

## Surface Science

### Room 120 - Session SS+2D+AMS-WeM

#### On-Surface Synthesis: Atomic and Molecular Ensambling on Surfaces

**Moderators:** Irene Groot, Leiden University, The Netherlands, Nan Jiang, University of Illinois - Chicago

8:00am **SS+2D+AMS-WeM-1 On-surface Synthesis of Porous Graphene Nanoribbons**, T. Qin, 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 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 work on the synthesis of porous graphene nanoribbon and nanosheet on different metal surfaces. We have successfully synthesized the one-dimensional graphene nanoribbons (GNRs) containing periodic [14]annulene pores on Ag(111) and the two-dimensional graphene nanosheets containing periodic [30]annulene pores on Au(111), originating from a same precursor. Two distinct reaction pathways on the two surfaces were regulated by different thermodynamic and kinetic mechanisms. With the combination of the scanning tunneling microscopy, synchrotron radiation photoemission spectroscopy and density functional theory (DFT) calculations, we identified the reaction products, intermediates precisely, and obtained insights into the reaction mechanism. On Ag(111), the formation of porous GNR is a thermodynamically favored pathway, by going through a flexible and reversible organometallic intermediate state. In contrast, on Au(111), because the debromination process is the rate-limiting step for the covalent coupling reaction and the generated covalent structures are irreversible, giving rise to the hierarchical formation of covalent chains and 2D porous nanosheet. The reaction mechanisms were confirmed by a series of control experiments, and the appropriate thermodynamic and kinetic parameters for optimizing the reaction pathways were proposed. Furthermore, DFT calculations revealed the influence of surface confinement on the band structures of these two nonplanar pores embed carbon materials, which enhances the conjugation of  $\pi$ -electrons thus shrinking the band gap.

8:30am **SS+2D+AMS-WeM-3 Tailoring Pt-Based Organometallic Nanomesh on Ag(111): A Model System for "Host-Guest" Chemistry**, V. Carreño-Díaz, A. Ceccatto, E. Ferreira, Abner de Siervo, University of Campinas (UNICAMP), Brazil

On-surface synthesis has been extensively used to produce complex functional nanostructures, such as Metal-Organic Frameworks (MOFs). MOFs are composed of highly ordered molecular structures, where metal adatoms act as connecting nodes, generating porous structures that exhibit a long-range order, offering a favorable environment for the adsorption and reaction of molecules in confined spaces, the so-called "host-guest" chemistry [2]. In the present work, we have studied the formation of bidimensional porous networks with hexagonal geometry (nanomesh) resulting from the combination of two molecular precursors: 1,3,5-tris[4-(pyridin-4-yl)-[1,1'-biphenyl]]benzene (TPyPPB) and dichloro-(1,10-phenanthroline)-platinum(II) ( $\text{Cl}_2\text{PhPt}$ ), deposited on the surface of Ag(111). Our results reveal that when the TPyPPB molecules are deposited on the Ag(111) surface, they adopt a porous arrangement with triangular packing mediated by hydrogen bonds [3]. On the other hand, in the presence of the  $\text{Cl}_2\text{PhPt}$  molecule, the chemical interactions between both molecules change upon annealing at 400K, which leads to various ordering patterns before stabilizing in a network with hexagonal geometry. After dehalogenation, the  $\text{Cl}_2\text{PhPt}$  molecule is transformed into a new complex, PhPt, maintaining the Pt atom in its structure. The Cl atoms dissociated from the  $\text{Cl}_2\text{PhPt}$  precursor decorate the periphery of TPyPPB molecules. PhPt molecules can interconnect TPyPPB molecules through metallic coordination between the Pt atom and the N from the pyridyl group (N–Pt–N). The present investigation is based on room temperature scanning-tunneling microscopy (STM) measurements. This experimental approach allows us to explore the properties and structure of these materials at the atomic and molecular levels, opening new perspectives on the design and properties of MOFs.

Acknowledgments:

This work was financially supported by FAPESP (2022/12929-3), CNPq, and CAPES from Brazil.

