Surface Science
Room Ballroom BC - Session SS-ThP
Surface Science Poster Session

**SS-ThP-1 Exploring the Oxidation State Void between Single-Atom Alloys and Single-Atom Catalysts: Insights from RhCu and PtCu Alloys*, Vinita Lal*[1]*,* *E. Charles H. Sykes,* Tufts University

Our aim is to explore the phase space between single-atom alloys (SAAs) and single-atom catalysts (SACs), where both the support and the single-site species exist in a partially oxidized state. SAAs have been extensively studied for hydrogenation, dehydrogenation, and coupling reactions, with growing interest in their potential for selective oxidation chemistry. However, their behavior under oxidizing conditions remains less understood. Since oxidation plays a crucial role in numerous catalytic processes, uncovering how oxygen interacts with SAAs and influences their reactivity and selectivity is essential for expanding their applicability in oxidation reactions. By investigating these interactions, we aim to provide new insights into the catalytic potential of SAAs and bridge the knowledge gap between SAAs and SACs.

To achieve this, we use well-defined model systems to study oxygen-mediated reactivity in SAAs. We investigate the oxidation of RhCu(111) SAAs using iodomethane as a probe molecule to examine how pre-adsorbed oxygen affects C-H activation and C-C coupling on both Cu(111) and RhCu(111). Through temperature-programmed desorption (TPD) and density functional theory (DFT) modeling, we show that C-H activation is inhibited on oxidized RhCu(111) compared to Cu(111) and that product selectivity follows distinct trends on SAAs relative to Cu(111) as a function of oxygen coverage. Expanding this framework, we explore O_2 activation and methanol oxidation on the PtCu(111) SAA system. TPD, X-ray photoelectron spectroscopy (XPS), and DFT analyses reveal that Pt slightly inhibits Cu(111) oxidation, contrasting with the promoting effect of Rh single atoms. However, Pt does not significantly alter Cu's selectivity in methanol oxidation, highlighting the complex role of different single-atom species in oxidation chemistry.

By shifting the focus from traditionally studied reducing conditions to oxidized environments, this work deepens our understanding of SAA reactivity and provides a foundation for tuning single-site catalysts for selective oxidation reactions. Our findings contribute to a broader understanding of how SAAs operate under oxidizing conditions, offering insights that could help guide the design of catalysts with enhanced functionality for industrially relevant oxidation processes.

SS-ThP-2 Development and Application of an Optimized Photo-Assisted Metal-Assisted Chemical Etching for Overcoming Fabrication Challenges in GaN Schottky Diodes*, Krystal Woodruff*, Kyma Technologies

Gallium nitride (GaN) has come up as a highly promising semiconductor material due to its wide band-gap, high breakdown voltage, and excellent thermal properties, making it ideal for high-power, high-frequency devices. Metal-assisted chemical etching (MacEtch) offers an adaptable approach to patterning GaN by combining the anisotropic control typical of dry etching with the cost-effectiveness and lower sidewall damage associated with wet etching. In this study, Kyma GaN wafers were subjected to MacEtch with a variety of solution concentrations, temperatures, and etch durations. The resulting etched structures were characterized using techniques such as scanning electron microscopy, white light interferometry, and optical microscopy.

The findings revealed a clear relationship between MacEtch parameters and subsequent GaN etch rates and surface morphologies. When applied as a trenching technique to Schottky diode structures, moderately etched devices showed improved reverse breakdown voltage, as expected from the trench architecture over planar structures. Ultimately, the work demonstrates how MacEtch can be used as an alternative to dry etching, as well as its ability to be used as a trenching technique to enhance the blocking voltage performance of GaN-based Schottky diodes. With refined processes and careful control of environmental factors, MacEtch holds significant promise for advancing GaN device fabrication, particularly in high-power applications.

SS-ThP-3 Product Promoted Acetylene Cyclotrimerization to Benzene and Propyne-Acetylene Coupling to Toluene on Ag(111)*, Nipun Kahagalla Dewage*, Tufts University*; Santu Biswas,* Tulane University*; Dennis Meier, Volkan Çinar,* Tufts University*; Matthew M. Montemore,* Tulane University*; Charles Sykes,* Tufts University

Benzene (C_6H_6) and toluene (C_7H_8) are irreplaceable chemical feedstocks for various products ranging from pharmaceuticals to building materials. They are primarily produced through petroleum cracking and reforming, which require high energy input, severe operating conditions, and lack 100% selectivity. With the shift from oil to shale gas as a hydrocarbon feedstock, there is an interest in alternative methods to produce C_6H_6 and C_7H_8. One promising pathway is the cyclotrimerization of acetylene (C_2H_2), which uniquely achieves 100% selectivity to C_6H_6 on the Ag(111) surface. However, it requires more than a monolayer (ML) of acetylene to initiate the benzene formation, necessitating high reactor pressures that could limit its industrial feasibility.

In the first study, acetylene cyclotrimerization on Ag(111) was investigated using Temperature Programmed Desorption (TPD), 12 Kelvin Scanning Tunneling Microscopy (STM), and Density Functional Theory (DFT) to explore how 2D compression by the reaction product benzene affects reaction rate. Isotopically labeled benzene (C_6D_6) was used to investigate the coadsorption of benzene and acetylene. Our results demonstrate that coadsorbed benzene (1/3 ML C_6D_6) enhances acetylene conversion and lowers the threshold acetylene coverage from 1 ML to ~0.3 ML. Increasing C_6D_6coverage up to 1 ML further enhances acetylene conversion, whereas an increase beyond 1 ML reduces both conversion and benzene yield due to decreased surface site accessibility for acetylene. DFT calculations show that the presence of two parallel and slightly overlapping benzene molecules with two acetylene molecules on a 4×4 Ag slab has the lowest energy for the rate-limiting step of forming the C_4 reaction intermediate compared to other possible coadsorbed configurations. The local organization was further investigated by STM confirming similar molecular density of acetylene and benzene as used for the DFT calculations.

