Surface Science
Room 209 CDE W - Session SS-WeM
On Surface Reactions

Moderators: Nathan Guisinger, Argonne National Laboratory, USA, **Yuan Zhang**, Old Dominion University

8:00am **SS-WeM-1 On-Surface Synthesis of Planar/Nonplanar Porous Graphene Nanoribbons and Nanosheets*, Junfa Zhu,*** University of Science and Technology of China **INVITED**

The low-dimensional porous graphene nanomaterials might have intriguing electronic properties and open exciting possibilities in the field of functional materials. By using rationally designed precursor molecules, on-surface synthesis (OSS) approach has emerged as a powerful platform for the synthesis of porous low-dimensional graphene-based nanostructures with atomic precision. In this presentation, we report our recent works on the synthesis of planar/nonplanar porous graphene nanoribbons and nanosheets on different metal surfaces. We have successfully synthesized the one-dimensional planar graphene nanoribbons (GNRs) containing periodic [14]annulene pores on Ag(111) and the two-dimensional non-planar graphene nanosheets containing periodic [30]annulene pores on Au(111), originating from a same precursor [1]. Two distinct reaction pathways on the two surfaces were regulated by different thermodynamic and kinetic mechanisms. In addition, a novel nonplanar porous [32]annulene graphene nanosheet that contains the narrowest periodic nanopores up to date was also successfully synthesized by the dissymmetrical debromination and regioselective coupling reactions of precursor molecules on an Au(111) surface [2]. With the combination of the scanning tunneling microscopy (STM), synchrotron radiation photoemission spectroscopy (SRPES) and density functional theory (DFT) calculations, we identified the reaction products, intermediates precisely, and obtained insights into the reaction mechanism. Moreover, the electronic properties of these porous graphene nanoribbons were also precisely characterized.

References:

[1] Qin T.; Guo D.; Xiong J.; Li X.; Hu L.; Yang W.; Chen Z.; Wu Y.; Ding H.; Hu J.; Xu Q.; Wang T.; Zhu J., Synthesis of a Porous [14]Annulene Graphene Nanoribbon and a Porous [30]Annulene Graphene Nanosheet on Metal Surfaces. An*gew. Chem., Int. Ed.*. 2023, 135: e202306368.

[2] Qin T.; Gao F.; Wu Y.; Liang B.; Hu L.; Yang W.; Ding H.; Hu J.; Xu Q.; Garcia-Lekue A.; Guo D.; Wang T.; Zhu J., Synthesis of Graphene Nanosheets Containing Ultra-Narrow Nonplanar Nanopores on Surfaces.*Submitted.*

8:30am **SS-WeM-3 In situ XPS Study of Pt-Grafted g-C3N4 as a Water-Splitting Photocatalyst***, Yu-Bin Huang,* National Synchrotron Radiation Research Center, Taiwan*; Ying-Huang Lai,* Department of Chemistry, Tunghai University, Taiwan*; **Bo-Hong Liu,*** National Synchrotron Radiation Research Center, Taiwan

The generation of hydrogen through solar-light-driven water splitting has acquired significant research interest, owing to the abundant availability of water as a raw material and the virtually limitless energy provided by sunlight. Graphitic carbon nitride (g-C_3N_4) has emerged as a promising catalyst due to its cost-effectiveness and eco-friendly characteristics.[1] When metal atoms are grafted onto g-C_3N_4, the chemical properties of the resulting metal/g-C_3N_4 composite can be optimized to enhance catalytic performance. Among various analogs, the single-atom Pt / g-C_3N_4 composite demonstrates exceptional catalytic reactivity.[2] This enhanced performance can be attributed to the metal-to-ligand charge transfer, which shifts the absorption spectrum toward the solar energy maximum. Additionally, the isolated Pt atom serves as a redox active site, significantly improving reaction kinetics.

