

Thin Films

Room 206 B W - Session TF2-TuM

VSHOP I - Porous Framework Materials & Membranes

Moderators: Siamak Nejati, University of Nebraska-Lincoln, Junjie Zhao, Zhejiang University

11:00am TF2-TuM-13 Synthesis of Electrically Conductive Metal-Organic Framework Thin Films, Sarah Park, Pohang University of Science and Technology (POSTECH), Republic of Korea

INVITED

Conducting metal-organic frameworks (MOFs) present a compelling prospect for the development of high-performance electronic devices, ranging from electrocatalysts and chemiresistive sensors to supercapacitors. Although MOFs typically exhibit low electrical conductivity due to flat bands determined by highly localized organic states and weak hybridization with inorganic units, significant advances have been made in engineering their electrical properties. Specifically, through precise control of symmetry and energy overlap, highly ordered infinite charge transport pathways in conducting MOF platforms have been established. Nevertheless, for practical device integration, a critical challenge lies in processing these materials into functional thin films. This presentation introduces two distinct approaches for synthesizing conductive two-dimensional MOF thin films: a single-step, all-vapor-phase chemical vapor deposition process, and a solution-processable synthetic approach.

11:30am TF2-TuM-15 Selective Breathing Behavior in Thin Films of Microporous Coordination Polymers, Greg Szulczewski, Hallie Matherne, The University of Alabama

Thin films in a family of pillared, microporous coordination polymers with the general formula $M_2(\text{BDC})_2\text{DABCO}$, where M is Ni^{2+} , Cu^{2+} and Zn^{2+} , BDC is benzenedicarboxylic acid and DABCO is 1,4-diazabicyclo[2.2.2]octane, were made by a hot vapor synthesis technique. The thin films were characterized by x-ray diffraction, vibrational spectroscopy and scanning electron microscopy. The films were activated by heating under high vacuum and adsorption/desorption isotherms were measured for several volatile organic alcohols. The shape of the isotherms strongly depend on the metal ion of the coordination polymer and the alcohol. In thin films of $\text{Ni}_2(\text{BDC})_2\text{DABCO}$, methanol adsorption isotherms exhibit a characteristic S-shape that is attributed to lattice expansion or breathing above a critical pressure. Upon removal of methanol from the thin film, the lattice relaxes back to the original structure. The breathing phenomena is attributed to the formation of a network of hydrogen bonds between the methanol molecules and BDC ligand.

11:45am TF2-TuM-16 Atomic Layer Deposition for Pore Engineering in Covalent Organic Framework Thin Films for Enhanced Membrane Gas Separation, Zhiwen Chen, Junjie Zhao, Zhejiang University, China

Covalent organic frameworks (COFs) are crystalline networks with ordered pores, large surface area and versatile topologies. Developing pore engineering strategies to fine tune the internal functionality and dimension of COF pores could offer proper pore size and affinity towards small gas molecules, which is crucial for applying COFs to membrane gas separation. Here, we report a pore engineering approach for COFs using atomic layer deposition (ALD). We prepared thin films of an imine-based COF (TPB-DHTA) on porous alumina supports via interfacial synthesis. We found that the amount of ZnO deposited into the COF pores can be precisely controlled by varying ALD cycles. Consequently, the original pore size (1.4 nm) was reduced to 1.05 nm, 0.85 nm, and even below 0.6 nm, leading to an improved the diffusion selectivity of H_2/CO_2 through the COF membranes from 93.9 to 278.6 after ALD modification. Moreover, the Zn-O moieties grown into the COF pores were found to shield the CO_2 -philic ketoenamine groups, which substantially reduced the CO_2 solubility in the COF membrane by 262%. Accordingly, the simultaneously increased diffusion selectivity and sorption selectivity for H_2/CO_2 led to a 430% improvement of permselectivity for membrane separation, demonstrating the efficacy of our strategy for pore engineering in COFs.

12:00pm TF2-TuM-17 Synthesizing Hydrophilic Membranes for PFAS Removal via Molecular Layer Deposition, Joelle V. Scott, Mathangi Venkatesh, Jocelyne Booth, David S. Bergsman, University of Washington

As the global water crisis continues to worsen, the increased need for access to clean water drives the need for better water treatment technologies, such as through the removal of per- and polyfluoroalkyl substances (PFAS). PFAS are a group of toxic compounds that do not

biodegrade due to their strong carbon-fluorine backbone. Common PFAS removal methods include absorption and ion exchange resins, but these require expensive and energy-intensive regeneration steps. A more efficient removal technology is membrane separation, which has been shown to be effective at removing PFAS from water. Short-chain PFAS are harder to remove than long-chain PFAS due to their decreased size and increased reliance on end group interactions. Due to the reduced hydrophobicity of PFAS as their carbon chain length decreases, increasing the hydrophilicity of the membrane selective layer may increase the rejection of both long- and short-chain PFAS by reducing hydrophobic interactions between the membrane and the PFAS compounds. However, interfacial polymerization, a traditional membrane synthetic approach, relies on identifying two monomers that can be dissolved in different solvents that are immiscible. The thickness of the resulting membrane also cannot be independently controlled, as it is defined by the monomer diffusion length into the counter solvent. In this work, we use molecular layer deposition (MLD) to synthesize thin film composite membranes with the aim to vary hydrophilicity. This approach avoids the issue of identifying appropriate solvents, allowing for a wider range of selective layer chemistries as well as independent control over film thickness. To demonstrate the effectiveness of this technique for controlling membrane properties, polymers based on polyurea, polyamide, and polyester were explored, measuring hydrophilicity and ability to remove long- and short-chain PFAS. Film composition is confirmed using FTIR and XPS. These are correlated with pure water permeability, salt rejection, and PFAS rejection to determine the impact of monomer chemistry.

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