In our second study, C_2H_2 and C_3H_4 were coadsorbed to examine the coupling between C_2H_2 and C_3H_4 by TPD and DFT. C_2H_2 and C_3H_4 undergo coupling at a full monolayer of coadsorbed molecules. However, C_7H_8 is just a byproduct (~5%), while C_6H_6 remained the main product (95%). C_3H_4 does not couple with itself to form either benzene or trimethylbenzene on Ag(111), which aligns with the high reaction barrier for C_3H_4 self-coupling suggested by DFT due to sterics.

These findings provide fundamental insights into product-driven promotion of acetylene cyclotrimerization and hetero-coupling of C_2H_2 and C_3H_4 on Ag(111), informing strategies for catalyst design and identifying a new reaction pathway for toluene production.

SS-ThP-4 Ni Nanocluster formation and Intercalation in Graphene/Ir(111) Heterostructures*, Shilpa Choyal*, University of Illinois at Chicago*; Michael Trenary, Nan Jiang,* University of Illinois - Chicago

The interfacial engineering of graphene-metal heterostructures through atomic intercalation presents a powerful approach for modulating electronic properties while preserving graphene's structural integrity. This investigation examines the temperature-dependent evolution of transition metal nanoclusters on epitaxial graphene/Ir(111) surfaces, with emphasis on intercalation mechanisms and their effects on the electronic structure of graphene.

Using high-resolution scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED), we characterized the structural transformations occurring when Ni is deposited onto graphene/Ir(111) at various temperatures. The pristine graphene layer exhibits a characteristic moiré pattern with 2.5 nm periodicity, resulting from lattice mismatch between graphene and Ir(111). Upon metal deposition at ambient temperature, Ni nanoclusters demonstrate remarkable site selectivity, exclusively nucleating at fcc sites among three possible adsorption positions. At ambient temperature, these nanoclusters form triangular islands aligned with the substrate's close-packed directions, spanning multiple moiré units with lateral dimensions of 10-15 nm and vertical heights of 1.4 nm.

Thermal annealing at 900 K induces Ni intercalation between graphene and Ir(111), as evidenced by the disappearance of surface clusters and emergence of a reverse moiré pattern compared to graphene on Ir(111). After intercalation, atop sites appear as bright protrusions instead of depressions. For Ni intercalation, we observe two distinct moiré patterns which are round and clover-like in shape, arising due to intercalation under

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two different adsorption sites. Upon further annealing to 1500 K, the intercalated metals adopt pseudomorphic growth on Ir(111), maintaining epitaxial registry despite significant lattice mismatch. This indicates substantial electronic interaction with both graphene and substrate. These insights advance the fundamental understanding of interfacial phenomena in two-dimensional materials and provide pathways for developing graphene-based electronic devices with tailored properties.

SS-ThP-5 Understanding Azide Modifications on Metal Oxides: A Window Into a New Class of Small Molecule Inhibitors*, **John Mason**, Andrew Teplyakov,* University of Delaware

Recent developments in area selective atomic layer deposition (AS-ALD) target requirements for smaller sized features as well as better control over surface chemical modification that governs the selectivity. This has brought attention to the use of small molecule inhibitors (SMIs) as a tool to assist in altering surface reactivity and thus enabling the miniaturization of these features. Azides are a common molecular species that has gained interest for surface modifications due to their non-reactive biproducts, nitrogen doping capabilities, and reactivity when brought into contact with a surface. This study aims to explore the reaction pathways for two different azides, trimethylsilyl azide and benzyl azide, and their reactions on metal oxide surfaces to see what conditions are needed to react with these surfaces, and what the surface species is afterwards. Using in-situ infrared spectroscopy and X-ray photoelectron spectroscopy we aim to observe the bonding configuration of these azide molecules on metal oxides and to explore the stability of the resulting surfaces as a pathway towards utilization of azides as SMIs.

SS-ThP-6 Surface Properties of Zirconium diboride (0 0 0 1) and Homoepitaxial Growth of Zirconium diboride as determined by Scanning Tunneling Microscopy*, Michael Trenary, **Ayoyele Ologun**,* University of Illinois - Chicago

Zirconium diboride, ZrB$_2$, a group-IV metal-terminated diboride, is an extremely hard material with a high melting point of 3246 °C and can be grown conformally via chemical vapor deposition (CVD) using zirconium borohydride Zr(BH$_4$)$_4$ as a precursor. Using ultrahigh vacuum scanning tunnelling microscopy (STM), we investigated the atomic-scale structure of ZrB$_2$(0001) and the homoepitaxial growth of ZrB$_2$ on this surface.After exposures of Zr(BH$_4$)$_4$ to ZrB$_2$(0001) at 1473 K and immediately cooling to room temperature, Zr-terminated bilayer islands of ZrB$_2$ were observed. Coalescence of the ZrB$_2$ islands was observed when the substrate was left for 60 minutes at the deposition temperature before imaging at room temperature. In contrast, exposure at 900 K resulted in high-density clusters. Stepwise annealing at 1400 K led to the transformation of these clusters into a continuous thin film via thermal-induced coalescence.

