NDnano Summer Undergraduate Research
2023 Project Summary

1. **Student name & home university**: Laura Schaffler, University of Notre Dame

2. **ND faculty name & department**: Dr. Nosang V. Myung, Chemical and Biomolecular Engineering

3. **Summer project title**: Electrochemical Synthesis of Metal-Organic Frameworks for Use in a Nano-Enabled Electronic Nose

4. **Briefly describe new skills you acquired during your summer research**:

This summer, I learned how to synthesize metal-organic frameworks using electrochemistry. I also learned how to characterize the synthesized materials using X-ray diffraction and a Scanning Electron Microscope.

5. **Briefly share a practical application/end use of your research**:

The end goal of my research is to create improved gas sensing materials for application in an electronic nose.

6. **50- to 75-word abstract of your project**:

Metal-organic frameworks (MOFs) have recently been studied and synthesized for implementation in gas sensing technology due to their high surface area, tunable morphology, and electrical properties of semiconducting materials. For my project, I have been synthesizing MOFs under different temperatures, applied voltages, and solvents using the method of anodic deposition for further use in gas sensing application, specifically for use in an electronic nose.

7**. References for papers, posters, or presentations of your research**:

1. Barandun G, Gonzalez-Macia L, Lee HS, Dincer C, Güder F. Challenges and Opportunities for Printed Electrical Gas Sensors. ACS Sensors. 2022;7(10):2804-22.
2. Jabarian S, Ghaffarinejad A. Electrochemical Synthesis of NiBTC Metal Organic Framework Thin Layer on Nickel Foam: An Efficient Electrocatalyst for the Hydrogen Evolution Reaction. Journal of Inorganic and Organometallic Polymers and Materials. 2019;29(5):1565-74.
3. Salehabadi A, Enhessari M, Ahmad MI, Ismail N, Gupta BD. Chapter 1 - Introduction. In: Salehabadi A, Enhessari M, Ahmad MI, Ismail N, Gupta BD, editors. Metal Chalcogenide Biosensors: Woodhead Publishing; 2023. p. 1-7.
4. Milligan JJ, Saha S. A Nanoparticle's Journey to the Tumor: Strategies to Overcome First-Pass Metabolism and Their Limitations. Cancers [Internet]. 2022; 14(7).
5. Kim T, Choi CH, Hur JS, Ha D, Kuh BJ, Kim Y, et al. Progress, Challenges, and Opportunities in Oxide Semiconductor Devices: A Key Building Block for Applications Ranging

from Display Backplanes to 3D Integrated Semiconductor Chips. Advanced Materials. 2022;n/a(n/a):2204663.
6. Liu Y, Wei Y, Liu M, Bai Y, Wang X, Shang S, et al. Electrochemical Synthesis of Large Area Two-Dimensional Metal–Organic Framework Films on Copper Anodes. Angewandte Chemie International Edition. 2021;60(6):2887-91.

One-page project summary that describes problem, project goal and your activities / results:

Gas sensors have many applications in everyday life. From air quality detectors to food spoilage sensors to breath monitoring devices, gas sensors are widely applicable in a world of rapidly improving technology. Among the different types of gas sensors, chemiresistive sensors are promising because of their rapid response, cost effectiveness, and simple configuration. The transduction of a chemiresistive gas sensor is based on the changes in resistance upon analyte exposure. This type of gas sensor is therefore suitable to integrate into a sensor array, known as an electronic nose, which mimics the olfactory system, identifying and quantifying individual analytes in mixtures. To fabricate an effective electronic nose, each sensor needs to have good sensitivity, and thereby, many recent studies have been focusing on improving the performance of sensing materials.

Multiple different types of materials can be used for gas sensing. Conducting polymers, for example, have fast response times and operate at room temperature; however, they have low selectivity, sensitivity, and stability. Carbon-based material is also synthesized for gas sensing purposes. While this type of material has a high surface area-to-volume ratio and high stability, it has a slow recovery time and a limited range of detection. Metal oxide-based material has high sensitivity and fast response and recovery times, but it has high energy consumption and requires high temperatures to synthesize. Finally, metal-organic frameworks (MOFs) have been synthesized for gas sensing due to their high porosity, high sensitivity, easily tunable morphology, and fast recovery times. While they have varied degrees of conductivity (depending on the MOF) and only moderate stability, their advantages outweigh the disadvantages, leading to the choice of synthesizing MOFs to create an improved gas sensor for this project.