1. Barth, J., Costantini, G. & Kern, K. Engineering atomic and molecular nanostructures at surfaces. *Nature* 437, 671–679 (2005).

2. Marta Viciano-Chumillas, et al. "Metal-Organic Frameworks as Chemical Nanoreactors: Synthesis and Stabilization of Catalytically Active Metal Species in Confined Spaces". *Accounts of Chemical Research* 53 (2020) 520–531.

3. Alisson C. dos Santos, Vanessa Carreño-Díaz, et al. "On-Surface Design of Two-Dimensional Networks through Nonmetal Atoms" (under preparation).

8:45am **SS+2D+AMS-WeM-4 Modulating the Reactivity of "Single-Atom Catalyst" Sites Within 2D Metal-Organic Frameworks by Small Structural Distortions**, Zdenek Jakub, CEITEC - Central European Institute of Technology, Czechia; J. Planer, D. Hruza, A. Shahsavar, P. Prochazka, J. Cechal, CEITEC, Czechia

Detailed atomic-scale understanding is a crucial prerequisite for rational design of next-generation single-atom catalysts (SACs). However, the sub-ångström precision needed for systematic studies is difficult to achieve on working SACs. We present a 2D metal-organic system featuring Fe- $\text{N}_4$  single-atom sites,<sup>1,2</sup> in which the height of the atomically-defined structure is modulated by the 0.4 Å corrugation of the inert graphene/Ir(111) support. We show that the support corrugation significantly affects the system reactivity, as the sites above the support "valleys" bind TCNQ (tetracyanoquinodimethane) much stronger than the sites above the "hills".<sup>3</sup> The experimental temperature stability of TCNQ varies by more than 60 °C on these seemingly identical sites. We expect that similarly strong effects of sub-ångström structural distortions will likely take place whenever large molecules interact with neighboring "single-atom catalyst" sites or when multiple reactants co-adsorb on such sites.

References

[1] Z. Jakub, A. Shahsavar, et al., *JACS*, **146**, 3471–3482 (2024)

[2] Z. Jakub, A. Kurowská, et al., *Nanoscale*, **14**, 9507-9515 (2022)

[3] Z. Jakub, J. Planer, et al., in preparation

9:00am **SS+2D+AMS-WeM-5 On-Surface Synthesis of Polycyclic Heteroatom-Substituted Nanocarbon Materials**, Willi Auwärter, Technical University of Munich, Germany **INVITED**

On-surface synthesis protocols provide elegant routes to individual molecular complexes, oligomers, and other nanocarbon materials on metal supports [1]. The resulting structural, physical, and chemical properties can be controlled by heteroatom-substitution.

In this talk, I will present an overview of our activities employing temperature-induced reactions on coinage metal supports in an ultrahigh vacuum environment, affording specific porphyrinoids and BN-substituted nanocarbon materials. On the one hand, routes to unsubstituted, square-type porphyrin tetramers [2] and peripherally O-doped porphyrins are addressed. On the other hand, dehydrogenation processes of borazine [3] and BN-functionalized carbon scaffolds will be discussed, in view of the synthesis and potential transfer of two-dimensional BNC materials.

[1] Grill, L.; Hecht S. *Nat. Chem.* **2020**, *12*, 115.

[2] Corral Rascon, E. *et al. J. Am. Chem. Soc.* **2023**, *145*, 967.

[3] Weiss, T. *et al.*, *Adv. Mat. Interfaces* **2024**, *11*, 2300774

9:30am **SS+2D+AMS-WeM-7 Atomic-Scale Investigation of the Highly Enantiospecific Decomposition of Tartaric Acid on Chiral Cu Surfaces**, Avery Daniels, C. Sykes, Tufts University