In this presentation, we report an Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) investigation of Pt-grafted g-C_3N_4 under the conditions of photocatalytic water splitting. The binding energy shifts observed upon exposure to solar light provide insights into the charge transfer dynamics between the Pt and the g-C_3N_4. Furthermore, the presence of water vapor during illumination induces changes in Pt, C, and N spectra, suggesting the existence of surface adsorbates and/or surface reaction intermediates. The work function shift of the catalyst is monitored through gas phase peaks under the reaction condition. These findings deepen our fundamental understanding of the mechanisms underlying g-C_3N_4-based water-splitting catalysts at the atomic level, providing valuable guidance for the development of g-C_3N_4-based photocatalytic systems.

References:

1. Zheng, Y.; Lin, L.; Wang, B.; Wang, X., Graphitic carbon nitride polymers toward sustainable photoredox catalysis. *Angewandte Chemie International Edition* **2015,** *54* (44), 12868-12884.

2. Kuang, P.; Wang, Y.; Zhu, B.; Xia, F.; Tung, C. W.; Wu, J.; Chen, H. M.; Yu, J., Pt single atoms supported on N-doped mesoporous hollow carbon spheres with enhanced electrocatalytic H2-evolution activity. *Advanced Materials* **2021,** *33* (18), 2008599.

8:45am **SS-WeM-4 Applying Gas Phase Ion Imaging Methods to Study Chemical Reactivity on Surfaces***, **Theofanis Kitsopoulos,*** University of Southern Mississippi

Velocity-resolved kinetics (VRK) is a versatile approach for investigating surface reaction dynamics by initiating surface chemistry with a pulsed molecular beam and detecting desorbed products through velocity-resolved ion imaging. In conventional setups, kinetic data were acquired by scanning the time delay between the molecular beam and a pulsed ionization laser, limiting observations to a single mass-to-charge (m/q) species per scan. We present a significantly enhanced VRK technique that employs a 100 kHz ionization laser in combination with an event-based camera, allowing quasi-continuous acquisition of complete kinetic traces from each molecular beam pulse. Crucially, this setup also enables simultaneous detection of multiple m/q species, greatly improving the duty cycle and expanding the technique's capability for real-time, multi-species analysis. This advanced VRK implementation is particularly well-suited for probing catalytic processes under time-varying conditions, offering powerful new opportunities to unravel surface reaction mechanisms.

9:00am **SS-WeM-5 DFT study of Transition-Metal Doping in Ni(OH)$_2$/NiOOH Catalysts for Enhanced Urea Oxidation***, Qiu Jin, Matteo Garcia-Ortiz,* School of Chemical, Biological, and Environmental Engineering, Oregon State University*; **Líney Árnadóttir,*** School of Chemical, Biological, and Environmental Engineering, Oregon State University. Physical and Computational Sciences Directorate, Institute for Integrated Catalysis, Pacific Northwest National Laboratory

Urea is commonly found in agricultural runoff and wastewater, where it can disrupt nutrient cycles and harm aquatic ecosystems. Urea is also a promising sustainable energy source for fuel cells and hydrogen generation through electrochemical urea oxidation (UOR). Identifying suitable catalyst material for UOR is challenging due to a complex six-electron transfer mechanism, with high overpotential, and competition with the oxygen evolution reaction (OER). Here we use density functional theory (DFT) calculations to investigate how five metal dopants (Mn, Fe, Co, Cu, Zn) influence UOR activity on basal-plane sites of β-NiOOH, the phase transition from β-Ni(OH)$_2$ to catalytically active β-NiOOH, and the UOR-OER selectivity.

We show that doping β-Ni(OH)$_2$ accelerates surface dehydrogenation, facilitating its transformation into the active β-NiOOH phase. Mn and Fe doping also enhances dehydrogenation and reduces the Gibbs free energy of UOR, promoting reaction efficiency. On the other hand, Cu doping reduces UOR activity and has little effect on the phase transition. Additionally, Mn increases the OER limiting potential, benefiting the competition between UOR and OER while Cu lowers the OER overpotential, reducing the potential window of higher UOR activity. These insights elucidate the interplay between dopants, phase stability, and reaction selectivity, advancing the design of high-performance catalysts for urea-rich wastewater treatment and energy conversion technologies.

