C, NH_2Cl molecularly adsorbs to the surface while the annealing leads to the loss of key vibrational modes, suggesting that either molecular desorption or dissociation occurs. These observations are contrasted with our findings at the solution/iron interface, where polarized modulated infrared reflection absorption spectroscopy (PM-IRRAS), ATR-FTIR, XPS, and XRD were used to assess the various regions after corrosion and their film growth. In solution, localized heterogeneous corrosion products were observed and identified, suggesting different reaction pathways exist in strongly oxidizing solutions. These findings are important for understanding the mechanism of chloramines and water disinfectants on iron interfaces relevant for water quality, material degradation, and other complex environmental processes.

9:00am SS+AMS+AS+CA+LS-FrM-4 Development of Tip-Enhanced Raman Spectroscopy for Solid-Liquid Interfaces, *Naihao Chiang*, University of Houston
Tip-enhanced Raman spectroscopy (TERS) combines the spatial resolution of scanning probe microscopy (SPM) with the chemical sensitivity of Raman spectroscopy. TERS with sub-nanometer resolution has been demonstrated under ultrahigh vacuum conditions. We aim to extend this unprecedented chemical mapping capability to interfacial studies under the solution phase. Specifically, we have developed a scanning ion-conductance microscope for TERS (SICM-TERS) capable of interrogating soft samples. In this presentation, the instrumental design will be discussed first. SICM-TERS probe fabrication and evaluation will be followed. Then, a distance-dependent SICM-TERS measurement on two-dimensional MoS_2 sheets will be used to assess the strain created by the SICM probe in close proximity. Our results demonstrate the potential of combining TERS with SICM for obtaining chemical information at interfaces, thus setting the stage for future investigation into soft materials in electrolytic environments.

9:15am SS+AMS+AS+CA+LS-FrM-5 Ion Based Pump-Probe: Probing the Dynamics Following an Ion Impact, *Lars Breuer*, L. Kalkhoff, A. Meyer, N. Junker, L. Lasnik, Universität Duisburg-Essen, Germany*; Y. Yao, A. Schleife*, University of Illinois at Urbana Champaign*; K. Sokolowski-Tinten, A. Wucher, M. Schleberger*, Universität Duisburg-Essen, Germany
The study of ion-surface interactions is crucial for understanding material properties and their atomic-level dynamic responses. The transient nature of these interactions, occurring on ultrafast time scales, has so far limited direct experimental observation and has left the field reliant on computer simulations. Existing experimental methods, such as pump-probe techniques, have faced challenges in generating and precisely timing short, monoenergetic ion pulses essential for capturing these ultrafast phenomena.

Our group has pioneered a novel approach that overcomes these limitations by generating the world's shortest monoenergetic ion pulses in the keV regime, with a current duration of approximately 5 ps. These pulses are produced using femtosecond photoionization of a geometrically cooled gas jet, coupled with miniaturization of the ionization section.

In our experiments, we conduct ion-based pump-probe experiments observing the emission of hot electrons post-ion impact, similar to processes studied in two-photon photoemission (2PPE) experiments. Our findings not only demonstrate the feasibility of our approach and provide direct measurements of the ion pulse characteristics but also offer insights into the non-equilibrium dynamics of electronic excitation in solids following an ion impact. We can track the electronic excitation and determine the temporal evolution of a pseudo electron temperature.

This research opens new avenues for understanding the fundamental processes underlying ion-solid interactions, with significant implications for semiconductor manufacturing and materials science. Our work sets a new standard for temporal resolution in the study of ion-induced phenomena and lays the groundwork for future innovations in the field.

9:30am SS+AMS+AS+CA+LS-FrM-6 How Hot Plasmonic Heating Can Be: Phase Transition and Melting of P25 TiO_2 from Plasmonic Heating of Au Nanoparticles, W. Lu, R. Kayastha, B. Birmingham, B. Zechmann, *Zhenrong Zhang*, Baylor University
Plasmonic heating has been utilized in many applications including photocatalysis, photothermal therapy, and photocuring. However, how high the temperature can be reached for the surrounding media due to the collective heating of the plasmonic nanoparticles (NPs) and the impact of the heat dissipation on the surrounding media is not clear. Herein we studied the impact of plasmonic heat generated by resonantly excited gold (Au) NPs on P25 TiO_2 nanoparticle film. Under 532 nm continuous laser irradiation at the surface of the Au-TiO_2, the surface evaporation of Au nanoparticles and phase transition of TiO_2 were observed at moderate laser power. More importantly, as high as the melting point of TiO_2 of 1830ºC is confirmed from the molten TiO_2 rutile phase. When Au/TiO_2 was irradiated with an off-resonance laser at 638 nm, no phase transformation or melting of TiO_2 was observed. The temperature calculation shows that the heating generated by Au nanoparticles is not localized. The collective heating from an ensemble of Au nanoparticles in the irradiated area produces a global temperature rise that melts TiO_2. Our results suggest that the photothermal