SS-ThP-7 Comparing Computational Methods for Predicting STM Images*, **Kaitlyn Handy**, Alex Kandel,* University of Notre Dame

Scanning tunneling microscopy (STM) allows for an image to be constructed of a molecular surface. STM utilizes a tunneling current that interacts with the electronic density of states to produce a topographic image of a surface. With the knowledge of how these STM images are created, then theoretical predictions for molecular surface STM images can be produced and compared to experimental data to verify predicted molecular geometries.

There are two different methods for predicting STM images that are being investigated through this work. The first method calculates molecular electron density from gas-phase calculations. The STM images are then generated by varying the tunnel decay, current, and molecular orbitals. The second method is VASP; calculating the full electronic structure of the molecule in the presence of a surface to create a predicted STM image. This study aims to determine the conditions that the gas-phase STM images, which are computationally cheaper, are able to produce results comparable to VASP. Thus far, the accuracy of these images has been found to depend on molecular planarity and the orientation of the molecule relative to the surface.

SS-ThP-8 Investigation of sub-Nanoscale Light-Matter Interactions in Carbon Nanomaterials Using Tip-Enhanced Raman Spectroscopy*, **Yuto Fujita**[1],* Keio University, Japan*; Norihiko Hayazawa,* RIKEN, Japan*; Maria Vanessa Balois-Oguchi,* Institute of Science Tokyo, Japan*; Satoshi Yasuda,* Japan Atomic Energy Agency, Japan*; Takuo Tanaka,* RIKEN, Japan*; Tomoko K. Shimizu,* Keio University, Japan

Tip-enhanced Raman spectroscopy (TERS) is a powerful technique for exploring novel optical phenomena, especially light-matter interactions at the nanometer scale [1]. It takes advantage of the near-field light generated at the apex of a sharp metallic tip. By utilizing the gap-mode between the tip apex and a metallic surface, spatial resolutions of approximately 1 nm [2] or even sub-nanometer resolution [3,4] can be achieved. In this study, we use a scanning tunneling microscope (STM)-based TERS system with sub-nanometer resolution in ambient conditions [4] to examine light-matter interactions in carbon nanomaterials under sub-nanometer scale light confinement in a working environment. While conventional far-field Raman spectroscopy of carbon nanotubes (CNTs) shows a weak D-band, typically attributed to defect-induced scattering, we found that TERS spectra revealed a significantly enhanced D-band, suggesting a different excitation mechanism. We propose that the high wavenumber of the near-field light preserves momentum conservation for electronic transitions associated with the D-band in TERS measurements, a role typically played by defects in conventional Raman scattering [5]. These findings highlight the unique effects of sub-nanoscale light confinement on electronic excitations in materials. Further discussions, including results for graphene, will be presented.

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SS-ThP-9 Localized Physical and Chemical Manipulation of Surfaces via Thermal Scanning Probe Lithography (t-SPL)*, **Nicholas Hendricks**, Emine Çağin,* Heidelberg Instruments Nano AG, Switzerland

Modification of thin film surfaces is of the utmost importance for various applications ranging from biosensors and spintronics to flat optics and magnonics. To push the performance of such applications to the next level, the optical, electrical, chemical, or magnetic properties need to be locally controlled at the sub-50nm length scale. To convert thin film surfaces, the use of direct-write lithography techniques is often employed where the film is manipulated by electrons, photons, or ions. These energetic particles can induce physical and chemical changes, however, the direct use of thermal energy as the stimulus could provide a more universal stimulus as well as an alternative route for such modifications. With thermal scanning probe lithography (t-SPL), enabled by the NanoFrazor from Heidelberg Instruments, the use of heat to perform direct-write patterning conversions is possible [1-5].

t-SPL generates patterns by scanning an ultrasharp tip over a sample surface to induce local changes with a thermal stimulus. By using thermal energy as the stimulus, it is possible to perform various conversion processes such as functional surface group deprotection, precursor conversion, and crystallization. Along with an ultrasharp tip, with a radius less than 10nm, the t-SPL cantilever contains several other important functions such as an integrated thermal height sensor, a capacitive platform for electrostatic activation, and an integrated heating element. By having a cantilever with such properties, it's possible to generate 2D and grayscale chemical gradients where surface chemistry is critical.

In this presentation, the background and workings of t-SPL will be introduced along with the lithography and processing steps necessary to create chemical gradients through the deprotection of functional groups for enzyme and protein patterning. The patterning of a phase change material (PCM) of GeSbTe (GST) will also be discussed where sub-300nm phase changes have been optically observed.

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SS-ThP-10 Probing the Oxygen-Driven Metal-Support Interactions in Pt/TiO_2 with Near-Ambient Pressure Spectroscopy and Microscopy*, **Gaurav Anand**, Florian Kraushofer, Matthias Krinninger, Marina de la Higuera-Domingo, Lorenz Falling, Barbara A.J. Lechner,* Technical University Munich, Germany

Platinum supported on titanium dioxide (Pt/TiO_2) is a prototypical model system for studying redox reactions and understanding metal-support interactions in surface science studies for heterogeneous catalysis. The Pt/TiO_2 interface serves as a dynamic active site, and can modulate catalytic activity, particularly under mild reaction conditions. However, as we approach more realistic environments - where elevated temperatures and pressures introduce complex, intertwined interactions between the metal particles, the oxide support, and gas-phase species - more sophisticated experimental probes are required. For example, in oxidizing environments the behavior of Pt on rutile TiO_2 remains debated. While encapsulation via classical strong metal support interaction (SMSI) - where Pt is buried by a reduced TiO_x ($x < 2$) overlayer[1] - has been well-documented in reducing conditions, recent observations suggest that oxidizing conditions can also lead to encapsulation via a "non-classical" mechanism.[2] In the latter scenario, a stoichiometric TiO_2 layer is observed to overgrow Pt, but the driving forces behind this phenomenon remain unclear, partly due to ill-defined defect densities within the oxide support.

