Surface Science
Room 305 - Session SS-MoM

Precision On-Surface Synthesis

Moderators: Dr. Nathan Guisinger, Argonne National Laboratory, USA, **Pavel Jelinek**, Institute of Physics of the Czech Academy of Sciences

10:00am **SS-MoM-1 Porous Graphene Nanoribbons and Nanomeshes**, ***Alexander Sinitskii,*** University of Nebraska-Lincoln **INVITED**

Atomically precise porous graphene nanostructures provide a versatile platform for tailoring electronic properties through controlled structural design. Here, we present a bottom-up synthetic strategy that provides access to a family of nanoporous graphene nanomaterials, including porous nanographenes, porous graphene nanoribbons (pGNRs), and extended nanoporous graphene (NPG) networks, all derived from closely related triphenylene-based molecular precursors [1]. By varying the synthetic environment, the same molecular building blocks can be directed toward distinct carbon architectures: solution-phase coupling yields cyclotrimeric porous nanographenes, whereas on-surface synthesis on Au(111) promotes linear polymerization and cyclodehydrogenation into atomically precise pGNRs. At high surface coverage and elevated annealing temperatures, these ribbons laterally fuse into extended nanoporous graphene sheets, establishing a modular and broadly tunable synthetic framework for porous carbon nanomaterials.

This platform further enables systematic investigation of how nanopore incorporation influences GNR properties [2]. By comparing a pristine N = 15 armchair GNR (15-AGNR), its periodically perforated analogue containing [18]annulene pores (15-pGNR), and the more extensively carved chevron GNR (cGNR), we track the evolution of the electronic structure with progressive pore opening. STS and ARPES measurements, as well as theoretical calculations, reveal that introducing periodic nanopores into the 15-AGNR produces a greater-than-twofold increase in bandgap, while further evolution toward the cGNR architecture results in comparatively smaller changes. These findings provide direct insight into the combined roles of geometric confinement and periodic lattice perforation in tuning GNR electronic structure.

We further expand the structural complexity of these systems by laterally fusing pGNRs into NPG networks containing periodically spaced biphenylene units, representing a novel 2D carbon allotrope [3]. STM, nc-AFM, and DFT calculations demonstrate that incorporation of biphenylene motifs into a porous graphene framework gives rise to distinct electronic behavior, including reduced and indirect bandgaps. Collectively, these studies establish a unified molecular design strategy for structurally related porous graphene nanomaterials with tunable topology and electronic functionality, spanning 0D, 1D, and 2D carbon architectures.

[1] M. Sarker, *et al*., *J. Am. Chem. Soc.*, **2024**, *146*, 14453.

[2] J.D. Teeter, *et al*., *ACS Nano*, **2026**, *20*, 8372.

[3] P. Angulo-Portugal, *et al*., *Adv. Mater.*, **2026**, e11706.

10:30am **SS-MoM-3 On-surface Synthesis of Porphyrin-Based MONs: a Model System for -Artificial Spin Lattices**, *Eidsa Brenda Costa Ferreira,* University of Campinas (UNICAMP), Brazil*; Rafael Reis Barreto,* university of campinas (UNICAMP), Brazil*; Otavio Rodrigues de Oliveira, Iago Aedon Silva Prior, Isabela Costa Tonon,* University of Campinas (UNICAMP), Brazil*; Vanessa Carrenõ-Diaz, Breno Santimaria Sertori,* university of Campinas (UNICAMP), Brazil*; Igor Stein Weiler, **Abner de Siervo**,* University of Campinas (UNICAMP), Brazil

Over the past decade, significant advances have been achieved in the on-surface synthesis of atomically precise one-dimensional (1D) and two-dimensional (2D) metal–organic networks (MONs) using selected molecular precursors as modular building blocks in a "molecular LEGO" approach. This strategy exploits substrate properties, precursor molecular geometry, functional groups, diffusion behavior, and thermal activation energies to steer hierarchical reactions and the formation of novel nanostructures [1]. Porphyrins have well-defined geometry, rich electronic properties, and the ability to accommodate a central metal atom within their mycrocycles, making them particularly promising building blocks. When their molecular periphery is terminated with cyano, pyridyl, carboxylic, or halogen groups, deposited or substrate-derived adatoms can be trapped to form metal–organic coordination nodes. This leads to MONs with linear, square, rectangular, hexagonal, or kagome lattices, with geometries dictated by the molecular structure and substrate registry. Such architectures serve as important model systems for two-dimensional artificial spin lattices, among other phenomena. In this work, we present recent examples of MON formation using two types of free-base porphyrins: 5,10,15,20-tetra(4-pyridyl)porphyrin (2H-TPyP) on Ag(100) [2] and 5,10,15,20-tetrakis[4'-(4-pyridyl)phenyl]porphyrin (2H-TPyPP) on Ag(111)[3]. In both cases, the introduction of Fe promotes de formation of different MONs with well-ordered and extended spin lattices. These different structures can be selectively realized by controlling the annealing protocol and the Fe deposition sequence [2,3]. These studies combine scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) experiments, supported by density functional theory (DFT) calculations.