9:15am **SS-WeM-6 Visualizing Self-Metalation Mediated Cyclodehydrogenation of a Nonplanar Tetrabenzoporphyrin Molecule by Tip-Enhanced Raman Spectroscopy***, **Soumyajit Rajak*** [1]*, Nan Jiang,* University of Illinois, Chicago

Opto-electronic properties of functional molecular materials are controlled by local nanostructures constructed by the molecular arrangements at the nanoscale and their local chemical environment. Metal surface-supported physicochemical transformations facilitate the tuning of structural and electronic properties of functional materials. To obtain a higher degree of control over the reaction outcome, submolecular scale characterization of the chemical intermediates and their local environment is required. Determining the real-space surface adsorbed configurations of molecules is challenging using ensemble-averaged surface science techniques. Again,

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

probing the effect of the local environment of chemical species is challenging because the spatial resolution of conventional optical spectroscopic techniques is limited by the diffraction limit of light. Coupling light with plasmonic nano-objects creates highly localized surface plasmons (LSPs), which allows us to break the diffraction limit. Herein we explore tetraphenyl-tetrabenzoporphyrin molecules as one of the most widely studied model molecules in organic optoelectronics for modern-age electronic device applications and catalysis. We present a combined topographical and chemical analysis of different surface-adsorbed configurations and surface-sensitive arrangements of a tetrabenzoporphyrin molecule and their chemical reactivity on a metal surface using angstrom-scale resolution scanning tunneling microscopy (STM) and ultra-high vacuum tip-enhanced Raman spectroscopy (UHV-TERS). Low temperature (77K) scanning tunneling microscopic images and localized surface plasmon resonance enhanced Raman signals reveal different adsorbate configurations of molecular entities and their thermal reaction products with a fundamental view of adsorbate-substrate binding interactions. The atomic scale insights obtained into the local environment enable precise control over the fabrication of molecules with tailored optoelectronic properties.

9:30am **SS-WeM-7 Band Engineering Low Energy States in 1D and 2D Carbon Nanomaterials***, Felix Fischer,* UC Berkeley **INVITED**

Our research focuses on the rational design, deterministic assembly, and detailed investigation of the physical phenomena emerging from quantum confinement effects in carbon nanomaterials. We pursue a highly integrated multidisciplinary program, founded on synthetic bottom-up approaches toward functional materials with precisely defined structure. We control their assembly into hierarchically ordered architectures and evaluate inherent physical properties using modern scanning probe techniques cross multiple length, time, and energy scales.

Here we describe two new classes of low-dimensional carbon nanomaterials: The first represents a dual-square carbon-oxide lattice featuring a Dirac nodal-line semimetal (DNLSM) band structure. Orbital engineering guided by Wannier function analysis guided the design of a *d4mm* symmetrictetraoxa[8]circulene (TOC) covalent-organic framework linked through cyclobutadiene groups. A second example describes the realization of phase frustration induced flat bands in a diatomic Kagome lattice. The chemical stabilization of the energetically unfavorable open-shell high-spin ground state of aza-[3]triagnulene within the lattice of a COF forms the basis for a degenerate set of molecular orbitals that give rise to hopping frustrated topological flat bands near the Fermi level.

References

[1]Liu, F.; Yan, Y.; Tang, W.; Qie, B.; Chen, J.; Wang, Z.; Louie, S. G.; Fischer F. R. Orbital Engineering Band Degeneracy in a Dual-Square Carbon-Oxide Framework, **2025**, *under review*.

[2]Yan, Y.; Liu, F.; Tang, W.; Qie, B.; Louie, S. G.; Fischer F. R. *Engineering Phase-Frustration Induced Flat Bands in an Aza-Triangulene Covalent Organic Kagome Lattice*, **2025**, *under review*.

