Novel synthesis apparatus for the growth of Cu-BTC, an HKUST-1 Metal-Organic Framework

***Itzel Esparza*, Jonathan Valenzuela, Nathan Stoddard, Siddha Pimputkar**

Department of Materials Science and Engineering, P.C. Rossin College of Engineering and Applied Science, Lehigh University, Bethlehem, PA, 18015

Introduction

- Metal-Organic Frameworks (MOFs) are porous materials composed of metal ions connected by organic ligands.
- Copper Benzene-1,3,5-tricarboxylate (Cu-BTC), due to its **high surface area, controllable pore size, and crystalline structure**, finds applications in carbon sequestration gas storage. [1,2]
- Optimizing synthesis conditions is crucial for enhancing MOF properties.
- Our research focuses on developing a closed synthesis apparatus to **improve Cu-BTC crystal quality and size.**

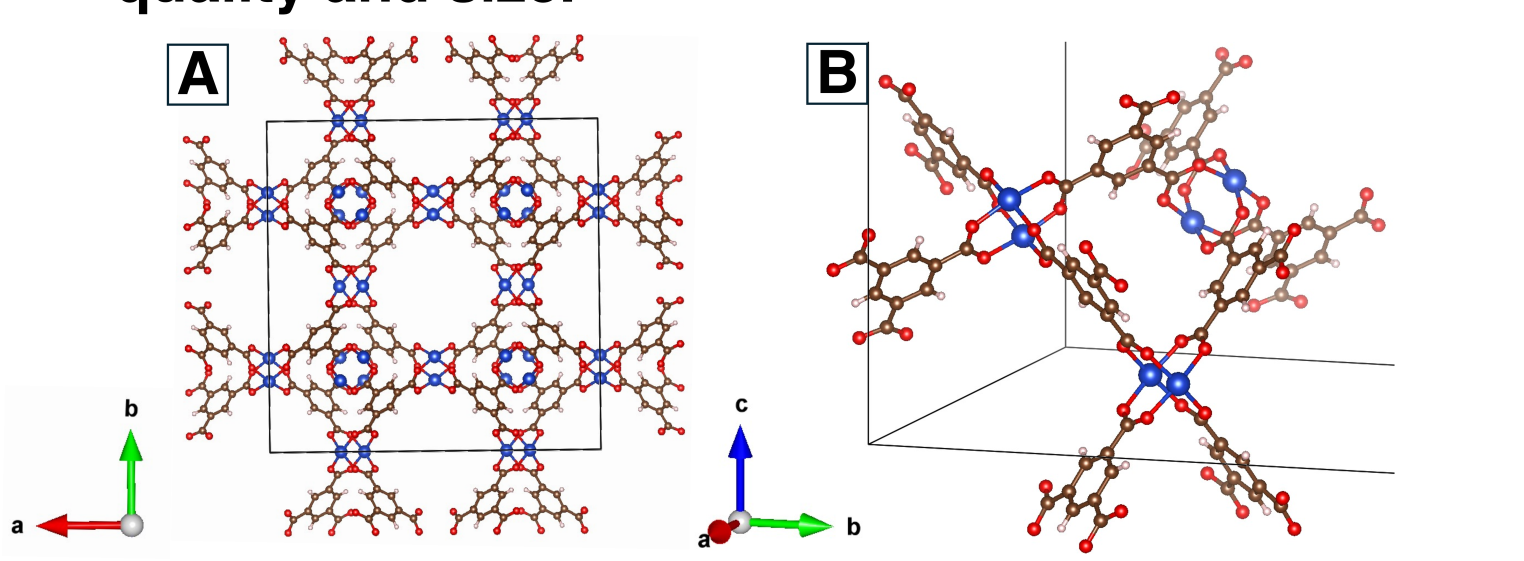

Figure 1. The atomic structure of Cu-BTC was modeled using Vesta. The atoms are color-coded, with Cu^{2+} represented in blue and the organic ligand BTC shown with brown carbon, red oxygens, and off-white hydrogens.