Enantioselectivity is the quintessential form of structure-sensitive surface chemistry, as differences in reactivity arise solely from the lack of mirror symmetry of the surface. Studying enantioselectivity on chiral surfaces provides insight into the design of enantioselective heterogeneous catalysts, which are important in pharmaceutical, agrochemical, and other industries. To determine the optimum surface facet for a given chemical reaction, it is essential to study the reaction on a wide variety of surface facets. Given the serial nature of surface science experiments on single crystals, high-throughput methods to study multiple facets at the same time would circumvent this issue. We have designed surface structure spread single crystals (S4Cs) that expose a vast variety of different surface facets on a single sample. Interestingly, a large portion of these facets are also chiral and therefore the use of S4Cs is ideal for studying for enantioselective surface chemistry. Tartaric acid decomposition on chiral Cu surfaces is known to be highly enantiospecific. With spatially resolved X-ray photoelectron spectroscopy (XPS), we have previously investigated the

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decomposition of tartaric acid on a Cu(110) ± 14o S4C where surfaces vicinal to Cu(14,17,2) were found to be the most enantiospecific. We have now combined these XPS results with scanning tunneling microscopy (STM) imaging to unveil the atomic-scale origins of the highly enantiospecific decomposition of tartaric acid on chiral Cu surfaces. We found extensive enantiospecific surface restructuring of surfaces vicinal to Cu(110) leading to the formation of facets vicinal to Cu(14,17,2). This reconstruction of the surface depends on both the TA enantiomer and the chirality of the surface itself, and is therefore enantiospecific. These results provide valuable insight into the origins of structure sensitivity for enantioselective reactions and demonstrate the efficacy of S4Cs in performing high-throughput surface science investigations.

9:45am **SS+2D+AMS-WeM-8 Competition between Hydrogen Bonding and van der Waals Interactions During Binary Self-Assembled Monolayer Formation**, *Rachael Farber, L. Penland, H. Hirushan, N. Dissanayake*, University of Kansas

Binary self-assembled monolayers (SAMs) comprised of polar and nonpolar molecules, such as 3-Mercaptopropionic Acid (MPA) and 1-Decanethiol (DT), offer the ability to carefully tune the interfacial properties of Au surfaces. The formation of molecularly precise binary SAMs through the displacement of one molecule with another *via* solution phase processing requires fine control over the structure and composition of the initial SAM. While DT has been extensively characterized using ultra-high vacuum (UHV) surface science techniques, the structural properties of MPA SAMs are less well understood. The relationship between solution phase processing procedures of MPA and island vacancy density, domain size, film uniformity, and the subsequent displacement behavior when exposed to DT, has not been established.

In this work, the effects of solution phase incubation temperature and time on MPA SAM formation and subsequent DT displacement behavior were determined using UHV scanning tunneling microscopy. Three MPA incubation procedures were studied: 3 hr MPA incubation at 35 °C (**MPA-1**), 3 hr MPA incubation at 25 °C (**MPA-2**), and 24 hr MPA incubation at 25 °C (**MPA-3**). While **MPA-1** and **MPA-2** both showed the characteristic MPA lattice, **MPA-1** had fewer domain boundaries and vacancy islands compared to **MPA-2**. **MPA-3**, which had the fewest domain boundaries and vacancy islands, showed regions of an MPA bilayer species across the surface. To determine the consequences of defect density and the presence of an MPA bilayer on DT displacement, **MPA-1**, **MPA-2**, and **MPA-3** were subsequently placed in a 2 μM DT solution for 20 min, 60 min, 3 hr, and 24 hr. **MPA-1** and **MPA-2** had comparable rates of DT displacement, with the formation of a high-density DT film across the surface within 3 hr. **MPA-3** had markedly slower DT displacement. Following a 24 hr incubation of **MPA-3** in the DT solution, small regions of the low-coverage, lying down phase (β) and 2-D gas phase (α) of DT were found across the surface. Only after a 48 hr incubation of **MPA-3** in DT did the high-density DT phase form. These results highlight the significance of the bonding interactions of the initial SAM on displacement kinetics during the formation of binary SAMs.

