Tuesday Morning, September 23, 2025

Surface Science
Room 209 CDE W - Session SS+2D-TuM
Complex Phenomena on Surfaces

Moderators: Te-Yu Chien, University of Wyoming, **Bo-Hong Liu**, National Synchrotron Radiation Research Center

8:00am **SS+2D-TuM-1 Atomically Precise Synthesis and Characterization of Defect Structures in Graphene***, An-Ping Li,* Oak Ridge National Laboratory **INVITED**

Atomically precise engineering of defects and interfaces in graphene, along with a detailed understanding of its structure-dependent electronic properties, is essential for the advancement of graphene-based quantum electronic applications. Here we present recent progress in the controlled synthesis and atomic-resolution characterization of defect structures in graphitic nanomaterials. The first approach involves bottom-up synthesis of graphitic nanostructures using on-surface chemical reactions using rationally designed molecular precursors. Particularly, graphene nanoribbons (GNRs) are obtained on a non-metallic substrate, showing entangled magnetic states that are decoupled from the substrate. The multistep thermally triggered transformations rely on highly selective and sequential activations of C-Br, C-F bonds, followed by cyclodehydrogenation. Scanning tunneling microscopy and spectroscopy (STM/S) are used to monitor the formation of intermediates and GNRs, revealing a weak interaction between GNRs and the substrate. The second approach employs a top-down strategy to introduce oxygen (O) substitutions into epitaxial graphene grown on SiC. Techniques including ion implantation and STM tip-assisted manipulation are used to create sp^2-hybridized O dopants and control its configuration. A combination of chemical-bond-resolved non-contact atomic force microscopy (ncAFM) and STM is used to investigate the structural and electronic properties of the O-related defects. The STM/S measurements, supported by DFT calculations, indicate that the sp^2-hybridized O dopant hosts a characteristicπ-orbital electronic state below the Dirac point. Tuning the Fermi level with electric field may achieve single-electron occupancy of these atomically defined centers. Such control opens the door to the realization of long coherence electron-spin qubits, providing pathway toward graphene-based quantum technologies.

The research was conducted at the Center for Nanophase Materials Sciences (CNMS), a US Department of Energy User Facility.

8:30am **SS+2D-TuM-3 Fabrication of Graphene Nanoribbons/Organic Molecules Interface***, **A.M. Shashika D. Wijerathna,** Markus Zirnheld,* Old Dominion University*; He Zhao,* Central South University, China*; Rockwell Li,* Old Dominion University*; Pingshan Wang,* Central South University and Guangzhou University, China*; Yiming Li,* Central South University, China*; Yuan Zhang,* Old Dominion University

Graphene derivative materials are great superlubricant candidates that can be potentially utilized in molecular devices. Therefore, it is essential to understand the mechanical property at the interface that is formed by organic molecules and graphene derivatives materials. In this study, we fabricated an interface formed by organic molecules with armchair graphene nanoribbons and studied its mechanical properties.

15-carbon-wide armchair graphene nanoribbons (15-AGNRs) were synthesized on Au(111) substrate in a bottom-up approach with dibromo-p-pentaphenyl (DBPPP) as precursor molecules. Precursor molecules, DBPPP exhibit two different self-assembly patterns on Au(111) substrate, forming rectangular domains and hexagonal domains. Both self-assembly structures can be successfully transformed into 15-AGNRs through polymerization at 370 K and, subsequently, cyclodehydrogenation at 470 K. 30-GNRs were also observed in some cases.

Subsequently, pentacene molecules, a linear polycyclic aromatic hydrocarbon consisting of five linearly-fused benzene (C_6H_6) rings, were deposited onto the AGNRs to form the interface pentacene/AGNRs. Pentacene molecules exhibited a preference for adsorption on the Au(111) substrate than the graphene nanoribbons. Therefore, they first fill in gapping areas formed in between graphene nanoribbons, and once the metallic surface sites are fully occupied, they adsorb onto the ribbons. Pentacene is adsorbed on AGNRs in different orientations, which include nearly transverse, oblique, and nearly axial. Among these, the most energetically favorable and stable orientation is nearly transverse, where the pentacene molecular long axis is approximately 93° clockwise relative to the GNR axis. Notably, external mechanical energy facilitated the movement of pentacene molecules along the GNRs, suggesting low molecular-scale friction. These findings provide critical insights into the adsorption behavior of pentacene on AGNRs and mechanical properties of the interface, which is essential for advancing their applications in organic electronics.