Synthesis Procedure

- Solvothermal synthesis methods have explored the dependence of the pH of the solution as well as temperature on growth. [3]
- We repeated a hot plate synthesis recipe, as seen in Figure 2. This involved the solutes $Cu(NO_3)_2$ $6H_2O$ and H_3BTC and the solvents Water, Ethanol, and N,N dimethylformamide (DMF). Glacial acetic acid was the chosen modulator. [4]

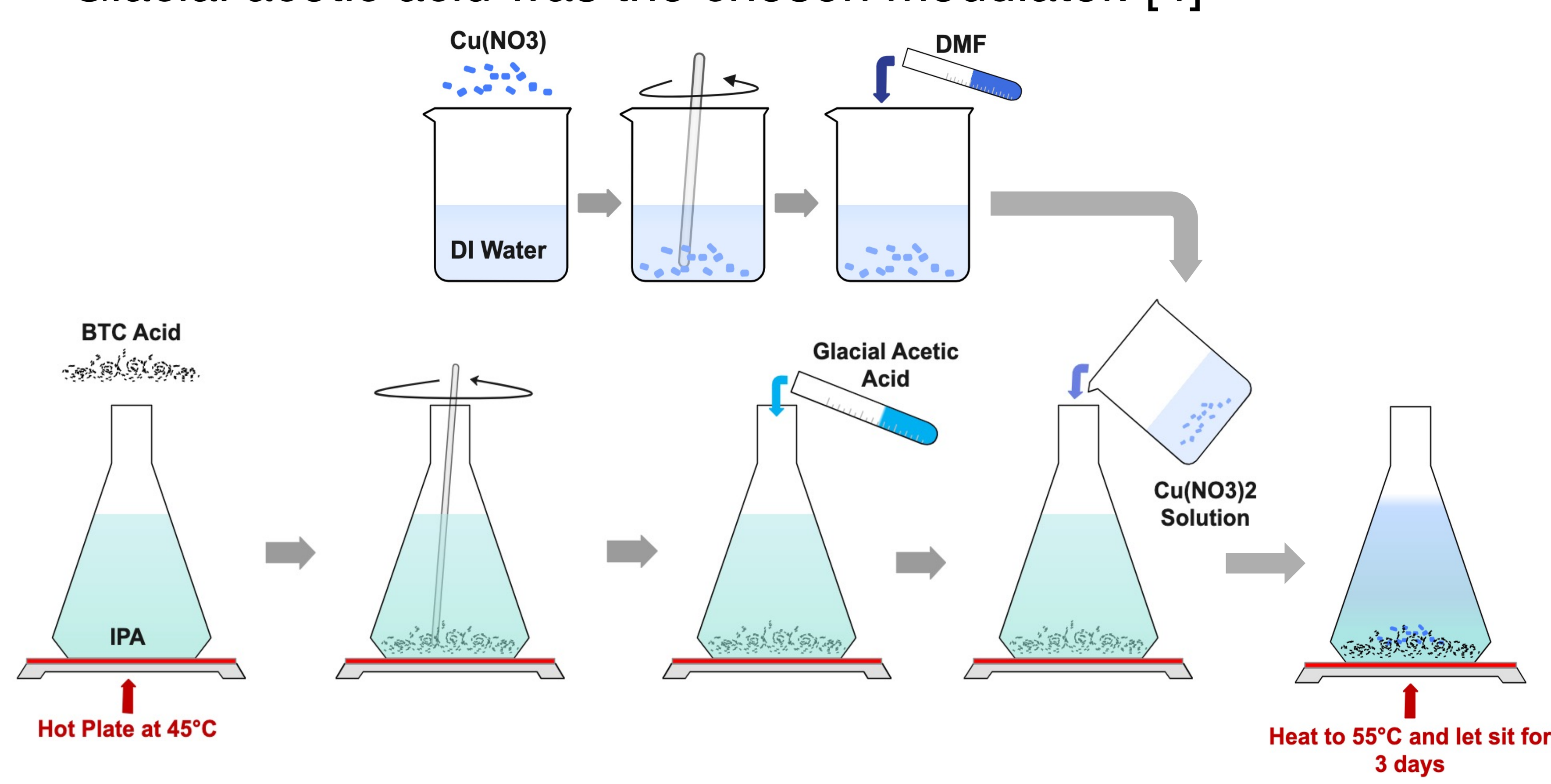

Figure 2. Schematic representation of the hot plate synthesis process involved mixing a Cu(NO3) solution in deionized water and DMF with a solution of BTC acid in isopropyl alcohol and glacial acetic acid. The final solution was left for three days on a heated stir plate at 55 °C.