effect could be a major mechanism in the plasmon-assisted photocatalytic reactions. The experimental observation of the high temperature of the supporting media suggests new applications for utilizing plasmonic heating, for example, additive manufacturing.

9:45am SS+AMS+AS+CA+LS-FrM-7 Kinetics and Dynamics of Recombinative Desorption of Oxygen from Silver and Rhodium Surfaces, *Dan Killelea,* Loyola University Chicago

The ability to obtain velocity distributions of molecules desorbing from surfaces with both high temporal precision and angular resolution provide newfound insight into both the kinetics and the dynamics of recombinative desorption and subsurface emergence.

I will discuss our observations of subsurface oxygen emerging from beneath Rh(111) and how the velocity distribution shifts in comparison to the thermally-dominated desorption pathways found for surface-adsorbed oxygen. In addition, it was recently discovered that decomposition of oxygenaceous surface phases on Ag(111) also exhibit pronounced shifts in the energetics of the desorbing oxygen molecules. I will discuss these observations and their potential impacts in oxidation reactions in heterogeneously catalyzed reactions over transition metal surfaces.

10:00am SS+AMS+AS+CA+LS-FrM-8 Mort Traum Award Announcement,

10:30am SS+AMS+AS+CA+LS-FrM-10 Unveiling Surface Mysteries with XPS Lab from Scienta Omicron, *T. Sloboda,* Scienta Omicron, Sweden*; P. Amann,* Scienta Omicron, Germany*; B. Gerace, F. Henn,* **Andrew Yost**, *X. Zhang,* Scienta Omicron*; M. Lundwall,* Scienta Omicron, Sweden

Surface analysis is paramount for understanding material properties, and Scienta Omicron's XPS Lab system excels in this realm. Featuring a compression unit for superior count rates and sensitivity, it offers unparalleled quantitative XPS enabled by a true counting multi-anode detector inside the Argus CU analyser.This unique detector employs 128 individual counters connected to a striped-anode array. With a linear response extending to the highest count rates and an exceptional dynamic range, it ensures high resolution precise measurements across various sample types.

The versatility of XPS Lab is evident through its scanning, imaging, snapshot, and dynamic measurement modes (see Figure 1), enabling researchers to tailor their experiments to specific needs. The chemical state mapping capability of the XPS Lab provides comprehensive insights into surface chemistry, empowering researchers to unravel complex phenomena.

Illustrating its prowess, case studies span catalysis, energy storage, semiconductor technology, and biomaterials, showcasing its ability to address diverse research challenges. Recent enhancements further strengthen its capabilities, solidifying XPS Lab as the premier choice for XPS analysis.

In summary, Scienta Omicron's XPS Lab system offers unmatched precision, sensitivity, and versatility, driving advancements in surface science and materials research.

10:45am SS+AMS+AS+CA+LS-FrM-11 Investigation of Stannane (SnH$_4$) Decomposition and Sticking Coefficient on Varied Metal Surfaces in EUV Lithography Environments, *Emily Greene,* N. Barlett, D. Qerimi, D. Ruzic, University of Illinois at Urbana-Champaign

In the context of extreme ultraviolet (EUV) lithography, the evaporation of tin droplets frequently leads to the deposition of tin on various chamber surfaces, including collector mirrors. A prevalent method to remove this tin deposition involves hydrogen plasma etching, which transforms the deposited tin into stannane (SnH$_4$). This compound, existing in a gaseous state under operational conditions, can be evacuated from the chamber using a vacuum pump. However, stannane is characterized by its instability, tending to decompose and adhere to various surfaces within the chamber.