This work is conducted with a low-temperature (~77 K), ultra-high vacuum (10^{-10} mbar) scanning tunneling microscopy (LT-UHV-STM).

Keywords: Armchair Graphene Nanoribbons, Pentacene, Friction at Molecular Interface, Adsorption Orientation, Scanning Tunneling Microscope

8:45am **SS+2D-TuM-4 Visualizing the Products of Scattering at Surfaces: Hot Transient Motion of N on Ru(0001) and Coverage Dependent Mobility and Placement of O on Moiré Graphene***, **Joshua Wagner**[1][2], Steven Sibener,* University of Chicago

Diffusion of atomic species is a pivotal process in surface chemistry for topics ranging from catalysis to material stability. This presentation focuses on two types of atomic mobility: the nonthermalized “hot” atomic motion of N atoms following dissociative chemisorption of N_2 and the highly correlated coverage-dependent diffusion of oxygen atoms on moiré patterned graphene. Overall, results provide spatially rich and atomically resolved insight to on-surface dynamics and illustrate a new direction in the study of interfacial reaction dynamics where outcomes such as site-specific reactivity and non-thermalized diffusion can be examined using incident kinetic energy and angle of incidence as reaction control parameters.

Ruthenium based materials serve as more energy efficient catalysts for the dissociative chemisorption of N_2, the rate limiting step of ammonia synthesis *via* the Haber-Bosch process. Despite the global importance of this chemical process, open questions remain concerning the dissipation of energy following dissociation. Answering these questions may inform catalyst design and will enrich our understanding of fundamental surface dynamics.

To probe the energy dissipation pathways of N_2 dissociation on Ru(0001), tight control of the energy and angle of incident N_2 is achieved *via* supersonic molecular beam fluxes of N_2 molecules. An in-line and *in situ* scanning tunneling microscope (STM) provides atomic-scale visualization of surface products. Analysis of the spatial distributions of N adatoms from the same molecule as a function of incident energy and angle provides insight to the energy dissipation pathways such as energy transfer to phonons and electron hole-pair excitations following dissociative chemisorption.

Exchanging a resistively heated pinhole nozzle for an RF plasma source, the molecular beam can also deliver supersonic ground state atomic oxygen. The site-specificity of atomic oxygen binding on the graphene-Ru(0001) moiré lattice is shown here to be coverage dependent. Furthermore, the stability of oxygen species on epitaxial graphene varies with the number of proximal O atoms as shown by STM imaging. Effects of multiparticle interactions appear in pair-distribution functions, oxygen binding distributions on the moiré lattice, and the diffusivity of O atoms. Comparison of monolayer versus bilayer graphene additionally demonstrates the role that spin-flipping dynamics play in the adsorption of $O(^3P)$ on graphitic surfaces. Overall, results provide insight to the stability of moiré-patterned two-dimensional materials which show promise as platforms for next-generation quantum materials and catalysts.

9:00am **SS+2D-TuM-5 Oxygen Diffusion Dynamics on a Rh(111)/(322) Multifaceted Surface***, **Alexis Gonzalez**, Elizabeth Serna-Sanchez, Maxwell Gillum, Stephanie Danahey, Dan Killelea,* Loyola University Chicago

The diffusion of oxygen on multifaceted Rhodium (Rh) crystals is of significant interest due to the importance of Rh in heterogeneously catalyzed reactions, such as surface-facilitated oxidation reactions. In this study, we investigate the diffusion dynamics and oxygen species on these two surfaces using temperature-programmed desorption (TPD) and low-energy electron diffraction (LEED) techniques. Despite the structural differences between the (111) and (322) facets, our experiments reveal that the oxygen species on both surfaces are similar, with oxygen existing on the surface as atomic oxygen shortly after adsorption. TPD experiments show that oxygen desorption occurs at comparable temperatures on both surfaces, indicating similar binding energies for oxygen species on each facet. However, LEED shows that there may be different structures forming on either side of the crystal and the orientation of oxygen species are

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[1] **AVS Dorothy M. and Earl S. Hoffman Awardee**

[2] **SSD Morton S. Traum Award Finalist**

dissimilar. These findings suggest that the oxygen species formed on both (111) and (322) surfaces are essentially the same even though the two surfaces have different atomic arrangements. This observation highlights the importance of other factors, such as surface defects and temperature, in governing the oxygen diffusion process. The study provides information on how surface structure influences the diffusion behavior of oxygen on Rh crystals and emphasizes the need for considering both surface morphology and adsorption characteristics in the design of catalytic materials.