In addition to material selection, dimensionality is also an important aspect of gas sensors. This can be tuned in the synthesis of the MOFs, and therefore the pros and cons of each dimensionality need to be taken into account when determining a synthesis method. Zero-dimensional material has a high surface area-to-volume ratio but low conductivity and high agglomeration. Two-dimensional material has high conductivity but only a moderate surface area-to-volume ratio and moderate agglomeration (depending on the MOF thickness), while three-dimensional material has high conductivity but a low surface are-to-volume ratio. Finally, one-dimensional material has a high surface area-to-volume ratio and low agglomeration with moderate conductivity. Because the one-dimensional structure has the most advantages and fewest disadvantages concerning important attributes of gas sensing material, this is the best structure for this project.

Since most MOFs have thin film structures or particle shapes, synthesis of MOFs using a template is required to form 1-D structures. The first part of the process is electrodepositing the 1-D metals (*i.e.*, metal filling the hollow structure of template) followed by removing the template and dissolving the deposited metal to form the MOF. To maintain the 1-D structure of the sacrificial metal, the MOF formation must be confined on top of the sacrificial material. This further allows the formation of a 1-D multi-segmented MOF, alternating between two different types of MOF. My work this summer has focused on finding the synthesis conditions for various types of MOFs in order to find two with similar conditions that could be combined and formed into a bamboo-like structure.

To synthesize these MOFs, I have been using an electrochemical method. For each MOF, a strip of metal is placed in a plastic container with a solution containing an organic linker and an electrolyte touching a small circle of area on the metal strip. Next, a coil of the same metal is placed in the solution, and a specific voltage is applied to the system. Once the voltage is induced through a two-electrode system of the metal strip and coil, the metal begins to dissolve into metal ions and diffuse into the solution with the electrolyte employed to improve the conductivity of the solution and lower the ohmic drop due to solution resistance. The metal ions then react with the organic linkers in the solution, and the new MOF particles form back on the depleted metal strip. This specific method for forming MOFs is called anodic dissolution, with the metal strip and coil being the anode and cathode respectively.

This summer, I tested copper, zinc, and nickel metals with solutions of mixed MTBS (tributyl methyl-ammonium methyl sulphate) as the electrolyte and BTC (1,3,5-benzenetricarboxylic acid) as the organic linker, one having a ratio of 50:50 water to ethanol and the other being 100 % ethanol. Additionally, the three metals were tested with solutions of MTBS as the electrolyte and MeIM (2-Methylimidazole) as the organic linker in both 100 % methanol and 50:50 water to methanol. These were tested over a range of applied voltages (-0.5 V to 9 V, at a constant voltage, sometimes being pulsed to optimize the adhesion of MOF on the metal strips), and two different temperatures (room temperature and 55 ^{o}C).

To characterize these synthesized samples, X-ray diffraction (XRD) was run on all the resulting MOFs to test whether any MOF actually formed on the surface of the metal and to confirm the composition of the MOF formed. Additionally, half of the metal strip exposed to the solution was passivated by applying a microshield layer for measuring the thickness of the synthesized MOF. After the reaction, this film was removed, and the thickness of the synthesized MOF was measured. Some of the promising samples were also tested using a Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) to look into their specific morphology and chemical composition, respectively.

While over fifty reactions were run this summer using three different metals and four different organic linker/electrolyte solutions, more reactions under different conditions need to be tested to find two different MOFs successfully synthesized under similar conditions. They will ultimately be formed into a bamboo-like structure to create an improved gas sensor for implementation in the electronic nose. In the future, I plan to continue my work in the lab, creating gas sensing material and contributing to the burgeoning field of nanotechnology.