We employ near-ambient pressure scanning tunneling microscopy (NAP-STM), X-ray photoelectron spectroscopy (NAP-XPS), and low-energy ion scattering (LEIS) to investigate the Pt/TiO_2(110) interface under oxygen pressures ranging from ultra-high vacuum (UHV) to 1 mbar. Our results reveal a strong correlation between the oxidation state of Pt, the stability of Pt nanoparticles, and the stoichiometry of the TiO_2 support.[3] Under low oxygen pressures and on reduced TiO_2 substrates, Pt nanoparticles become encapsulated by stoichiometric TiO_2 overlayers, likely driven by substrate reoxidation and the presence of metallic Pt, while the classical SMSI-driven TiO_x ($x < 2$) overlayer remains unchanged. In contrast, at higher oxygen pressures, Pt nanoparticles exhibit increased resistance to encapsulation, potentially due to Pt oxidation.[4] Furthermore, on near-stoichiometric TiO_2 substrates, encapsulation is suppressed even at near-ambient oxygen pressures, allowing Pt nanoparticles to undergo oxidation instead. These findings provide new insights into the complex nature of metal-support interactions in oxidizing environments and offer a more nuanced understanding of Pt/TiO_2 catalysts under realistic reaction conditions.

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SS-ThP-12 Methanol Dehydrogenation on Pt / Cu (111) Single Atom Alloy Surface*, Michael Trenary, **Vishwa Don Lokugan Hewage**,* University of Illinois - Chicago

Pt/Cu(111) single atom alloys (SAAs) have been reported to catalyze the non-oxidative dehydrogenation of alcohols, selectively forming the corresponding aldehydes and hydrogen. They do so by facilitating O-H bond cleavage to form an alkoxy intermediate and C-H bond cleavage of the alkoxy to form the aldehyde. In this study, methanol dry dehydrogenation reactions on Pt/Cu(111) SAA surfaces were investigated using reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) to determine reaction intermediates and pathways. Although no formaldehyde desorption was observed from Cu(111), 0.02 ML of formaldehyde desorbs from a Pt/Cu(111) surface at 375 K. A RAIRS peak at 1005 cm^{-1} on the SAA surface, observed at 250 K, was assigned to the C–O stretching mode of methoxy, compared to the corresponding methoxy C–O stretching peak(1005 cm^{-1}) on an oxygen-pre-adsorbed Cu(111) surface. The methoxy yield (0.001 ML), estimated from the CO stretching peak area on the SAA surface, was lower than the number of Pt single atoms (0.04 ML), contrary to the expectation that a single Pt site could form multiple methoxy molecules via spillover onto Cu sites. To assess the effect of background CO, the formaldehyde yield was compared to an SAA surface where Pt sites were blocked by CO dosed at 250 K. The formaldehyde yield decreased by approximately 50%, confirming that background CO suppresses the reaction yield on the Pt/Cu (111) SAA surface. These findings provide insights into the mechanistic role of Pt sites in methanol dehydrogenation and the impact of surface species on catalytic efficiency.

SS-ThP-13 Automated Workflows in Photoelectron Spectroscopy: Enhancing Reproducibility and Efficiency*, **Jonathan Counsell**, Liam Soomary,* Kratos Analytical Limited, UK*; Chris Moffitt,* Kratos Analytical Inc.

The widespread application of X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS) in materials characterization necessitates automation to improve workflow efficiency and analytical consistency. Reproducibility challenges, stemming from operator-dependent data processing and spectral interpretation, threaten the reliability and broader utility of these techniques. Automated data handling systems mitigate analyst bias, reduce errors, and enhance the comparability of results across different laboratories.

This work explores the implementation of automated workflows in XPS and UPS, focusing on large-area analysis, depth profiling, and data compilation. We examine key challenges such as X-ray-induced damage, transmission and analysis area calibration, surface uniformity, and quantification consistency. Case studies will highlight automated solutions for handling complex material systems, demonstrating the role of advanced data processing in standardizing spectral interpretation. Furthermore, we discuss recent developments in high-throughput XPS systems that incorporate automated spectral fitting, background subtraction, and large-scale data integration, improving data reliability and reducing manual intervention [1,2].

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SS-ThP-14 Single-Atom Cu-Embedded Mo_2Ct_x Mxene for Selective Reduction of Co_2 to Methane*, **Dinushika Kotudura Arachchige**,* University of Florida, Gainesville

The electrochemical reduction of CO_2 (CO_2RR) is a promising approach to mitigating carbon emissions while generating value-added products under ambient conditions. However, achieving high selectivity and efficiency remains challenging due to the competing hydrogen evolution reaction (HER) and the strong correlation of binding energies among reaction intermediates. Single-atom (SA) catalysts, with their unique electronic properties, have emerged as promising candidates for CO_2RR. However, their performance is often limited to CO production at high overpotentials, and their stability is compromised due to atom aggregation.

