Emerging Materials
Room Jan & Hubert Van Eyck - Session EM-WeM

Organic and Organic-Inorganic Hybrid Materials I

Moderators: Steven M. George, University of Colorado at Boulder, Mato Knez, CIC nanoGUNE

11:00am **EM-WeM-2 Vapor-Phase Synthesis and Surface Area Analysis of ZIF-8 Metal Organic Framework (MOF) on Fibrous Substrates via Atomic Layer Deposition***, R Nye, S Smith,* ***Nicholas M. Carroll****, G Parsons,* North Carolina State University

Solvent-free synthesis methods for metal-organic frameworks (MOFs) will help expand their applications in catalysts, gas adsorption, and sensors. Unfortunately, methods of using atomic layer deposition on silicon wafers to convert a metal oxide to MOF prevent surface area measurements, which are critical in the aforementioned applications. In this work, we describe low-temperature formation of zeolitic imidazolate framework (ZIF-8) MOF on high-surface area polypropylene polymer fiber substrates via vapor-directed conversion of ALD ZnO. The resulting MOF-fiber structures are highly stable and withstand robust mechanical deformation, demonstrating excellent MOF adhesion to the polymer fiber surface. Moreover, for the first time, our synthesis approach enables direct gas adsorption analysis of vapor-derived MOFs, including determination of net surface area by Brunauer-Emmett-Teller (BET) analysis. To form the MOF-fiber structure, approximately 10 nm of zinc oxide is deposited at 90°C via ALD on nonwoven polypropylene fiber mats. The coated mats are then placed into a loosely sealed vessel containing 2-methylimidazole powder and heated at 100-135 C for 1-24 hours, enabling volatilization of the 2-methylimidazole and reaction with the solid ZnO to form ZIF-8 crystals. During the process, the pressure in the vessel is maintained at atmospheric pressure. The formation of ZIF-8 is confirmed by XRD, and SEM shows crystals of ~100-300 nm on the fiber surface. BET analysis on the MOF-coated fiber mats demonstrated surface area values of 400 m^2/g (fiber+MOF). Using the mass of MOF determined by sample weight before and after MOF growth, the surface area of the ZIF-8 on the fibers in 1500 m^2/g ZIF-8, which is comparable to ~1300 m^2/g expected for ZIF-8 powder, indicating good quality of synthesized MOF. To the best of our knowledge, this is the first report of surface area measurements on solvent-free MOFs. By tuning deposition and conversion parameters, the crystallinity and surface area of the ZIF-8 can be controlled. This MOF formation on fibers enables applications and measurements not otherwise available, such as incorporation into protective garments. Additionally, successful vapor-phase MOF synthesis opens the doors for selective deposition of MOFs for use in sensing and electronic applications.

11:30am **EM-WeM-4 Vapor Phase Infiltration for Transforming Polymers into Hybrid Materials: Mechanisms of Inorganic Entrapment and Structure-Property Implications***,* ***Mark Losego,*** Georgia Institute of Technology **INVITED**

Vapor phase infiltration (VPI) transforms polymers into organic-inorganic hybrid materials by infusing the polymer with inorganic constituents from the gas phase. Hybrid materials synthesized with VPI have been demonstrated for numerous applications ranging from energy harvesting to filtration media to photolithographic hard masks. The infiltration process consists of three basic steps: (1) sorption of the gaseous precursor molecule into the polymer, (2) diffusion of the precursor throughout the polymer, and (3) “entrapment” of that precursor within the polymer. This talk will focus on this final step: “entrapment”. The mechanism of entrapment informs both how to design an infiltration process and the final chemical structure of the hybrid material. Processes for entrapment can largely be understood by the energy landscape for precursor binding and reaction with the polymer. Most important to understand is the depth of the energy well for the bound state and the activation energy for the reaction pathway. These energetics determine whether a precursor is easily entrapped and whether the final hybrid has unbound or chemically bound inorganic constituents. In this talk, we will show evidence from our lab for infiltrated materials where the inorganic constituents are homogeneously distributed throughout the hybrid material but are chemically unbound to the organic – creating an interpenetrating, unbound organic-inorganic bicontinuous network. Similarly, we will show how increasing reaction temperature can increase the probability for chemical reactions and covalent bond formation. Subsequently, we will show how these different chemical states lead to differences in material properties including solubility, glass transition, thermal expansion, and interfacial adhesion strength.

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