Nano and 2D Materials
Room Naupaka Salon 4 - Session NM2-TuE

2D Materials Based on Carbon and Boron
Moderator: Akitoshi Shiotari, Fritz-Haber Institute

7:40pm **NM2-TuE-7 First-Principles Study of Adsorption and Reaction on the Hydrogen Boride Sheet***, Ikutaro Hamada,* Osaka University, Japan **INVITED**

The hydrogen boride (HB) sheet [1] is a newly synthesized two-dimensional material composed of hydrogen and boron atoms with their ratio of 1:1. The HB sheet has been attracted increasing attention, not only because of its high gravimetric hydrogen content as a hydrogen storage material and its ability to release hydrogen through light [2] and electrochemical [3] means, but also due to its catalytic activities [4]. Furthermore, the HB sheet has been shown to be chemically stable against water [5], unlike many boron hydrides that undergo hydrolysis reactions. The stability is a fascinating considering the practical application of the HB sheet. However, the molecular and mechanistic details of the chemical processes occurring on the HB sheet have yet to be fully addressed. In this talk, I will discuss the electronic and structural properties of the HB sheet [5], as well as the adsorption and reaction on the HB sheet based on our density functional theory calculations. Special emphasis is placed on the interaction with water molecules, and the mechanism of the stability of the HB sheet against water will be discussed [6,7].

References:

[1] H. Nishio, *et al.*, J. Am. Chem. Soc. **139**, 13761 (2017).

[2] R. Kawamura, *et al.*, Nat. Commun. **10**, 4880 (2019).

[3] S. Kawamura, *et al.*, Small **20**, 2310239 (2024).

[4] T. Goto, *et al.*, Commun. Chem. **5**, 118 (2022).

[5] L. T. Ta, Y. Morikawa, and I. Hamada, J. Phys. Condens. Matter **35**, 435002 (2023).

[6] K. I. M. Rojas, *et al.*, Commun. Mater. **2**, 81 (2021).

[7] K. I. M. Rojas, Y. Morikawa, and I. Hamada (submitted).

8:20pm **NM2-TuE-9 N-doped Graphene Synthesis through Nitrogen Ion Irradiation***, Zbynek Novotny,* Pacific Northwest National Laboratory*; B. Alupothe Gedara, P. Evans, Z. Dohnalek,* PNNL

Hydrogen (H_2) is one of the most promising clean and renewable energy sources. Nevertheless, the storage of hydrogen shows poor performance due to the low gravimetric and volumetric densities. Nitrogen-doped graphene (Gr) has been identified as a potential material for H_2 storage. We study the growth of Gr on a Ru(0001) surface by chemical vapor deposition (CVD) of pyridine (H_5C_5N) and N-doping through N_2^+ ion irradiation using scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS). A high-quality Gr film with low N densities was obtained by pyridine CVD on Ru(0001) at 1100 K. Higher concentrations of N-dopants were introduced on the Gr/Ru(0001) through low-energy N_2^+ irradiation at 100 eV. Nitrogen can be embedded in the Gr lattice preferentially in two configurations, namely graphitic N (N substituted in the C lattice) and pyridinic N (substitutional N next to a C vacancy). Atomically-resolved STM images of graphitic and pyridinic-N defects demonstrate their preferential locations within the Gr Moiré. XPS shows that coverage of up to 3.9% of pyridinic-N and 2.3% of graphitic N can be embedded into the high-quality Gr film using N_2^+irradiation at room temperature, indicating a preferential formation of pyridinic N over graphitic N. Only graphitic N was observed upon annealing the ion-irradiated Gr/Ru(0001) to 1063 K, revealing higher thermal stability of graphitic N over pyridinic N. Our current efforts center on the adsorption studies of atomic hydrogen, its interactions with N dopants, and thermally induced diffusion.

8:40pm **NM2-TuE-10 Nanoscale Investigation of N-Heterocyclic Carbene Monolayers on Metal Surfaces***, Francesco Tumino,* Queen's University, Canada, Italy*; E. DesRoche, M. Aloisio, D. Nanan, A. McLean, C. Crudden,* Queen's University, Canada

Molecular monolayers on metal surfaces are two-dimensional (2D) systems of great interest for advanced applications in several fields, such as molecular electronics, photovoltaics and catalysis[1]. The physical and chemical properties of these systems critically depend on the choice of the molecular unit that constitutes the basic building block of the resulting 2D assembly[2].

Recently, N-heterocyclic carbenes (NHCs) have been proposed for the fabrication of robust molecular monolayers, based on their ability to form strong covalent bonds with transition metals[3]. Studies conducted on gold surfaces have shown that NHC-based monolayers can have greater thermal and chemical stability than alkanethiolate 2D layers[4], making them promising for applications in biosensing, surface patterning and corrosion protection[3].

The fabrication of NHC-based monolayers, however, requires a detailed understanding of how the NHC structure and the surface properties affect the molecular adsorption and self-assembly behavior on metals.

Therefore, we have conducted a nanoscale investigation of NHCs on single-crystal metal surfaces under ultra-high vacuum conditions (UHV). Our study includes NCHs with different backbones and N-substituents, deposited onto atomically clean surfaces using a vapor phase method (supplemental document, Fig.1). Low-temperature scanning tunneling microscopy (STM) was used to image in situ the resulting monolayers and obtain molecular-scale information on binding modes, adsorption geometries, and self-assembly patterns.

We observed different supramolecular assemblies (Fig. 2), in which the binding mode and lattice geometry vary depending on the N-substituents, the backbone structure, and the molecular density on the surface. Moreover, the metal surface properties play an important role, affecting the ability of NHCs to extract metal adatoms from the surface and form mobile NHC-metal complexes.

By discussing different factors which influence the NHC behavior on metals, our work contributes to a wider understanding of the coordination of these ligands to metal surfaces and the formation of 2D NHC-based layers.

[1] Goronzy D.P., et al. "Supramolecular assemblies on surfaces: nanopatterning, functionality, and reactivity." ACS Nano 12.8 (2018): 7445-7481.

[2] Barth J.V., et al. "Engineering atomic and molecular nanostructures at surfaces." Nature 437 (2005).

[3] Smith C.A., et al. "N-heterocyclic carbenes in materials chemistry." Chem Rev 119 (2019).

[4] Crudden C.M., et al. "Ultra stable self-assembled monolayers of N-heterocyclic carbenes on gold." Nat Chem 6 (2014).

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