11:00am **SS-WeM-13 On-Surface Synthesis and Single-Molecule Manipulation for the Atomically Precise Fabrication of Carbon Nanomaterials***, **J. Michael Gottfried**,* University of Marburg, Germany **INVITED**

Recent advancements of on-surface synthesis techniques enable the fabrication and precise characterization of carbon-based nanomaterials with atomic-scale accuracy. These materials often exhibit novel (opto-)electronic and magnetic properties, which are partly derived from the inherent characteristics of the precursor molecules and partly emerge from the unique structures formed during synthesis. Therefore, on-surface synthesis presents a highly versatile alternative to conventional solution-phase chemistry, leading to novel products not obtainable by conventional chemical methods. Specifically, the quest for nonbenzenoid sp^2 carbon allotropes has stimulated substantial research efforts because of their predicted unique mechanical, (opto-)electronic, and transport properties. However, synthesis of these carbon networks remains challenging due to the lack of reliable protocols for generating nonhexagonal rings. We have developed various on-surface synthesis strategies by which polymer chains are linked to form nonbenzenoid carbon networks. In this way, we synthesized biphenylene network, a carbon allotrope with 4-6-8-membered rings, which is metallic already at very small dimensions, and other carbon networks. [1]

An especially rigorous protocol for the prototyping of new materials is the direct manipulation of atoms and molecules with the tip of a low-temperature scanning tunneling microscope. Here, we used this method to fabricated tridecacene (13ac) and pentadecacene (15ac), the longest acenes achieved to date, via multistep single-molecule manipulation. [2,3] Acenes are another important class of carbon materials with potential for use in organic electronics. We find antiferromagnetic open-shell ground state electron configurations for both acenes. Notably, 15ac shows a low-bias spin-excitation feature, indicating a singlet-triplet gap of around 124 meV. Investigation of 15ac complexes with up to 6 gold atoms suggest considerable multiradical contributions to the electronic ground state of 15ac. [3] Furthermore, doping with heteroatoms alters the electronic and magnetic properties of carbon-based nanomaterials. We present a variety of nitrogen-containing carbon nanostructures including planar and curved cycloarenes as well as N-doped graphene nanoribbons.

[1] Q.T. Fan, L-H. Yan et al., J.M. Gottfried, Science 372, 852-856 (2021).

[2] Z.L. Ruan et al., J.M. Gottfried, J. Am. Chem. Soc. 146, 3700-3709 (2024).

[3] Z.L. Ruan et al., J.M. Gottfried, J. Am. Chem. Soc. 147, 4862–4870 (2025).

11:30am **SS-WeM-15 Impact of Subsurface Oxygen on CO Oxidation over Rhodium Surfaces***, Arved Dorst,* University of Göttingen, Germany*; Maxwell Gillum, Daniel Killelea,* Loyola University Chicago*; **Tim Schäfer**,* University of Göttingen, Germany

Rhodium surfaces play a crucial role in heterogeneous catalysis, driving extensive research on their reactivity. In particular, CO oxidation is of great interest, where different oxygen species at the surface can influence catalytic activity. Under certain conditions, rhodium can also host subsurface oxygen species, further affecting reaction dynamics. In this work, we combine molecular beam surface scattering, ion imaging, and ultra-high vacuum techniques to investigate the impact of subsurface oxygen on CO oxidation on single-crystal Rh surfaces. When oxidizing CO at the (2 × 1)-O adlayer without subsurface oxygen, we observe hyperthermal velocity distributions of desorbing CO_2, indicating significant energy release along the translational coordinate directly from the transition state. In contrast, the presence of subsurface oxygen results in thermal velocity distributions, suggesting the formation of a temporarily trapped chemisorption state, which becomes energetically favorable in the presence of subsurface oxygen.

11:45am **SS-WeM-16 Structural Elucidation of Intermediates in the Selective Epoxidation Reaction of Ethylene on Ag(111) and NiAg(111)***, **Dennis Meier**, Elizabeth E. Happel,* Tufts University*; Matthew M. Montemore,* Tulane University*; E. Charles H. Sykes,* Tufts University

Ethylene epoxidation with molecular oxygen (O_2) to form ethylene oxide (EO) is a major industrial process. EO plays a significant role as a chemical intermediate for products such as pharmaceuticals, detergents, plastics, or antifreeze. Silver-based nanoparticles on alumina, enhanced with promoters like chlorine, rhenium, and cesium, are the primary catalysts for ethylene epoxidation. The key parameter for industrial ethylene epoxidation catalysts is their selectivity, as this reaction alone accounts for 3% of the CO_2 emissions from the chemical industry. There are two main surface oxygen species reported on silver: nucleophilic and electrophilic oxygen. The electrophilic species is thought to be selective for epoxidation, whereas nucleophilic oxygen is reported to be active for total combustion reaction of ethylene and EO to CO_2. Despite the significance of this reaction, the mechanism is still under debate. Recently, Ni was discovered to be a new promoter of the ethylene epoxidation adding 25% selectivity over pure Ag, an effect as large as Cl, the ubiquitous promoter.