MXenes, with their high surface electron density, provide a robust platform for stabilizing transition metal SAs, preventing aggregation under catalytic conditions. Herein, we report the design and synthesis of a Cu SA-embedded 2D Mo_2CT_x MXene electrocatalyst for the selective reduction of CO_2 to methane (CH_4) at low overpotentials. The successful incorporation of Cu SAs into the 2D MXene sheets led to a high Faradaic efficiency (~94%) for CH_4 formation at low applied potential (~ -0.3 V vs RHE), with significant suppression of HER. This enhanced selectivity is attributed to the strong CO adsorption on Cu SAs via back-donation, prolonging its residence time and facilitating further hydrogenation through MXene surface functional groups.

SS-ThP-15 Kevion: An Ion Irradiation Facility for Transformative Research in Space Science at the University of Virginia*, **Adam Woodson**, Catherine Dukes, Aubrey Carley, Robert Johnson,* University of Virginia*; Jeroen Terwisscha van Scheltinga,* Leiden University, Netherlands*; John Ihlefeld, Petra Reinke, Robin Garrod, Ilsedore Cleeves,* University of Virginia

The KiloElectron Volt ION (KEVION) irradiation facility for space science — a new NASA Planetary Science Enabling Facility — is under development within the Laboratory for Astrophysics and Surface Physics at the University of Virginia (LASP-UVa). This user-focused facility, available at no cost to NASA Planetary Science Division (PSD) grantees, is comprised of four integrated components: (1) a 25–300 keV Pelletron ion accelerator to provide positive atomic or molecular ions over a wide range of species, charges, and energies; (2) a novel, new ultrahigh vacuum (UHV) chamber called "GRAINS" that incorporates X-ray photoelectron spectroscopy, mass spectrometry, hyperspectral imaging, and more for holistic studies of geologic samples and other materials; (3) an established, well-tested cryogenic UHV chamber, aptly named "ICE", for studies concerning the irradiation of condensed gas targets; and (4) a minimally equipped, user-configurable UHV chamber called "TEST" for instrument testing, calibration, and prototyping. The KEVION is expected to facilitate transformative research in space weathering, radiolysis, radiosynthesis, sputtering, radiation damage, surface charging, and instrument development/response testing.

A full-time facility instrument scientist is available to assist with experiment planning, instrument operation, instrument training, and data analysis. The KEVION facility will be fully operational by the end of 2025, though the GRAINS chamber chamber will be ready for use without the Pelletron by the summer of 2025. The facility will be accessible both in person and remotely. Specific details of the Pelletron accelerator and analytical techniques associated with each end chamber are summarized on the KEVION website at https://engineering.virginia.edu/kevion, and on the NASA Science Mission Directorate website at https://smd-cms.nasa.gov/wp-content/uploads/2023/06/KEVION.pdf.

Investigators submitting proposals to any of the NASA PSD funding programs are encouraged to integrate the KEVION facility into their research plans. We also welcome non-PSD academic, governmental, and industrial clients to make use of the facility at a nominal, tiered hourly rate. For more information email Cathy Dukes at cdukes@virginia.edu or Adam Woodson at akw8r@virginia.edu.

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SS-ThP-16 The Importance and Reporting of NAP-XPS Instrument Parameters*, **Braxton Kulbacki**, Joshua Pinder, Jacob Crossman, Matthew Linford,* BYU

X-ray photoelectron spectroscopy (XPS) data acquisition is directly affected by a variety of instrumental and software parameters. Accordingly, gaining a full picture and proper understanding of the material being analyzed and reported on, requires adequate reporting of these parameters. With recent advancements in XPS technique, XPS has become more commonplace. Although XPS is being used at an increasing rate, the number of XPS experts has not increased at the same rate. Thus, inadequacies in reporting are becoming more prevalent. A variant of XPS, called Near-ambient pressure XPS (NAP-XPS) is important because it allows data to be taken at much higher pressures than is done conventionally. Many samples that cannot be analyzed by conventional XPS can be analyzed by NAP-XPS. This poster examines parameter reporting within NAP-XPS – containing publication results from 2021 to 2023, highlighting gaps in parameter documentation. The reported parameters include the electronic analyzer (spectrometer), photon flux, X-ray source (synchrotron or anode) and energy, spot size, pass energy, dwell time, incident angle, substrate temperature, aperture size and distance, background gas, and fitting parameters such as background and peak shape. The general findings show that, on average, less than 50% of instrument parameters are recorded. A survey of X-ray sources revealed that over 50% of NAP-XPS experiments are conducted at synchrotrons. There is considerable variation in the frequency of parameter reporting: for instance, the analysis chamber pressure is reported 94% of the time, while dwell time is only reported 6% of the time. The large majority (92%) of papers contain fit data, but fewer than 50% of the literature report fitting parameters. Less than 5% of NAP-XPS studies are operando, among other findings. By emphasizing the critical role of various NAP and XPS parameters, we aim to promote best practices and enhance data reliability across the field.

