Thin Film Division
Room A105 - Session TF1-TuA
Catalytic and Active Materials

Moderators: Mark Losego, Georgia Institute of Technology, **Richard Vanfleet**, Brigham Young University

2:20pm **TF1-TuA-1 MLD as a Sandbox for Photoactive Hybrid Materials***, **Ola Nilsen,*** University of Oslo, Norway **INVITED**

To an experimental chemist, the MLD approach is a desirable tool to explore chemical reactivity and to create structures that otherwise would not be possible. So, what are its limitations? And why should you use this approach? These, and other questions will be covered during this presentation where we will focus on volatilization of precursors, challenges with surface limited reactions when your material is porous, how to influence the growth during growth, and more. The MLD approach is highly effective in combining material classes that naturally do not combine. We use this approach to combine highly absorbing organic molecules with fluorides and oxides to design photoactive structures. By such manner, we have achieved complete energy transfer from the organic molecules to lanthanides without quenching. We also show drastic suppression of concentration quenching of multilayered structures of lanthanides as compared to solid solutions by confining energy migration in 2D planes. The flexibility of the MLD approach allows for exploration of exotic combinations of absorbers and emitters, but how far can you go with MLD?

3:00pm **TF1-TuA-3 Dry Pathways to Synthesize Thin Films of Covalent Organic Frameworks***, **Syed Ibrahim Gnani Peer Mohamed**, S. Nejati, M. Bavarian,* University of Nebraska - Lincoln

Covalent organic frameworks (COFs) are porous materials with potential applications in gas storage, catalysis, and electronics. However, traditional COF synthesis methods are limited by low solubility and poor processability. In contrast, oxidative chemical vapor deposition (oCVD) and oxidative Molecular Layer Deposition (oMLD) provide versatile and scalable approaches to deposit COFs on different surfaces. Porphyrins and their derivatives have attracted the attention of many researchers as precursors for COF preparation. Porphyrin and its metal complexes can serve as electrocatalysts, especially for oxygen reduction, nitrate reduction, and carbon dioxide reduction reactions. In addition, these materials have also been explored for photocatalysis, separation, optical switches, and other applications. Polymerization of porphyrins to create frameworks and networks increases the stability of these materials. Thus, preparing porphyrin-based COFs is essential for their widespread application. COFs are commonly synthesized via the solvothermal method, which involves a very long reaction time and the use of toxic organic solvents. Therefore, a dry synthetic pathway is highly desirable. Herein, we report the one-step, solvent-free synthesis of crystalline and porous porphyrin-based COFs. Both 5,10,15,20-tetra(4-aminophenyl)porphyrin (TAPP) or its transition metal complex (MPOR-COF, M = H_2, Cu^{2+}, Co^{2+}, Zn^{2+}) in the presence of antimony pentachloride ($SbCl_5$), as an oxidant, polymerized. The monomer TAPP undergoes polymerization via phenazine link formation (pTAPP) in the presence of $SbCl_5$, leading to the formation of well-ordered MPOR-COFs. Here, we describe the bottom-up and dry assembly of pTAPP and its derivatives to create active materials. We also report on the control achieved over the reaction selectivity and separation performance of the thin films deposited through the oxidative vapor phase polymerization pathway and explore various strategies to control the film structure and properties. The resulting materials were characterized using various techniques such as spectroscopy, microscopy, and gas adsorption. We also investigated the effect of substrate, deposition conditions, and post-synthesis treatment on the structure and properties of the resulting COFs. Our results show that oCVD and oMLD are promising methods for synthesizing COFs with tunable properties and potential applications in various fields.

3:20pm **TF1-TuA-4 Vapor Phase Infiltration of Titanium Oxide into P3HT to Create Organic-Inorganic Hybrid Photocatalysts***, **Li Zhang**, S. Gregory, M. Losego,* Georgia Institute of Technology

Chemical doping using vapor phase infiltration (VPI) of metal halide precursors and water has been shown to dope conjugated polymers (CP). The reacted product – metal oxide clusters – remain trapped within the CP and are often thought to just act as scattering centers that lower the electronic mobility of the CP. However, in this talk we will show how these metal oxides can be used as catalytic sites for photocatalytic reactions. Metal oxides such as TiO_x have been well documented for their good photocatalytic properties, with the drawback that they do not absorb in the visible region. In hybrid CP-MO_x systems, the CP can act as a sensitizer absorbing light in the visible regime and then injecting the photo-excited electrons into the MO_x to perform the catalysis. In this talk we will discuss our work in exploring the vapor phase infiltration of the CP poly(3-hexylthiophene-2,5-diyl) [P3HT] with $TiCl_4$ and H_2O to form P3HT-TiO_2 hybrid photocatalysts. Specifically, we examine how these photocatalysts perform in degrading the dye methyl blue in aqueous solutions, fitting the degradation to a first-order reaction and extracting the rate constant. XPS analysis of the VPI treated P3HT confirms that the inorganic infiltrants dope the polymer, which is confirmed by electrical measurements, and leave behind TiO_2 clusters. Photocatalytic measurements reveal that the P3HT-TiO_x hybrid material outperforms pure P3HT and pure TiO_2 by at least a factor of 4.5x, but only when illuminated. These results show a synergistic photosensitizing effect between the P3HT and TiO_2. To confirm that the electronic doping is not the sole source of enhanced photocatalytic activity, we also examined P3HT films doped with common oxidative dopants. While these doped P3HT show significantly higher electrical conductivity than the VPI treated P3HT, they had significantly lower photocatalytic activity (at least 3x lower). Dedoping of the P3HT-TiO_2 hybrids to reduce conductivity also did not eliminate the photocatalytic performance of these hybrids, providing further evidence that this photocatalytic effect is not simply due to higher electrical conductivity. To explore how catalytically active VPI could make the P3HT, the polymer was exposed to differing number of VPI cycles. It was found that the catalytic activity increased until 5 cycles, where the surface S:Ti ratio was 3, and then proceeded to gradually decrease for more cycles. Based on subsequent characterization, we will discuss why this design is optimal and to what extent the infiltrated TiO_x species need to be near the surface of the hybrid material. We will also demonstrate how this catalyst is amongst the best performing CP-MO_x photocatalysts to have been reported in the literature.

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