Acknowledgements

This work was financially supported by FAPESP (2022/12929-3; 2024/07409-6; 2025/02160-2), CNPq, and CAPES from Brazil.

References

[1] J. Barth, G. Costantini, K. Kern, *Nature* **437,** 671–679 (2005).

[2] Rafael Reis Barreto, et al., Surface Science 766, 122897 (2026).

[3] Eidsa Brenda da Costa Ferreira, et al., "Engineering Two-Dimensional Artificial Spin Lattice Based on Porphyrins Metal-Organic Networks" (under preparation).

10:45am **SS-MoM-4 Deciphering Atomic Layer Deposition in Materials Processing: A Surface Science Perspective**, ***Joerg Libuda,*** Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

Atomic Layer Deposition (ALD) enables controlled growth of ultrathin films with sub-nanometer precision, making it a key technique for nanoelectronics, catalysis, and energy applications. However, its success critically depends on the early stages of nucleation, which determine film continuity, uniformity, and defect density. Achieving uniform nucleation and atomic-level control remains challenging. Among the emerging materials accessible by ALD, transition-metal dichalcogenides (TMDCs) are of particular interest due to their tunable band gaps. Besides the extensively studied MoS_2, HfS_2 is a promising candidate, offering higher carrier mobility and a suitable band gap for electronic applications.

Here, we present our work on elucidating ALD nucleation mechanisms using a surface-science approach under ultrahigh vacuum (UHV). Atomically defined films and nanoislands of transition metal oxides (CoO(100), Co_3O_4(111)) on metal single crystals (Ir(100), Au(111)) serve as model substrates. HfS_2 growth is achieved via self-limiting reactions of tetrakis(dimethylamido)hafnium (TDMAH) with H_2S (or D_2S). The nucleation and growth processes are investigated in situ by combining scanning tunneling microscopy (STM) with time-resolved and temperature-programmed infrared reflection absorption spectroscopy (TR-IRAS, TP-IRAS).

Our results reveal that initial ALD nucleation is highly complex, involving multiple mechanisms and surface species. In the presence of surface OH/H_2O, mobile OH species induce full TDMAH hydrolysis (Brønsted acid–base mechanism). With increasing exposure, nuclei evolve dynamically through reactions of partially hydrolyzed species. While OH-functionalized self-assembled monolayers reduce OH mobility, substantial stoichiometric changes persist during early growth. Notably, nucleation also occurs on oxide surfaces in the complete absence of OH groups, indicating a Lewis acid–base mechanism with ligands bound to surface Co^{2+} sites. On CoO nanoislands, STM identifies initial intermediates, providing direct evidence for the Lewis acid–base mechanism. At elevated temperatures, dehydrogenation sets in as an additional reaction channel and generates OH groups that subsequently react via the Brønsted acid–base mechanism.

Overall, nucleation involves a highly complex interplay of Brønsted and Lewis acid–base pathways and dehydrogenation processes. These findings highlight that precise control over process parameters, surface structure, OH/H_2O chemistry, and reactant purity is essential for achieving controlled ALD nucleation.

11:00am **SS-MoM-5 Iterative Organic Modification of Pt Nanoparticles for Site-Selective Surface Engineering**, ***Yongju Yun,*** *Minji Yun,* Pohang University of Science and Technology (POSTECH), Republic of Korea

The controlled modification of surface chemical environments is important for understanding structure-sensitive reactions on metal nanoparticles. However, conventional single-step surface modification methods often lead to non-selective coverage of surface sites, limiting precise control over local surface environments. In this study, we present an iterative organic modification strategy using ethylenediamine (EDA) as a molecular modifier to tune the electronic and geometric properties of Pt/Al_2O_3 surfaces.

Successive cycles of molecular adsorption and mild thermal annealing progressively introduced N-containing surface species. X-ray photoelectron spectroscopy (XPS) showed an increase in the fraction of electron-deficient $Pt^{\delta+}$ species through Pt–N interfacial interactions. In parallel, CO diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) suggested preferential modification of under-coordinated (UC) sites, leading to a relative increase in the exposure of well-coordinated (WC) terrace sites. Compared with conventional single-step modification, the iterative approach resulted in a higher WC/UC ratio, indicating improved site selectivity. The modified catalysts exhibited enhanced enantioselective hydrogenation performance for α-keto esters, achieving an enantiomeric excess (ee) of up to 96.5%. These results demonstrate that iterative organic modification can provide an effective approach for tuning interfacial surface environments and surface-site distributions on heterogeneous catalysts.