11:00am **SS+2D+AMS-WeM-13 Learning More with Less: High-Throughput Screening of Molecular Layer Deposition Processes**, *David Bergsman*, University of Washington **INVITED**

Because of its ability to deposit organic, inorganic, and hybrid ultrathin films with sub-nanometer thickness and compositional control, molecular layer deposition (MLD) has seen growing interest for use in technologies where precise interfacial control is essential, such as in semiconductor processing, membrane separations, and catalysis. However, development of these technologies is inhibited by the relatively slow process times for MLD vs atomic layer deposition and the large number of combinations of inorganic & organic reactants available to MLD.

This presentation will highlight the intrinsic advantages of accelerating MLD process development, both for technology development and for fundamental research. First, previous work in MLD process development will be highlighted, focusing on areas where comparisons between processes yielded fundamental insight into film growth phenomena. Then, an approach for rapidly screening new materials deposited by MLD using a custom-built, high-throughput, multiplexing MLD-style reactor will be discussed. In such a system, multiple reaction chambers are connected to shared reactants and pumping lines, allowing for the elimination of redundant reactor components and reducing capital costs compared to an equivalent number of independent systems. Finally, an example of how this approach can be applied to future technologies, such as EUV photolithography, will be given, demonstrating how materials made using

these parallel systems can be screened for their properties of interest and be used to obtain process-structure-property relationships.

11:30am **SS+2D+AMS-WeM-15 Organic Molecular Architectures Synthesized on Si(001) by Means of Selective Click Reactions**, *T. Glaser, J. Peters, Justus Liebig University Giessen, Germany; D. Scharf, U. Koert, Philipps University Marburg, Germany; Michael Dürr, Justus Liebig University Giessen, Germany*

The concept of molecular layer deposition on solid surfaces is promising for the synthesis of layers with well-controlled physical and physicochemical properties. Molecules with two functional groups are suitable building blocks for covalent layer-by-layer synthesis. However, with symmetric bifunctional organic molecules, i.e., with two identical functional groups at one molecule, side reactions which hinder the well-controlled layer-by-layer growth, e.g., by chain termination, may occur.

Here we solve this problem using a combination of two selective and orthogonal click reactions for controlled covalent layer-by-layer growth on Si(001). In order to do so, we combine ultrahigh-vacuum- (UHV)-based functionalization of the Si(001) surface with solution-based click chemistry for the attachment of the further layers. The starting point is the Si(001) substrate which is functionalized via selective adsorption of the bifunctional ethynylcyclopropylcyclooctyne (ECCO) molecule under UHV conditions [1]. This first-layer sample is then transferred into solution [2] in order to perform the subsequent layer-by-layer synthesis using the two orthogonal click chemistry reaction steps in an alternating fashion: First, a diazide is coupled in acetonitrile via a copper-catalyzed azide-alkyne click reaction; second, a layer of ECCO molecules is coupled via a catalyst-free, strain-promoted azide-alkyne click reaction. Without contact to ambient conditions, the samples are analyzed by means of X-ray photoelectron spectroscopy in UHV after each reaction step in solution; the N 1s spectra clearly indicated in the first step the selective click reaction of the primary azido group of the diazide molecule, whereas the tertiary azido group stayed intact. In the second step, this tertiary azido group was reacted selectively with the strained triple bond of the ECCO molecule in solution, forming a third layer of organic molecules on Si(001) with the terminal triple bond of ECCO available for further reactions according to this cyclic reaction scheme. Alternating application of the two orthogonal reaction steps then led to a well-controlled layer-by-layer growth up to 11 layers [3]; it opens the possibility for the controlled synthesis of layers with physical or physicochemical properties that alternate on the molecular scale.

[1] C. Länger, J. Heep, P. Nikodemiak, T. Bohamud, P. Kirsten, U. Höfer, U. Koert, and M. Dürr, *J. Phys.: Condens. Matter* 31, 34001 (2019).

[2] T. Glaser, J. Meinecke, C. Länger, J. Heep, U. Koert, and M. Dürr, *J. Phys. Chem. C* 125, 4021 (2021).

[3] T. Glaser, J. A. Peters, D. Scharf, U. Koert, and M. Dürr, *Chem. Mater.* 36, 561 (2024).