Therefore, there is a great opportunity to understand the effect of Ni and the catalytic mechanism by which it operates to further improve process efficiency. We have performed an atomic-scale investigation of how Ni promotes oxygen activation and spillover on Ag as well as the surface intermediates of the reaction. Using a surface science approach in ultra-high vacuum (UHV) we investigated Ag(111) and NiAg(111) surfaces as a function of oxygen and ethylene exposure, Ni loading and the effect of temperature. An advantage of the NiAg system is that reactive species like NO_2 or ozone are not required to form atomic oxygen on silver in UHV meaning the system can be prepared without impurities. Using low-temperature scanning tunneling microscopy we directly image carbonate structures that are reported to be present in significant amounts on working epoxidation catalysts and may affect selectivity. We also report a precursor to surface carbonate formed from CO and electrophilic oxygen. The electronic structure of these species is probed with scanning tunneling spectroscopy and reactivity with temperature-programmed desorption measurements. Density functional theory is used to model the structure and formation of these carbonate structures and their precursors. Together, these data provide detailed insights into the structure and energetics of several chemical intermediates in the ethylene epoxidation reaction, which is crucial information for modeling and understanding the mechanism.

12:00pm **SS-WeM-17 Metal-Oxide Interfaces and Their Role in Methane Conversion to Fuels***, **M. Verónica Ganduglia-Pirovano**, Pablo G. Lustemberg,* Institute of Catalysis and Petrochemistry-CSIC, Spain

Methane dry reforming (MDR), which converts CH_4 and CO_2 into syngas (CO/H_2), is attracting increasing interest due to its environmental benefits. In parallel, the direct conversion of CH_4 to CH_3OH represents a key goal in sustainable catalysis. Among the most promising candidates for these transformations are metal-ceria systems, particularly those involving Ni, Co, and Pt supported on CeO_2. This presentation highlights recent theoretical and experimental advances in understanding these catalysts, combining DFT+U simulations with in situ/operando techniques, including AP-XPS, XRD, XAFS, and catalytic performance testing.[1-4]

A central finding is that low metal loadings, together with ceria's ability to stabilize oxidized metal species via electron re-localizing on *f*-states, enable CH_4 activation at room-temperature and efficient MDR at relatively mild conditions (~700 K). Notably, CH_4 activation in these systems deviates from conventional linear scaling relationships, suggesting that nanostructured metal-ceria interfaces can overcome the "*tyranny of linear scaling*"and offer a rational route toward designing highly active and stable systems.

We further demonstrate that low Ni loadings on CeO_2 catalyse methanol production at 450 K with high selectivity using O_2 and H_2O as oxidants.[5] In addition, carbon-modified Pd-CeO_2 (Pd-*i*C-CeO_2) achieves 100% methanol selectivity in the liquid phase at 350 K, using H_2O_2 as the oxidant.[6] The critical roles of carbon and solvent-surface interactions in tuning product selectivity are also discussed. Together, these findings highlight the transformative potential of tailored metal–oxide catalysts for the selective conversion of methane and CO_2 into value-added chemicals under mild conditions.

References

[1] Liu Z. et al. *Angew. Chem. Int. Ed.***55**, 7455-7459 (2016)

[2] Liu Z. et al. *Angew. Chem. Int. Ed.* **56**,13041–13046 (2017)

[3] Lustemberg, P. G. et al. *J. Phys. Chem. Lett.* **11**, 9131−9137 (2020)

[4] Zhang, F. et al. *ACS Catal.* **11**, 1613−1623 (2021)

[5] Lustemberg P. G., et al. *J. Am. Chem. Soc*. **140**, 7681−7687 (2018)

[6] Jiménez J. D., et al. *J. Am. Chem. Soc*. **146**, 25986−25999 (2024)

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