O 39: Poster Session III: Poster to Mini-Symposium: Free-standing functional molecular 2D materials I

Time: Tuesday 10:30–12:30 Location: P

O 39.1 Tue 10:30 P

Electronic and Optical Properties of Protonated Triazine Derivatives — Michele Guerrini[1,2], •Enrique Delgado Aznar[2], and Caterina Cocchi[1,2] — [1]Carl von Ossietzky Universität Oldenburg, Institute of Physics, 26129 Oldenburg, Germany — [2]Humboldt-Universität zu Berlin, Physics Department and IRIS Adlershof, 12489 Berlin, Germany

The peculiar electronic and optical properties of covalent organic frameworks (COFs) are largely determined by protonation, a ubiquitous phenomenon in solution environments. Resulting effects are non-trivial and yet crucial for the intriguing functionalities of these materials. We investigate from first principles the impact of protonation of triazine and amino groups in molecular building blocks of COFs in water solution. We find that proton uptake leads to bandgap reduction and to a reorganization of the electronic structure. The interplay between bandgap renormalization and exciton binding strength determines whether the absorption onsets is red or blue shifted with respect to the pristine species. Structural distortions induced by protonation are found to play only a minor role.Our results [1] offer a quantitative and microscopic insight into the role of protonation in the electronic and optical response of triazine derivatives as building blocks of COFs and to the rationalization of the relationship between structure, property, and functionality in these materials.

[1] M. Guerrini, E. D. Aznar, C. Cocchi J. Phys. Chem. C 2020 DOI: 10.1021/acs.jpcc.0c08812

O 39.2 Tue 10:30 P

Controlled Electron-Induced Fabrication of Metallic Nanostructures on 1 nm Thick Membranes — Christian Preischl[1], •Linh Hoang Le[2], Elif Bilgilisoy[1], Florian Vollnhals[1], Armin Gölzhäuser[2], and Hubertus Marbach[1] — [1]Physikalische Chemie II, Friedrich-Alexander Universität Erlangen-Nürnberg, 91058 Erlangen, Germany — [2]Fakultät für Physik, Universität Bielefeld, 33615 Bielefeld, Germany

Functional metallic nanostructures precisely deposited on insulating 2D materials are desired in many applications in optics, electronics, and magnetics. Such miniaturized details can be realized by using focused electron beam induced deposition (FEBID). With this technique, we directly deposit iron structures from Fe(CO)5 precursors onto terphenylthiol self-assembled monolayers (SAMs). We then apply electron irradiation to crosslink the functionalized SAMs into porous carbon nanomembranes (CNMs) while the iron structures remain on their surfaces. The resulting ultrathin, flexible and mechanically stable CNMs preserves the written iron patterns. They can be transferred onto either solid substrates or onto grids to obtain free-standing metal/CNM hybrids. In this way, we can achieve clean iron nanostructures of arbitrary size and shape on top of the 1 nm thick CNMs. Combining the ease and versatility of CNMs with the flexibility of FEBID leads to a promising route for the fabrication of functional hybrid nanostructures.

O 39.3 Tue 10:30 P

Ru(II) polypyridine nanomembranes by low-energy electron irradiation of SAMs — •Maria Küllmer[1], Felix Herrmann-Westendorf[1,3], Stefan Götz[2], Christof Neumann[1], Patrick Endres[2], Rebecka Glässner[1], Andreas Winter[2], Ulrich Sigmar Schubert[2,4], Benjamin Dietzek[1,3,4], and Andrey Turchanin[1,4] — [1]Institute of Physical Chemistry, Friedrich Schiller University Jena, Germany — [2]Institute of Organic Chemistry and Makromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Germany — [3]Leibniz Institute of Photonic Technology e. V., Jena, Germany — [4]Center for Energy and Environmental Chemistry Jena (CEEC Jena), Germany

Artificial photosynthesis is of great importance for the development of sustainable energy sources. Due to their unique chemical and physical properties molecular 2D materials are highly promising building blocks to this end. Here we present two different concepts for the introduction of the Ru(II) polypyridine photosensitizers into Carbon Nanomembranes (CNMs) - a molecular nanosheet generated by electron irradiation induced cross-linking of self-assembled monolayers (SAMs). The photoactive units are either incorporated into the SAMs before or covalently attached after the crosslinking. We characterize the developed molecular nanosheets using high-resolution X-ray photoelectron spectroscopy and surface-enhanced Raman scattering. The combination of atomic force and scanning electron microscopy shows the formation of 2D nanomembranes. Photothermal deflection spectroscopy (PDS) is employed to characterize the absorption properties.