9:15am **SS+2D-TuM-6 CO Adsorption on Gr/Ni(111) Single Point Defects*, Francesco Armillotta*[1]**, EPFL, Switzerland

Single atom catalysis (SAC) has attracted great interest due to its potential high selectivity, reduced material consumption, and activity. However, a detailed atomistic insight into the active sites and reaction details is still limited, which is fundamental for the understanding and engineering of SAC. We show that even simple molecular adsorption and desorption can reveal non-trivial aspects that affect, for example, the overall sticking probability. We study the CO chemisorption on a model single atom catalyst, where single Co and Ni atoms are adsorbed (or stabilized) in graphene (Gr) vacancies during graphene growth by chemical vapor deposition (CVD) on a Ni single crystal.[1,2]The study is carried out using a custom designed high-resolution Thermal Desorption Spectroscopy (TDS) instrument in combination with a Variable Temperature STM. In particular, the TDS instrument allows for the study of active sites with a very low surface coverage, of the order of 10^{-3} monolayers. We provide a thorough characterization of the active sites for CO adsorption on Gr (Fig. 1a).[3,5] In particular, the identification of Ni and Co in Gr di- and tri-vacancies, the dependence on the azimuthal Gr orientation, and an unreported CO chemisorbed state on pristine Gr. We show that the nature of the single point defect can have a huge impact on the CO adsorption probability, accounting for differences up to a factor of 10^4. We explain the existence of very different main adsorption channels, such as a reverse spillover (Fig. 1b) and activated adsorption *via* a precursor state (Fig. 1c), both known for extended surfaces but never reported for single atoms.[4,5] The well-defined geometries allow for direct and reliable comparison with *ab initio* simulations, revealing important thermodynamic and kinetic aspects.

(1) Chesnyak, V.; Perilli, D.; Panighel, M.; Namar, A.; Markevich, A.; Bui, T. A.; Ugolotti, A.; Farooq, A.; Stredansky, M.; Kofler, C.; et al. *Sci. Adv.* **2024**, *10* (45), eado8956

(2) Carnevali, V.; Patera, L. L.; Prandini, G.; Jugovac, M.; Modesti, S.; Comelli, G.; Peressi, M.; Africh, C. *Nanoscale* **2019**, *11* (21), 10358–10364

(3) Perilli, D.; Chesnyak, V.; Ugolotti, A.; Panighel, M.; Vigneri, S.; Armillotta, F.; Naderasli, P.; Stredansky, M.; Schied, M.; Lacovig, P.; et al. *Angew Chem Int Ed* **2025**, e202421757

(4) Armillotta, F.; Naderasli, P.; Chesnyak, V.; Brune, H., *J. Phys. Chem. C* **2025**, *129* (10), 4915–4922

(5) Armillotta, F.; Naderasli, P.; Chesnyak, V.; Panighel, M., Carnevali, V., Africh, C., Peressi, M., Brune, H. Carbon monoxide adsorption on intrinsically defected graphene on nickel*in preparation*

9:30am **SS+2D-TuM-7 Spin and Transport in Graphene Nanostructures with π-Magnetism*, Thomas Frederiksen,*** Donostia International Physics Center (DIPC), Spain **INVITED**

The emergence of π-magnetism in open-shell graphene nanostructures—long anticipated from theoretical models—has seen remarkable experimental breakthroughs in recent years, driven by advances in on-surface synthesis and scanning probe techniques. These developments have enabled the realization and manipulation of localized spin states with atomic precision, opening new opportunities in spin-dependent phenomena at the nanoscale. In this talk, I will highlight recent progress in understanding and engineering π-magnetism in graphene nanostructures through three complementary theoretical perspectives. First, I will discuss theoretical efforts to interpret scanning tunneling microscopy (STM) experiments that probe spin-resolved phenomena in atomically precise nanographenes. Second, I will present theoretical results on hyperfine interactions in π-magnetic nanographenes, where significant and anisotropic couplings suggest promising avenues for detection via techniques such as ESR-STM and for studying coherent nuclear dynamics. Finally, I will introduce a proposal for a spin-polarizing electron beam splitter based on crossed graphene nanoribbons, showing how such structures could serve as building blocks for spintronics and quantum interference devices. Together, these directions underscore the potential of graphene nanostructures for both fundamental quantum science and future quantum technologies.