SS-ThP-17 Landing Energy Dependent Surface Conformation of Electrosprayed Foldamer Molecules*, **Dennis Meier**,* Tufts University, Germany*; Shengming Zhang, Benedikt Schoof,* Technical University Munich, Germany*; Patrick Lawes,* Karlsruhe Institute of Technology (KIT), Germany*; Pengfei Zhao, Andreas Walz, Annette Huettig, Hartmut Schlichting, Joachim Reichert,* Technical University Munich, Germany*; Anthoula C. Papageorgiou,* Technical University Munich, Greece*; Ivan Huc,* Ludwig-Maximilians-University of Munich, Germany*; Johannes V. Barth,* Technical University Munich, Germany

Biomimetic molecules hold great potential for molecular devices, where preserving their secondary structure is crucial for maintaining functional properties. When assembled in well-ordered two-dimensional configurations, such molecules can exhibit unique characteristics. For example, helical aromatic foldamers are promising for molecular recognition and molecular machinery. Many of these macromolecules, however, cannot be sublimed by, e.g., organic molecular beam epitaxy onto surfaces in ultra-high vacuum (UHV). Electrospray controlled ion beam deposition (ES-CIBD) combines non-destructive landing onto surfaces with a low level of contaminants in UHV, due to soft ionization *via* electrospray ionization, mass filtering and control of the landing energy. We addressed the deposition of two oligoamides of 8-amino-2-quinoline-carboxylic acid with different lengths on metallic surfaces in a UHV environment using ES-CIBD. In particular, we investigated how their landing energy during deposition influences the helical conformation. On the surface, the conformation of the molecules was unambiguously identified through real-space single-molecule imaging *via* scanning tunneling microscopy. At a low landing energy, the helix of the molecular structure was preserved after adsorption. Thermal treatment of the surface induces unfolding of the molecules. Increasing the landing energy resulted in mostly unfolded and partially folded molecules. At high surface coverages, a well-ordered self-assembly of the unfolded molecules was formed. We thus unravel the influence of the landing energy upon adsorption of complex molecules and provide a pathway for depositing intact molecules with well-defined secondary conformations on surfaces in UHV.

SS-ThP-18 Understanding Pt-Based Catalysts for Dehydrogenation of Methylcyclohexane for Use in Liquid Organic Hydrogen Carriers*, **Mengxiong Qiao**, Bhawana Rayamajhi, Andreas Heyden, Donna A. Chen,* University of South Carolina

Hydrogen is a promising source of clean and renewable energy, but a major challenge lies in its storage and transportation. The use of liquid organic hydrogen carriers (LOHC) allows hydrogen to be stored in organic molecules that are liquids at room temperature and therefore suitable for transportation through the existing infrastructure for petroleum. For example, the methylcyclohexane (MCH)-toluene pair has been used for the catalytic cycle of hydrogenation to store hydrogen and dehydrogenation to release hydrogen. While inexpensive and efficient catalysts are already available for hydrogenation, there is still the need for the development of selective dehydrogenation catalysts that inhibit deactivation due to carbon fouling.

In this work, model surfaces consisting of Pt(111), supported Pt clusters, and single-crystal Pt-Sn alloy surfaces were prepared in ultrahigh vacuum (UHV, $P \leq 2x10^{-10}$ Torr) and then transferred directly into a high-sensitivity flow reactor operated in recirculation mode for kinetic studies under realistic pressure conditions. The turnover frequency for MCH dehydrogenation on the Pt(111) surface was four times lower than for Pt clusters supported on highly oriented pyrolytic graphite (HOPG) at 300 °C, and this behavior is attributed to the higher activity of undercoordinated sites that exist on the clusters. Furthermore, the ordered Pt-Sn alloy surfaces prepared by depositing and annealing Sn films on Pt(111) had less carbon deposition compared to on Pt(111) itself, as determined by post-reaction X-ray photoelectron spectroscopy.

The reaction mechanism of MCHdehydrogenation to toluene was also investigated using a combination of DFT and microkinetic modeling techniques on Pt(111), Pt(100), and Pt(211). A microkinetic analysis with a continuous stirred tank reactor (CSTR) model identified the intrinsic catalytic activity, dominant reaction mechanism, and rate-controlling steps for the conversion of MCH to toluene. These results suggest that for Pt catalysts, the more open (100) and (211) facets are more active. However, the calculations also suggest that thermodynamically all Pt surfaces favor coke formation although the kinetic barriers for Pt(111) are at least 1 eV higher than for the more open surface facets.Thus, the most coke-resistant Pt surface should be the one in which the step sites are blocked, perhaps by an inactive metal like Sn.

SS-ThP-19 Structural Study of Rhodium-Based Metal Surfaces*, **Elizabeth Serna-Sanchez**, Alexis Gonzalez, Maxwell Gillum, Stephanie Danahey, Dan Killelea,* Loyola University Chicago

Heterogeneously catalyzed oxidation reactions, such as the catalytic process of converting CO to CO_2, are extensively utilized for the production of modern commodities. However, there is little information known about the atomic level details of these catalytic processes. In order to further our understanding of the process at an atomic level, the investigation herein will focus on characterizing structures of oxygen on Rh model catalysts. Scanning tunneling microscopy (STM) images illustrate how the behavior of oxygen is affected by features such as surface defects and step width. Alongside the STM, other techniques such as temperature programmed desorption (TPD), and low energy electron diffraction (LEED) are used to identify the various species of oxygen and the structures they form on the surface.