11:15am **SS-MoM-6 Probing the Role of Anodization Leading to Improved Sn Uptake for the Creation of High-Performance Nb_3Sn SRF Cavities**, ***Jasper Brown***, *Van Do,* University of Chicago*; Liana Shpani,* Cornell University*; Helena Lew-Kiedrowski,* University of Chicago*; Matthias Liepe,* Cornell University*; Steven Sibener,* University of Chicago

One of the primary obstacles to implementing Nb_3Sn in the creation of high performance superconduction radio frequency cavities (SRF) for use with high gradient particle accelerators is the presence of film-growth inhomogeneities, which promote vortex pinning and generate localized surface hot spots that degrade cavity performance. Studies have shown that pre-anodizing Nb enhances Sn nucleation, leading to the formation of more stoichiometric and uniform Nb_3Sn coatings. Although anodized Nb surfaces have been widely investigated, there remains limited understanding of the chemical and structural evolution of these surfaces under Sn nucleation conditions. In this work, we employ in-situ X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) to examine the thermal evolution of anodized polycrystalline Nb samples annealed to 773 K at heating rates of 3 K/min and 7 K/min in the absence of Sn. We find that compared to the control sample, the anodized Nb surface exhibits an RMS roughness an order of magnitude greater and displays an isotropically rough and porous morphology that persisted throughout the annealing process. Additionally, XPS measurements revealed persistent surface contamination associated with the anodizing electrolyte both prior to and following annealing. Through this study, we quantified surface roughness, chemical composition, and the oxide dissolution activation energy for both anodized and native Nb surfaces. These findings provide important insight into the role of anodization in influencing Sn nucleation behavior and the subsequent Nb_3Sn alloying process.

11:30am **SS-MoM-7 Methods and Mechanisms to Engineer Monodispersed Noble Metal Single Atoms, Dimers, Trimers, and Bi-atomic Metal–Oxygen Dimers on TiO_2(110)-(1×1) Surface for Catalysis**, ***Xiao Tong***, BNL

Monodispersion of size-selected nanoclusters supported on metal oxide is critical for catalytic activity, selectivity, and stability, but small clusters often diffuse and aggregate into 3D structures after adsorption, losing their size specificity. This study examines how oxygen vacancy density, cluster landing energy, and environmental water influence the adsorption of Au_1, Ag_n (n = 1–3), and VO clusters on TiO_2(110)-(1×1). High landing energies of clusters or elevated substrate temperatures promote monodispersion of monomers, dimers, trimers, and 2D sheet growth by creating transient defects that pin clusters while thermal dissipation heals surrounding damage, or by preserving oxygen vacancies from passivation by environmental water. Water can displace Au_1 from oxygen vacancies to nearby 5-fold Ti sites and passivate the vacancies through hydroxyl formation. VO clusters stabilize water dimer strings that act as barriers and spacers, preventing aggregation of incoming clusters and enabling control over monodispersion density by modulating string length. These findings demonstrate how tuning physical and chemical parameters can stabilize the monodispersion of size- and composition-selected clusters, advancing novel catalytic design.

11:45am **SS-MoM-8 Ni Porphyrin as a Model Single Atom Catalyst for CO_2 Adsorption**, *J. Sanchez,* The University of Texas at San Antonio*; J. Martinez, P. Sharma, H. Wang,* University of North Texas*;* ***Fang Xu***, The University of Texas at San Antonio

Metalloporphyrin is an ideal model for fundamental studies of single atom catalysis (SAC), becaues the electronic structure of the central metal atom is tunable by electron donating or withdrawing substituents.In this work, we investigate the self-assembly and electronic structure of Ni-tetraisopropylporphyrin (Ni-TIPP) and its substituent Ni-tetrabromoisopropylporphyrin (Ni-TBTIPP) for CO_2 activation on Au(111) surface. Scanning tunneling microscopy and spectroscopy (STM/STS) were employed to qualitatively probe changes in local density of states associated with variations in the porphyrin substituents and central metal environment. STS detects a large band gap associated with the strong insulating porphyrin molecules. The STM results show that Ni-TIPP forms a 2D network of porphyrin islands with an upward tilted phenyl in each molecule due to possible tension, while molecules at the edge of the islands appear relaxed and more planar to the surface. The tilt was not observed in the case of Ni-TBTIPP which self-assembles planarly and flatly to the Au(111) substrate. The assembled Ni-TIPP was subsequentially exposed to CO_2 through a direct dosing tube with enhanced pressure effect. Control experiments of STM and temperature desorption indicate the formation of formate as the intermediate of CO_2 activation. This work visualizes CO_2 activation to formate over Ni metalated porphyrins for the first time, and the fundamental understanding provides key insight toward catalytic designs of CO_2 conversions.

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