O 39.4 Tue 10:30 P

Gas permeation through a series of chemically inert carbon nanomembranes — •Vladislav Stroganov[1], Daniel Hüger[1], Monika Kruk[2], Christof Neumann[1], Krzysztof Kozieł[3], Piotr Cyganik[2], and Andrey Turchanin[1] — [1]Friedrich Schiller University Jena, 07743 Jena, Germany — [2]Smoluchowski Institute of Physics, Jagiellonian University, 30-348 Krakow — [3]Faculty of Chemistry, Jagiellonian University, 30-387 Krakow

Due to their unique physical and chemical properties, atomically or molecularly thin sheets are promising nanomaterials for future energy conversion and separation technologies. In this study, we investigate carbon nanomembranes (CNMs) synthesized by low energy electron beam irradiation cross-linking of self-assembled monolayers based on a homologue series of biphenyl substituted carboxylic acids (C_6H_5-C_6H_4-$(CH_2)_n$-COO/Ag, n=2-6). Their permeation properties for various gases (He, Ar, D_2, D_2O, O_2) were studied by highly sensitive mass spectrometry measurements. The results demonstrate that the permeation of CNMs can be intimately tuned by structure of the molecular precursors. A difference of only one aliphatic carbon unit can significantly modify the permeation of gases with various kinetic diameters. Based on the conducted measurements, we evaluate the size and the density of nanopores in CNMs. Both quantities are otherwise hardly accessible for the studied molecular nanosheets by conventional microscopy techniques.

O 39.5 Tue 10:30 P

Preparation of Carbon Nanomembranes without Chemically Active Groups — Christof Neumann[1], Monika Szwed[2], •Martha Frey[1], Zian Tang[1], Krzysztof Kozieł[3], Piotr Cyganik[2], and Andrey Turchanin[1] — [1]Institute of Physical Chemistry, Friedrich Schiller University Jena, 07743 Jena — [2]Smoluchowski Institute of Physics, Jagiellonian University, 30-348 Krakow — [3]Faculty of Chemistry, Jagiellonian University, 30-387 Krakow

The electron-irradiation-induced synthesis of carbon nanomembranes (CNMs) from aromatic thiol-based self-assembled monolayers (SAMs) on gold substrate is a well-established method to form molecular thin nanosheets. These molecular two-dimensional materials can be prepared with tunable properties; therefore, they find a variety of applications in nanotechnology ranging from ultrafiltration to nanobiosensors. However, having advantages for some applications, chemically inert CNM cannot be prepared from thiol-based SAMs, as the reactive thiol group is present on the membrane surface even after transferring it to other substrates. Here, we study the electron irradiation of carboxylic acid-based SAMs on a silver substrate as an alternative route for CNM formation. Our analysis, based on a combination of X-ray photoelectron spectroscopy and scanning electron microscopy demonstrates that for this type of SAMs, purely carbonaceous CNMs with tunable porosity can be obtained. Neumann et al. ACS Appl. Mater. Interfaces 11 (2019) 31176.

O 39.6 Tue 10:30 P

Optically triggered control of carrier density in hybrid graphene-carbon nanomembranes field effect transistors — •Antony George[1], Zian Tang[1], Andreas Winter[1], David Kaiser[1], Christof Neumann[1], Thomas Weimann[2], and Andrey Turchanin[1] — [1]Friedrich Schiller University Jena, Institute of Physical Chemistry, 07743 Jena, Germany — [2]Physikalisch-Technische Bundesanstalt (PTB), 38116 Braunschweig, Germany

Field effect transistors (FETs) based on 2D materials are of great interest for applications in ultrathin electronic and sensing devices. Here we demonstrate the possibility to add optical switchability to graphene FETs (GFET) by functionalizing the graphene channel with optically active azobenzene molecules. The azobenzene molecules have been incorporated to the GFET channel by building a van der Waals heterostructure with carbon nanomembrane (CNM) which is used as a molecular interposer to attach the azobenzene molecules. Under exposure with 365 nm and 455 nm light, azobenzene molecules undergo cis- and trans- molecular conformations respectively, resulting in a switching of the molecular dipole moment. Thus the effective molecular field acting on the GFET channel is switched by optical stimulation and the carrier density is modulated.