SS-ThP-20 Self-assembly and On-surface Reactivity of β-diketonato Molecules on Au(111), ***Chamath Siribaddana,*** *Nan Jiang,* University of Illinois Chicago

Self-assembly and on-surface reactions of organic molecular building blocks are two versatile processes that can be utilized to synthesize well-defined nanostructures with functional properties. It is essential to study the intricate details of these processes at the nanoscale to achieve their controllability. This would enhance the ability to create defect-free nanoarchitecture with long-range order and the desired symmetry. The final nanoarchitecture depends on the properties of the molecule/molecules used as the building block, i.e., symmetry, functional groups, and intermolecular interactions; properties of the substrate, i.e., crystallinity, symmetry, catalytic activity, and molecule-substrate interactions, and reaction conditions, i.e., substrate temperature and byproducts. Ultra-high vacuum (UHV) conditions and single-crystalline surfaces offer a pristine and controlled environment to synthesize nanostructures and investigate how these factors influence their formation. Scanning tunneling microscopy (STM), with its sub-molecular resolution, enables detailed probing of these factors at the local scale. In this study, the self-assembly and on-surface reactivity of a β-diketonato molecule on Au(111) were explored using UHV-STM across a range of substrate temperatures. At room temperature, the molecules self-assemble primarily through intermolecular halogen bonding, with minimal influence from molecule-substrate interactions. At higher substrate temperatures, an Ullmann coupling reaction via a surface-assisted activation of C-I leads to the growth of a robust self-assembly stabilized by intermolecular C-C bonds. The symmetry of the underlying substrate has a templating effect on the symmetry of this resultant robust covalent organic network type self-assembly despite not affecting its precursor assembly, which is conformationally flexible. The progression of the reaction with respect to the substrate temperature reveals thermodynamically favorable conditions for network units with varying sizes and symmetry. These insights into self-assembly and on-surface reactivity enhance the design of synthetic pathways that lead to nanomaterials with desired functionalities.

SS-ThP-21 Transformation of TiN to TiNO films via In-situ Temperature-dependent Oxygen Diffusion Process and their Electrochemical Behavior, ***Sheilah Cherono,*** *Dhananjay Kumar,* North Carolina A&T State University

Titanium oxynitride (TiNO) thin films represent a multifaceted material system applicable in diverse fields, including energy storage, solar cells, sensors, protective coatings, and electrocatalysis. This study reports the synthesis of TiNO thin films with controlled amount of oxygen using pulsed laser deposition. A comprehensive structural investigation was conducted by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Non-Rutherford backscattering spectrometry (N-RBS) and X-ray absorption spectroscopy (XAS), which facilitated a detailed analysis that determined the phase, composition, and crystallinity of the films. Structural control was achieved via temperature-dependent oxygen in-diffusion, nitrogen out-diffusion, and the nucleation growth process related to adatom mobility. The XPS analysis indicates that the TiNO films consist of heterogeneous mixtures of TiN, TiNO, and TiO_2 phases. The correlation between the structure and electrochemical behavior of the thin films was examined. The TiNO films with relatively higher N/O ratio, meaning less oxidized, were more electrochemically active than the films with lower N/O ratio (more oxidized films). Films with higher oxidation levels demonstrated enhanced crystallinity and greater stability under electrochemical polarization. These findings demonstrate the importance of substrate temperature control in tailoring the properties of TiNO film, which is a fundamental part of designing and optimizing an efficient electrode material.

This work was supported as part of the Center for Electrochemical Dynamics and Reactions on Surfaces (CEDARS), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences at the North Carolina A&T State University under award DE-SC0023415. The work also used resources at the ALS of LBNL, supported by the Director, Office of Science, Office of Basic Energy Sciences, of the US Department of Energy under Contract No. DE-AC02-05CH11231. Part of the work was performed using the resources of NSF-PREM Collaborative Research and Education in Advanced Materials Center (grant number DMR-2425119) and the Joint School of Nanoscience and Nanotechnology, a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the National Science Foundation (Grant ECCS-2025462). Also, the work was partially supported by project ELI-RO/RDI/2024-015 and National Nucleu Program LAPLAS VII – contract no. 30N/2023.

SS-ThP-22 XPS Study of Initial Oxygen Adsorption on ZrB2 (0001) at Room Temperature, ***Cosmic Gober,*** University of Illinois - Chicago

Zirconium diboride (ZrB_2) is an ultra-hard material with a melting point of 3246 °C, making it suitable for extreme environment applications such as hypersonic vehicles and cutting tools. Understanding its interactions with molecular oxygen (O_2) is crucial for predicting its performance. This study investigates the nascent stages of oxygen uptake on the ZrB_2(0001) surface at room temperature. A clean, well-ordered ZrB_2(0001) surface, confirmed by a characteristic (1x1) low energy electron diffraction (LEED) pattern, was exposed to O_2 dosages ranging from 0.01 to 1.0 L. X-ray photoelectron spectroscopy (XPS) was employed to track the evolution of surface composition. Analysis of the O 1s spectra following even minimal exposures reveals multiple distinct oxygen species. Two primary components were identified: one at a binding energy of 533.8 eV corresponding to oxygen adsorbed on the surface, and another at 531.4 eV attributed to oxygen incorporated into the subsurface region. These findings indicate that even at very low O_2 exposures at room temperature, oxygen not only dissociatively adsorbed onto the ZrB_2(0001) surface but also begins to penetrate the subsurface layers. This work demonstrates the capability of XPS to distinguish initial surface and subsurface oxygen species on ZrB_2(0001). The observation of subsurface oxygen at room-temperature exposures provides critical experimental data for understanding the onset of its oxidation pathway.