Apparatus Design

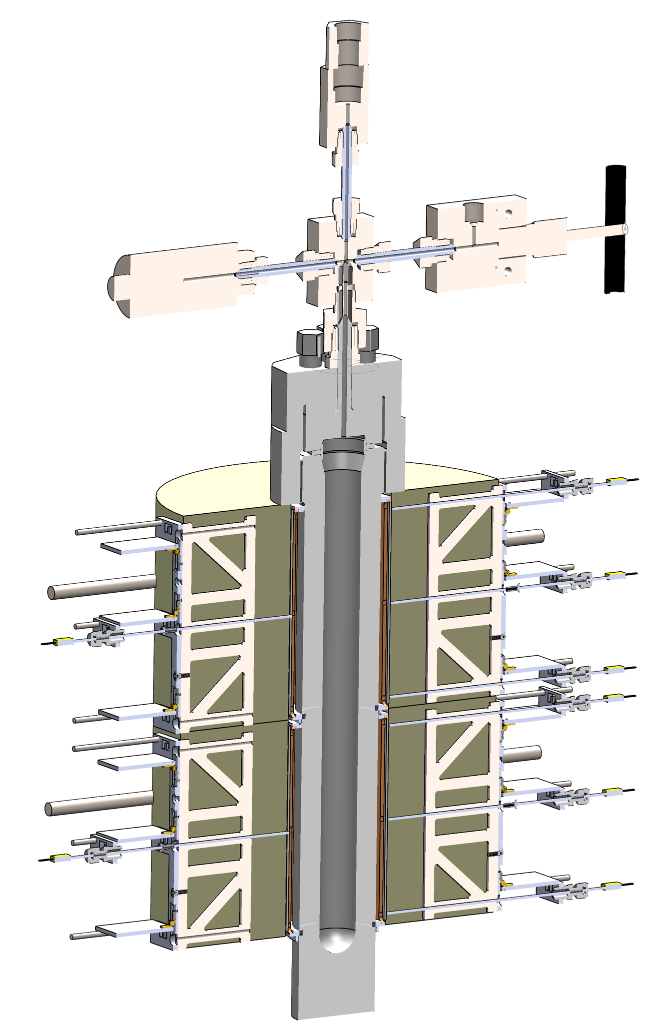

Figure 3. A Solidworks rendering of the mechanical design of the autoclave

- Our apparatus aims to provide a closed system for controlled temperature and pressure conditions to drive crystal growth.
- The autoclave has been designed for growth conditions of **500 K and 5 MPa**. The **partial pressure of our solvents at different temperatures** determined these parameters.
- We designed an autoclave using **Hastelloy C276** due to its **corrosion resistance** to glacial acetic acid up to 500 K and its **mechanical strength** which withstand the safety regulations at high pressure.