11:45am **SS+2D+AMS-WeM-16 Confinement Effects at Surfaces**, *J. Anibal Boscoboinik*, Brookhaven National Laboratory

Nanosized spaces at surfaces offer an interesting playground to understand the effect of confinement in chemistry and physics. Two examples will be described in this talk. In the first one, the water formation from hydrogen and oxygen is studied on a metal surface both in its bare state and also covered with a two-dimensional porous silicate. A change in reaction pathway is observed due to confinement effects. In the second example, nanosized silicate cages supported on a metal are shown to trap single atoms of noble gases through a new ionization-facilitated trapping mechanism. In this case, the gas phase species are first ionized. These ions can then enter the nanocages, at which point they get neutralized by an electron donated by the adjacent metal, resulting a neutral species that are kinetically trapped inside the confined space.

12:00pm **SS+2D+AMS-WeM-17 Facilitating CO<sub>2</sub> Capture Enabled by Weak Intermolecular Interactions Among CO<sub>2</sub>, Water and PEEK-Ionene Membrane**, *Jennifer Yao, L. Strange, J. Dhas, PNNL; S. Ravula, J. Bara, University of Alabama; D. Heldebrant, Z. Zhu, PNNL*

Poly (ether ether ketone) (PEEK)-ionene membranes have shown significant potential for direct CO<sub>2</sub> capture due to their high selectivity, durability, and efficiency.<sup>1</sup> Despite their promise, the mechanisms of CO<sub>2</sub> transport through these membranes and the impact of water vapor on its CO<sub>2</sub> capture and diffusion remain poorly understood. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) can detect and distinguish the characteristic molecular ions,<sup>2,3</sup> making it an ideal tool for studying complex intermolecular interactions of the CO<sub>2</sub>, water and the membrane. In this study, a combination of isotopic labeling and SIMS provides a unique

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method to track small molecules in organic matrixes at nanoscale. We investigated the interactions of PEEK-ionene membranes with  $^{13}\text{CO}_2$  and  $\text{D}_2\text{O}$  using cryo ToF-SIMS. ToF-SIMS 3D imaging provided chemical mapping of the distribution of these species from the surface down to several micrometers into the membrane. The cryo ToF-SIMS data did not show any significant enhancement of the  $^{13}\text{C}/^{12}\text{C}$  ratio, implying weak  $\text{CO}_2$ -membrane interactions and  $\text{CO}_2$  vaporization even at  $-130\text{ }^\circ\text{C}$  in vacuum condition. In contrast, cryo ToF-SIMS revealed a relatively uniform distribution of  $\text{D}_2\text{O}$  within the heavy water-loaded membrane. This suggests that water-membrane interactions are stronger than  $\text{CO}_2$ -membrane interactions. Additionally, the presence of  $\text{D}_2\text{O}$  in the membrane did not enhance  $^{13}\text{CO}_2$  retention, indicating weak  $\text{CO}_2$ - $\text{D}_2\text{O}$  interactions and minimal impact of water vapor on  $\text{CO}_2$  diffusion within membrane. For comparison, ToF-SIMS data demonstrated that  $^{13}\text{CO}_2$  readily reacts with a basic  $\text{Na}_2\text{CO}_3$  solution to form  $\text{NaH}^{13}\text{CO}_3$ , highlighting the potential for modifying  $\text{CO}_2$ -membrane interactions via functional group modifications. Specifically, introducing basic functional groups may enhance  $\text{CO}_2$ -membrane interactions, whereas acidic modifications may reduce them.

## References:

1. K. O'Harra, I. Kammakakam, P. Shinde, C. Giri, Y. Tuan, E. M. Jackson and J. E. Bara, ACS Applied Polymer Materials, 2022, 4, 8365-8376.
2. L. E. Strange, S. Ravula, Z. Zhu, J. E. Bara, P. Chen, D. J. Heldebrant and J. Yao, Surface Science Spectra, 2024, 31.
3. L. E. Strange, D. J. Heldebrant, S. Ravula, P. Chen, Z. Zhu, J. E. Bara and J. Yao, Surface Science Spectra, 2024, 31.

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