SS-ThP-23 Enhanced Electrocatalytic and Supercapacitance Performances of Transition Metal Oxynitride Thin Films, ***Brianna Barbee,*** North Carolina A&T State University

The importance of research in the field of non-conventional energy generation and storage cannot be overemphasized in order to be less dependent on limited resources in nature. Our research has established the effectiveness of the pulsed laser deposition (PLD) method for the synthesis of an emerging class of transition metal oxynitride (TMON) material systems in epitaxial thin film form. The material systems cover a wide range of compositions that exhibit the physicochemical properties needed in electrocatalysis and extended-life electrochemical energy storage. The attraction of TMONs over more widely studied transition metal oxides (TMOs) is rooted in the polarizability, electronegativity, and anion charge of nitrogen versus that of oxygen, which induces an enormous change in the physical and chemical properties of the resulting compounds. TMON films were deposited in the absence and presence of liquid nitrogen stage in the PLD chamber, which is capable of adsorbing the residual oxygen in the PLD chamber. The films were characterized using high resolution x-ray diffraction, x-ray reflectometry techniques, and x-ray photoelectron spectroscopy. The electrochemical supercapacitor measurements on the TiNO films using cyclic voltammetry have shown that the specific capacitance values are amongst the highest values reported for the recently top-tier nanoscale electrode materials.

SS-ThP-24 The Initial Oxidation Reactions of Compositionally Complex Alloys, (Cr-Mn-Fe-Co-Ni), ***Farzad Bastani,*** University of Virginia, USA; *Keithen Orson, John R. Scully,* University of Virginia; *Petra Reinke,* University of Virginia, USA

The Cr-Mn-Fe-Co-Ni alloy with near-equimolar composition, known as the Cantor alloy, is a single-phase face-centered cubic solid solution and a compositionally complex alloy (CCA). These materials are stable as high configurational entropy solid solutions. CCAs can phase-separate into multi-phase systems and thus form compositionally and structurally complex surfaces. This complexity presents challenges for understanding surface reactions, particularly in catalysis and oxidation. This work examines the oxidation of polycrystalline Cantor, focusing on the composition and evolution of surface oxides as a function of time and temperature. Samples are sputter-annealed, and SRIM simulations model defect generation to consider near-surface defects in oxidation. Oxidation is studied under three conditions: (i) native oxide formed in ambient conditions, (ii) oxygen exposure in vacuum at variable temperatures, and (iii) cryogenic oxidation to “freeze” kinetics, suppress bulk diffusion, and isolate surface-limited reactions and O_2 dissociation. In-situ angle-resolved X-ray photoelectron spectroscopy (AR-XPS) is used to track chemical composition and layering in the alloy and oxide. Ni oxide formation is consistently suppressed, and Cr and Mn preferentially form stable oxides under all conditions. Co oxide appears only in the native oxide, which also contains Cr hydroxide and Cr, Mn, and Fe oxides in proportions similar to those formed under vacuum oxidation, highlighting its role as a persistent surface state. Vacuum-grown oxides display temperature-dependent selectivity: at 77K, oxidation is limited and surface-bound; at 298K, Fe oxide is still observed; and at 600K, only Cr and Mn oxides persist, suggesting enhanced thermodynamic control and surface Fe depletion. Oxide structure varies by route: native oxides are chemically mixed and layered, while elevated temperature vacuum oxides form binary (Cr-Mn) phases.

These results show that surface oxide chemistry is governed more by kinetic and thermodynamic factors than by bulk composition. We also examine how surface enrichment and segregation (induced by identical treatments at different fixed temperatures) affect oxide structure and stability. Activation barriers are tracked by correlating temperature-dependent XPS data with selective oxide formation to map energy thresholds for surface composition changes. Future work will extend the materials space to multiphase alloys and explore the effects of crystallographic orientation, mechanical properties, and microstructural stability of Cantor alloys at cryogenic temperatures, including potential embrittlement, phase separation, and aqueous corrosion.

SS-ThP-25 Atomic-Scale Investigation of Electron-Induced Processes at Single-Atom Alloy Active Sites*, **Nima Rajabi**, Charles Sykes,* Tufts University*; Phillips Hutchison, Emily Carter,* Princeton University

Single-atom alloys (SAAs) have captured significant interest as promising thermo- and electro-catalytic materials and most recently in the plasmonic photocatalytic field due to their unique electronic and chemical properties. Unlike thermal catalysis, plasmon photocatalysis enables energy-efficient, selective molecular activation via localized surface plasmon resonance (LSPR), which reduces energy consumption and provides more control over the reaction. However, the details of the mechanism by which adsorbates react or desorb are still unclear. Using scanning tunneling microscopy (STM) and spectroscopy (STS), we investigate the topography and electronic structure of four different SAAs—NiAg(100), PtAg(100), PdAg(100), and RhAg(100)—and their role in electron-stimulated CO desorption. STS and density functional theory (DFT) allow us to correlate local density of states with electron energy and probe the mechanism of desorption. Specifically, we can identify states associated with transient negative ion (TNI) formation, which plays a crucial role in facilitating plasmon-induced charge transfer. In plasmon-driven photocatalysis, this TNI state can arise from chemical interface damping (CID) or Desorption Induced via Electronic Transition (DIET), key decay pathways of LSPR. Our results indicate that SAAs exhibit drastically different CO desorption rate dependence on electron energy.

Moving forward, we explored the possibility that the TNI state contributes to bond weakening, leading to more efficient CO removal—a major challenge in catalytic processes. To further support our experimental findings, we employed DFT calculations and embedded correlated wavefunction (ECW) methods. These studies provide additional insights into the electronic structure modifications induced by CO adsorption and desorption. DFT results align with experiments, showing similar desorption trends for RhAg, PtAg, and PdAg, while NiAg deviates, suggesting a different mechanism possibly linked to TNI state formation via electron injection. Our findings provide deeper insights into the electronic and catalytic properties of SAAs and offer guidance for designing more efficient and sustainable photocatalysts that minimize the use of precious metals.

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