Growth Results

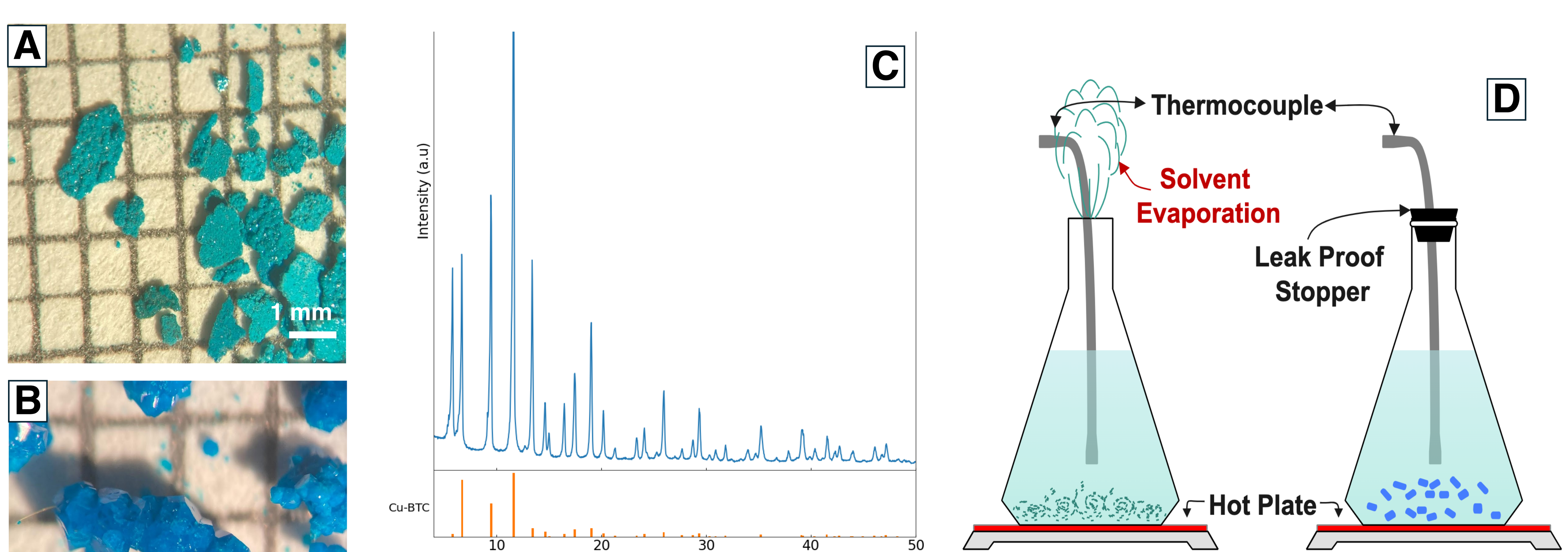

Figure 4. Powder-like blue-green crystals are produced in the non-leakproof run (A), and bright blue crystals are produced during the leakproof run (B). The XRD plot and Cu-BTC pdf file of the leak-proof run crystals (C). Schematic demonstrating the non-leakproof synthesis, which has solvent evaporating and produces small powder blue-green (left). The leakproof run has a rubber stopper, reducing evaporation and producing bright blue crystals (right) (D).

- We conducted hot plate synthesis twice. We placed a rubber stopper at the beaker opening the second time, as seen in Figure 3.
- We observed that all crystals synthesized at the bottom surface of the beaker, indicating preferential growth at the heat source.
- The desired output for Cu-BTC crystals was modeled with the leakproof run, **verifying that limiting solvent evaporation (e.g. increasing pressure) is key to bulk crystal growth**.

Conclusions and Future Work

Throughout this experiment, we verified that Cu-BTC can be synthesized using a solvothermal method. We also observed that a leakproof system grew large crystals of Cu-BTC.

Our next steps include the following:

1. Fabricate the autoclave and safety test to 550 K and 15 MPa
2. Grow Cu-BTC crystals in the autoclave using the hot plate synthesis conditions.
3. Explore the effects of high temperature on growth

LEHIGH UNIVERSITY | P.C. Rossin College of Engineering and Applied Science

NSF

References: [1] Lin, R.-B., Xiang, S., Zhou, W. & Chen, B. Microporous metal-organic framework materials for gas separation. *Chem* 6, 337–363 (2020). [2] Peedikakkal, A. M. & Aljundi, I. H. Mixed-metal Cu-BTC Metal–organic frameworks as a strong adsorbent for molecular hydrogen at low temperatures. ACS Omega 5, 28493–28499 (2020). [3] Yang Zhao, Zhongxin Song, Xia Li, Metal organic frameworks for energy storage and conversion, Energy Storage Materials, V2, 2016, Pages 35-62, ISSN 2405-8297 [4] Tovar, T. M. *et al.* Diffusion of CO2 in large crystals of Cu-BTC MOF. *Journal of the American Chemical Society* 138, 11449–11452 (2016).

Acknowledgments: The authors acknowledge the facilities and support of the Lehigh University Department of Materials Science and Engineering. The authors also thank the David and Lorraine Freed Undergraduate Research Symposium at Lehigh University. The authors gratefully acknowledge the support from NSF DMR (CAREER) under Award No. 2046468 and Lehigh Faculty Startup Funds.

DAVID AND LORRAINE FREED UGRS UNDERGRADUATE RESEARCH SYMPOSIUM