PRF# 57951-UNI10
Project Title: Mechanism-Guided Design and Synthesis of Metal-Organic Frameworks with Optimized Pores for Methane Storage
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Research Progress:

From 9/1/2018 to 8/31/2019, we have been focusing on the synthesis of new organic linkers and metal-organic frameworks (MOFs), as well as the characterizations of the new materials for their gas storage properties. We have also used a green chemistry approach to synthesize MOF hybrid materials for methane storage applications. One MOF we synthesized exhibited excellent high pressure (65 bar) methane uptake under room temperature. Computational work is being conducted to understand the methane adsorption sites in this MOF.

An organic linker (L1) with reduced symmetry was obtained via Suzuki reaction. The solvothermal reaction between copper salts and L1 in *N,N'*-dimethylformamide (DMF) produced blue crystals, namely CSLA-1. Single-crystal X-ray diffraction revealed this MOF has a three-dimensional (3-D) cavity structure which was shown in Figure 1a and 1b. CSLA-1 can be synthesized in bulk by scaling up the reaction to 100 mg, and the purity of the bulk material was confirmed by Powder X-ray Diffraction (PXRD), as shown in Figure 1c. After washing with DMF, the MOF was activated by solvent exchange using methanol and dichloromethane (to remove coordinated DMF), followed by vacuum drying. Based on 77 K N_2 sorption experiment, the surface area of CSLA-1 was calculated to be 2872 $m^2 g^{-1}$ (Figure 1d). Additionally, CO_2, CH_4 and N_2 sorption isotherms were also collected at 195 K to study the porosity and gas selectivity of the MOF (Figure 1e). Like most MOFs, CSLA-1 is the most favorable for the adsorption of CO_2. Meanwhile, it showed a high CH_4 uptake at 195 K and 1 bar. This led us to study the high pressure (up to 65 bar) methane uptake of this MOF under room temperature. HKUST-1 was used as a benchmark in this study as it was reported as one of top performers for methane storage. As presented in Figure 1f, CSLA-1 exhibited even higher total methane uptake than HKUST-1 at 65 bar and room temperature, which is 16 mmol/g. The manuscript for this work is being prepared, and collaboration with computational lab will help reveal the mechanism for the high methane uptake. In addition, we are also currently optimizing the experimental conditions for the solvothermal synthesis of MOFs constructed from high valent metals (Al^{3+}, Fe^{3+} and Zr^{4+}) and L1, as MOFs based on these metals tend to be very stable to moisture.

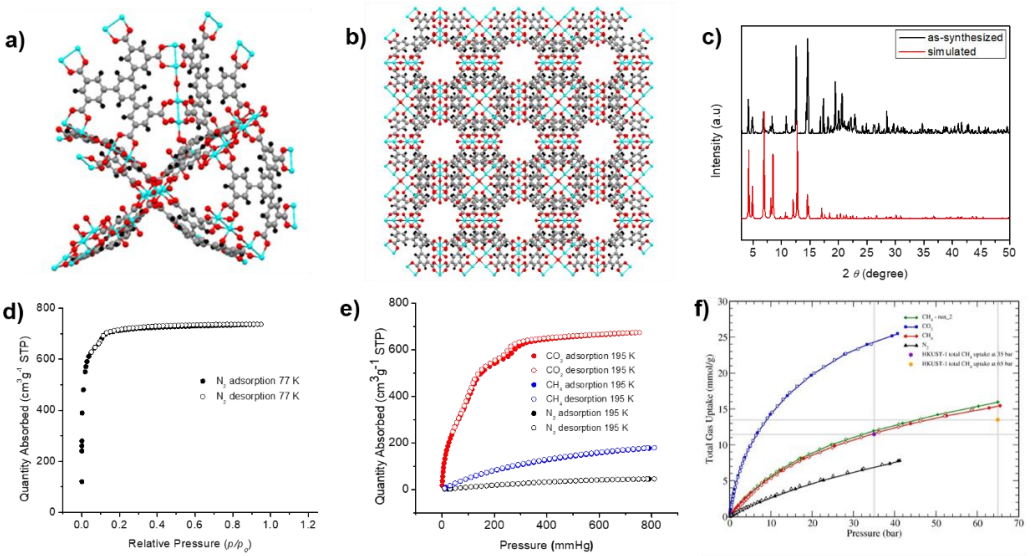

Figure 1. The crystal structure of synthesized MOF, CSLA-1 (a and b). c) Powder X-ray Diffraction of as-synthesized CSLA-1 compared to simulated patterns. d) 77 K N_2 sorption of CSLA-1. e) 195 K CO_2, CH_4 and N_2 sorption of CSLA-1. f) High pressure CH_4, CO_2 and N_2 uptake at 298 K.