To systematically study the decomposition behavior of stannane, a specialized experimental chamber has been designed. This chamber integrates a load-lock mechanism for inserting a test tube containing liquid stannane into a loading section, which is isolated from the main vacuum chamber by a valve. Within the main chamber, a quartz crystal microbalance (QCM), regulated by a cartridge heater, measures the mass of stannane deposits. The QCM will be set to temperatures between 30-300°C. Upon opening the valve, the stannane vaporizes and interacts with the temperature-controlled QCM, facilitating the quantitative determination of the sticking coefficient as a function of both the surface material and the temperature.

Stannane is synthesized through the reaction of LiAlH$_4$, SnCl$_4$, C$_8$H$_{18}$O, and C$_4$H$_{10}$O$_2$. The four chemicals are mixed in a 3-neck flask while under vacuum. The reaction produces SnH$_4$which is flows through three U-tubes traps. The first trap is held at -96°C to trap precursors, the second two traps are help at -196°C and trap the stannane. The stannane is increasingly pure the more traps are used.

This investigation aims to understand and quantify the mechanisms of stannane deposition and decomposition, enhancing the maintenance and efficiency of EUV lithographic systems by optimizing the cleaning protocols for tin contamination.

11:00am SS+AMS+AS+CA+LS-FrM-12 First Principles Methods for Predicting Surface Reaction Mechanisms for Chemical Functionalization of Semiconductor Surfaces, *Roberto Longo,* S. Sridhar, P. Ventzek, Tokyo Electron America Inc.,

The density of semiconductor devices continues to increase, accompanied by the subsequent scaling down of the critical dimension (CD) size, which is now on the order of a few nanometers. This results in device structure changes, from two-dimensional (2D) to three-dimensional (3D) structures, because the CD size has reached its limit of reduction. To accomplish this, precise chemical modification of the required surfaces with atomic scale precision is key to obtain the desired geometric control. Precise modification implies being able to leverage knowledge of individual plasma born species and surface interactions. Unfortunately, species specific chemical interaction mechanisms in the context of reactive ions and chemical etching are still poorly understood for the full range of chemical environments at play. Once dissociated in plasma radicals, there might be a wide array of compositions. For similar atomic compositions, variations in the molecular structure of the chemical precursor can also result in significant differences as to the surface modifications and subsequent etching characteristics. The chemical nature of the surface including coverage and chemical activity add significant dimensionality to the problem of controlling plasma surface interactions in general. We divide the problem of elucidating plasma surface interactions into two major categories for practical purposes: hydrofluorocarbon driven for oxide etch and halogen driven for silicon etch. We present here semiconductor surface modeling with general characteristics and investigate the reaction mechanisms undergone by a large variety of hydrofluorocarbon molecular precursors using density-functional theory (DFT), with a focus on reactive halogen adsorption. Given the large parameter space of this problem, we describe computational approaches that efficiently and accurately generate fundamental data. Physical and chemical surface reactions and the corresponding byproducts are identified, obtaining self-limitation thresholds for each specific functionalizing chemistry. Therefore, our computational results provide valuable insights on the complex physical, chemical, and dynamic molecular and ion interactions with functionalized semiconductor surfaces, paving the road for designing tailored strategies with the desired outcome for each specific system.

11:15am SS+AMS+AS+CA+LS-FrM-13 A Model Interstellar Medium Reactivity Study: Low Energy Electron Induced Chemistry of CH$_3$OH@H$_2$O, *Ahmad Nawaz,* M. Asscher, The Hebrew University of Jerusalem, Israel

The desorption kinetics for MeOH@H$_2$O sandwich films from Ru(0001) surfaces are investigated using temperature-programmed desorption (TPD) at ultrahigh vacuum, with a base pressure of 2×10^{-10} Torr and temperature 25K. The TPD spectra of all the prominent stable molecular products were well detected by an in-situ quadrupole mass spectrometer (QMS). However, variation of the QMS signals were observed to be lower at different exposure to the negative charges in different time interval. Further, the MeOH parent molecules decompose, upon exposure to electrons at energies of 100 eV and 6.4 eV. Molecules at m/z of 2, 28 and 44, assigned to H$_2$, CO and CO$_2$, were the most abundant products. The typical mass spectra of the parent molecules within the sandwich layer (16 ML) are shown in Figure 1. Here, the MeOH peaks appears at ~140K while the water desorption peak is at ~160K.

Author Index

Bold page numbers indicate presenter

Author Index