11:00am **SS+2D-TuM-13 Simultenous Electron Spectroscopy and X-Ray Scattering on Model Ceria Catalysts*, Baran Eren,*** Weizmann Institute of Science, Israel **INVITED**

Heterogeneous catalysis is a timely and critical research field in basic and applied energy sciences, due to its potential to provide solutions to global environmental issues. However, there is still a lack of a profound understanding of the molecular and structural processes at the interfaces between solids and reactant gases. A detailed understanding of the correlation between the chemistry, structure, and function in these materials requires a multimodal investigation. Over the past few years, scientists at the at the Advanced Light Source, the Berkeley synchrotron facility, have developed a unique setup attached to an X-ray beamline where chemically-sensitive ambient pressure X-ray photoelectron spectroscopy (APXPS) and structure-sensitive grazing incidence X-ray scattering (GIXS) experiments can be performed simultaneously. Here, we showcase that this tool can provide mechanistic insights that are unparalleled in the literature.

This novel approach allows us to probe the changing surface and bulk chemistry, and surface and bulk structure of the model ceria catalysts in the presence of H_2 and CO_2 gases. In addition to the method itself, the electron density, surface chemistry, and roughness trends observed in ceria during the reaction will be discussed in this talk.Access to such a variety of data from working catalysts in a single experiment can have far-reaching implications, because changes in surface roughness, ability to store hydrogen in the bulk in various forms, and the chemical state of the surface, which all depend on the reactive environment, can directly affect the catalyst performance.

11:30am **SS+2D-TuM-15 Vibrational Spectroscopic Identification of Carbon Absorbed Beneath the Metal Surface*, Santosh K. Singh*[2]***, Volkan Cinar, Sylvia T. Ceyer,* Massachusetts Institute of Technology

Carbon dissolved in transition metals, also known as subsurface or bulk carbon, plays a critically important role in many technological processes. Subsurface carbon atoms have been recognized as essential for the catalytic growth of carbon nanotubes, graphene synthesis, and operation of direct carbon fuel cells. Despite the recognition of carbon bound beneath the surface of a metal as a crucial species in many chemical and catalytic processes, it has not been identified spectroscopically using methods that do not destroy the sample. We report the first vibrational spectroscopic identification of bulk carbon in a Au-Ni(111) surface alloy by high-resolution electron energy loss spectroscopy (HREELS) and its unambiguous synthesis via collision-induced absorption (CIA). The vibrational modes of carbon embedded beneath the surface alloy are shown to be distinguishable from surface-bound carbon based on their intensity dependence on the incident electron energy. Three distinct peak features, centered around 690, 500, and 380 cm^{-1}, are assigned to modes of subsurface carbon atoms that are located at octahedral sites and triangular misfit dislocation loops of the second layer of Au/Ni surface alloy. Additional confirmation of these assignments come from their appearance after CIA experiments, in which surface bound carbon atoms are hammered into the bulk by collisions with energetic gas phase Xe atoms, accompanied by a decreased intensity of the surface carbon mode at 540 cm^{-1}.This work reports for the first time a new method to spectroscopically identify interstitial carbon below the surface of a solid metal and a non-thermal method to synthesize it.

11:45am **SS+2D-TuM-16 Pt-Sn Catalysts for Selective Hydrogenation of Furfural*, Donna Chen***, *Sharfa Farzandh,* University of South Carolina*; Wenrui Chai, Katherine Mader, Graeme Henkelman,* University of Texas at Austin*; Mengxiong Qiao,* University of South Carolina

The production of high value chemicals from biomass is an attractive option for reducing economic dependence on fossil fuels, and the development of new catalysts for selective transformation of highly functionalized biomass derivatives has become an important area of research. For example, furfural is a platform chemical derived from biomass reforming, and catalysts are needed for the desired selective hydrogenation of furfural to furfuryl alcohol, which is a high-value chemical used in adhesives, resins, and coatings. In this work, model Pt-Sn surface alloy catalysts were prepared in ultrahigh vacuum (UHV) by vapor-depositing Sn on Pt(111) and annealing to various temperatures. Specifically, a $\sqrt{3}$x$\sqrt{3}$-R30 low energy electron diffraction pattern was observed after annealing one monolayer of