With partial support from PRF, a MOF-hydrogel hybrid was synthesized and characterized. A green chemistry approach was utilized in the preparation of this hybrid, in which only water was used as the solvent. The Scanning Electron Microscope (SEM) images (Figure 2) showed the MOF-hydrogel hybrid has higher density than the hydrogel, indicating

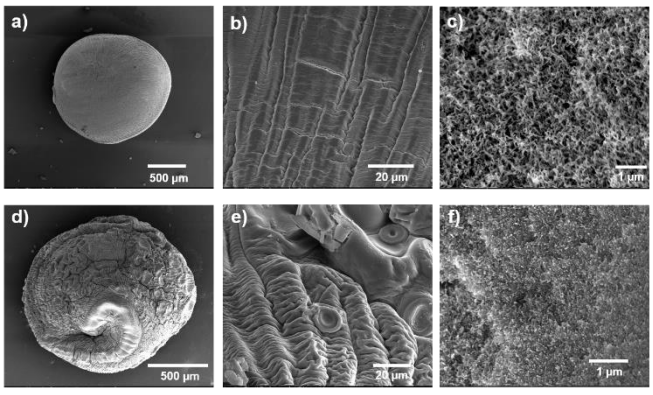

Figure 2. The Scanning Electron Microscope images of hydrogels (a-c) and MOF-hydrogel hybrid (d-f).

the microporous MOF components were uniformly embedded in the mesoporous hydrogel through cross-linking. FT-IR, PXRD and gas sorption studies further confirmed the hybrid structure. Due to the combination of meso- and micropores in this MOF-hydrogel hybrid, we believe it is a great candidate for methane storage application. While the mesopores can facilitate the diffusion of gas molecules, the micropores can enhance the interactions between the framework and the methane molecules. This hybrid was activated by supercritical CO_2 drying which is a method of removing solvent slowly from highly porous materials while maintaining their 3-D framework. The methane uptake of this material will be measured, and the methane adsorption sites will be studied through collaboration with computational research laboratory. A manuscript on the hybrid composites have been completed and will be submitted to an ACS journal for review. We are also currently synthesizing other MOF hybrid materials and studying their gas sorption properties.

Impact of Research:

Impact on the PI's Career: With the support of the PRF fund, the PI was able to establish collaborations with other universities as well as other research groups at Cal State LA. For example, the PI has maintained a close relationship with her collaborators in Pennsylvania State University via working on a project that was partially funded by PRF. This collaboration has led to the idea of hybrid materials. All the publications resulted from this project and the collaborations will help the PI to get her tenure on time. More importantly, the ideas and results obtained from this project also inspired new research directions and explorations. While working on this project, the PI has come up with several new ideas and has submitted grant proposals to various funding agencies and foundations (e.g. National Science Foundation, Department of Defense and Environmental Research & Education Foundation). With the feedback from the ACS-PRF proposal reviewers and the skills learned throughout the project, the PI was able to obtain two more external grants to support her research. Some of the ideas and materials obtained from this project were also applied to other projects in the PI's lab, which has led to a synergistic growth of her research group and a highly collaborative environment of her lab. While working on this project, the PI has learned how to manage students, projects and time. All these skills gained from this project will benefit her through her entire career as a professor and have made the PI become a more confident, more creative and more independent Assistant Professor.

This project also helped the PI to recruit students and grow her research group. By incorporating her research into her lectures and by posting research topics on her website, the PI has attracted both undergraduate and graduate students to joining her research laboratory to perform the proposed research. The PI's laboratory currently has nine graduate students and eight undergraduate students. The dynamic research environment in the PI's lab has led to some interesting scientific discoveries which will further benefit the PI's career development.

Impact on the Students: Many of the students working on this project were getting research experience for the first time. They became interested in research by being involved in this project and many of them decided to pursue a career in science afterwards. Several of them have already got into graduate programs and are continuing their journey in science. Due to the research experience they gained in this project, many of the students have also been awarded Research Fellowships that financially support them to complete their degrees in science.

Additionally, all the involved students have gained important scientific communication and writing skills, by presenting their research and by writing monthly research progress report. They have learned how to use some important research tools, such as ChemDraw, Sci-Finder, Endnote and Mercury. They have also been trained on organic synthesis, materials synthesis and characterizations, Schlenk line techniques, glovebox and various instruments, such as PXRD, thermogravimetric analysis, gas sorption, supercritical CO_2 drying.

With the support of the PRF, one undergraduate student working on this project has successfully obtained his Bachelor's Degree in Chemistry and was admitted to the Chemistry PhD program at University of California, Davis. He already started his PhD studies in Chemistry this Fall and is planning to pursue a career in science afterwards.

Due to the research experience this project has offered, another undergraduate student was awarded an NIH undergraduate Fellowship which offers financial support throughout her undergraduate studies. Before joining my lab, this student had no prior research experience, but this project attracted her to research. She has presented her research in multiple symposiums in the forms of both poster and oral presentations. Her goal is to get into a top PhD program after she graduates next summer.

One graduate student supported by this fund gained research experience in the synthesis of water-stable MOFs and was awarded a National Science Foundation Fellowship, which financially supports him to pursue his Master's Degree. He has also decided to pursue a PhD after his Master's Degree in Chemistry.