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[1] **JVST Highlighted Talk**

[2] **JVST Highlighted Talk**

Sn on Pt(111) to 800 K, while a p(2x2) pattern was observed after annealing to 1000 K. Low energy ion scattering studies confirmed that these two ordered overlayers have compositions roughly corresponding to Pt_2Sn and Pt_3Sn, respectively. Furfural hydrogenation was studied in a microreactor coupled directly to the UHV chamber under reaction conditions of 0.1% furfural/balance H_2 at 160 °C. On Pt(111), conversion was low (~5%), with THF and furan as the main products and no furfuryl alcohol produced.However, on the p(2x2) surface, the desired furfuryl alcohol product was formed with ~70% selectivity, and conversion was ten times higher than on Pt(111). Furfuryl alcohol was also observed on the $\sqrt{3}x\sqrt{3}$-R30 alloy surface, but the yield was only 25% of that on the p(2x2) surface. Furthermore, furfuryl alcohol production was even lower on annealed Pt-Sn surfaces with lower Sn coverages or unannealed surfaces with the same coverage. Density functional theory and minimum energy pathway calculations showed that in the first hydrogenation step, hydrogenation at the carbonyl oxygen is both kinetically and thermodynamically favored on the Pt, Pt_3Sn, and Pt_2Sn surfaces. In the second step, hydrogenation at the C-OH carbon has a low energy barrier (0.3 eV) on the Pt_3Sn surface but is not favorable on Pt(111) or Pt_2Sn ($\geq$0.8 eV). These differences are explained by a combination of electronic effects that decrease the binding energy of hydrogen on the Pt-Sn alloy surface and adsorption geometries. Furfural hydrogenation was also studied on bimetallic Pt-Sn clusters supported on TiO_2(110), but these surfaces were always rich in Sn and not active for furfuryl alcohol formation.

12:00pm **SS+2D-TuM-17 Bimodal Sputter Depletion of Adsorbed Na from Granular, Regolith-Like, Olivine Targets***, **Adam Woodson**, Cassandre Morel, Noah Jäggi, Catherine Dukes,* University of Virginia

Regolith roughness is expected to modulate the sputter flux of surface atoms into the exospheres of airless bodies such as Mercury. Studies have shown that roughness—from the nanometer scale upward—promotes redeposition and diminishes total sputtering yields. Experiments involving irradiation of minerals and single-element powders demonstrate yield reductions anywhere from 15% to 70% as compared to smooth targets, but the grain size dependence of this effect has not been adequately parameterized. Understanding this mechanism is therefore of critical importance for quantifying desorption and sputter ejection and for predicting the relative contributions of release processes from planetary surfaces.

We measured the sputter depletion of adsorbed Na from polished natural olivine and from synthetic granular forsterite targets with narrow grain size distributions from 45 µm up to 520 µm. Na vapor was deposited onto each target in an ultrahigh vacuum system and then irradiated at either 15° or 60° incidence (from global surface normal) to prescribed fluence steps using 4 keV He^+ ions. All experimental steps were carried out at room temperature (~300 K). After each fluence step an XPS spectrum was acquired and used to quantify the remaining Na surface concentration. Depletion cross sections were then extracted from the concentration vs. fluence data for each target, and sputtering simulations were conducted using SDTrimSP to recreate experimental observations and corroborate target surface structure and stoichiometry.

For the polished targets, Na concentrations exhibited single-exponential decay with increasing fluence, and depletion at 60° incidence outpaced that at 15° as expected from theory. Conversely, for all granular samples the Na concentrations exhibited at least double-exponential decay and depletion occurred more quickly at 15°. We propose that this reflects faster removal of Na that is directly exposed to the incident ion flux, convolved with slower removal of shadowed Na by—primarily—reflected incident ions. We found that the shadowed sodium was sputtered away 10–100 times more slowly than the exposed Na, with a transition from single-exponential to double-exponential decay at some threshold between nanoscale roughness (polished targets) and microscale roughness. These results may help to explain, for example, why current models underestimate the persistence of Na density enhancements in Mercury's dayside exosphere, as observed by the MESSENGER spacecraft's UltraViolet and Visible Spectrometer.

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