NDnano Summer Undergraduate Research
2024 Project Summary

1. Student name & home university:
Marie Schafer, University of Notre Dame

2. ND faculty name & department:
Kaiyu Fu, Department of Chemistry and Biochemistry
William Phillip, Department of Chemical and Biomolecular Engineering

3. Summer project title:
Biocompatible membrane coated nanoelectrode for sweat analyte measurements

4. Briefly describe new skills you acquired during your summer research:
Through research this summer, I learned how to cast thin membranes utilizing a spin coating process in which rotational speed determines thickness of the membrane. Additionally I learned how to functionalize these membranes and grow zwitterionic polymer brushes on this surface. Then I tested permeability and flux using a stirred cell. From here, I was able to pick up analysis skills through learning how to use a Shimadzu TOC-L total organic carbon analyzer as well as Fourier Transform Infrared Spectroscopy. Through oral presentations within both research labs and poster presentation for the 2024 University Summer Research Symposium, I was able to gain skills in how to demonstrate my research in different settings and styles.

5. Briefly share a practical application/end use of your research:
Membranes that resist fouling of various molecules and proteins from different biofluids will increase longevity of biosensors collecting data such as cortisol excreted from human sweat. These cortisol measurements can provide individualized health data to the user over long periods of time, not only informing of stress changes but also exercise and in some cases different disease risks.

6. 50- to 75-word abstract of your project:
Longevity issues of biosensors arise due to fouling (non-specific adsorption of molecules and proteins) on their interface. This project focuses on eliminating such sensor fouling though developing a biocompatible nanostructured membrane, functionalized with an antifouling zwitterionic polymer brush. The thin membrane was cast using spin coating and the monomer sulfobetaine methacrylate was grown on the membrane. A Continuous assessment of the permeability for these enhanced membranes was obtained allowing for comparison with a control membrane.

7. References for papers, posters, or presentations of your research:\Zhu, B.; Edmondson, S. ARGET ATRP: Procedure for PMMA Polymer Brush Growth. *Millipore Aldrich* **(2019)** https://www.sigmaaldrich.com/US/en/technical-documents/protocol/materials-science-and-engineering/polymer-synthesis/arget-atrp-procedure-for-pmma-polymer-brush-growth.

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

As a rise in individuals turn towards wearable devices to monitor and collect personal health data ranging from heart rate to stress levels, the longevity of the biosensors that continuously collect accurate data has become increasingly important. Issues in performance of such devices arise due to the continuous exposure to excreted sweat, in which an assortment of unwanted molecules and proteins can adsorb non-specifically to the interface of the sensors, blocking membranes that facilitate the transport of target solutes to the sensors. This blockage leads to a decrease in the accuracy of valuable data readings over time. In response, this project focuses on eliminating such sensor fouling by developing a biocompatible nanostructured membrane functionalized with an antifouling zwitterionic polymer brush.

Utilizing a spin coater, a laboratory synthesized P(HEMA-GMA-TFEMA-OEGMA) copolymer was cast onto a silicon wafer to form a thin membrane. Due to the limitations of experimentation and analysis that can be performed on the membrane while on a silicon wafer, it was deemed necessary to transfer the membranes to a new porous support. The characteristics of two different membrane supports, polyvinylidene fluoride (PVDF) and polyethersulfone (PES) were examined, and PVDF was found to be the support that could provide the most continuous data. With this decision made, the cast membranes were transferred to the PVDF support via a sacrificial transfer process. Now it is possible to evaluate the relationship between membrane throughput versus applied pressure on the PVDF.

With control measurements determined, the zwitterionic polymer brush sulfobetaine methacrylate was grown on the membrane through a surface-initiated ARGET ATRP method. Further assessment of the permeability of these enhanced membranes was obtained through filtration experiments, allowing for comparison with the previously collected data for the control HEMA membrane. As shown in Figure 1, there was minimal difference (a 6% decrease in flux) in the relationship between applied pressure and flux for both the membrane with a zwitterionic brush layer and the control membrane. When doubling the width of the membrane there was a 101% decrease in flux which is significantly greater.

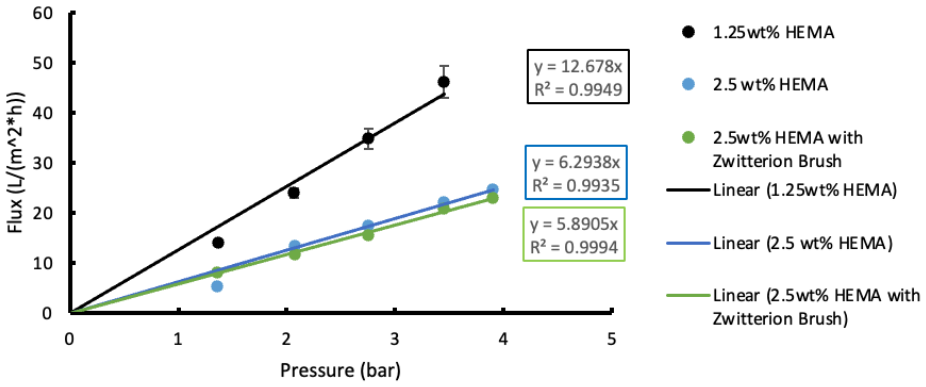

Figure 1. A comparison of three unique HEMA membranes. Adding a zwitterionic layer caused a 6% decrease in flux when compared to a membrane of similar thickness.

The secondary filtration experiment involved pushing five unique feed solutions with molecular sizes of 0.925nm, 1.406nm, 1.707nm, 2.126nm and 2.869nm through the membranes. A Shimadzu TOC-L total organic carbon analyzer was used to determine the concentration of organic carbon in both the permeate and retentate, allowing for the calculation of percent rejection. Due to a strong similarity in the percent rejection trends between the control membrane and the membrane with zwitterionic growth, as seen in Figure 3, it is highly likely that there is no change in the physical membrane as a result of polymerization. Further data must be collected to determine if the results are reproducible.

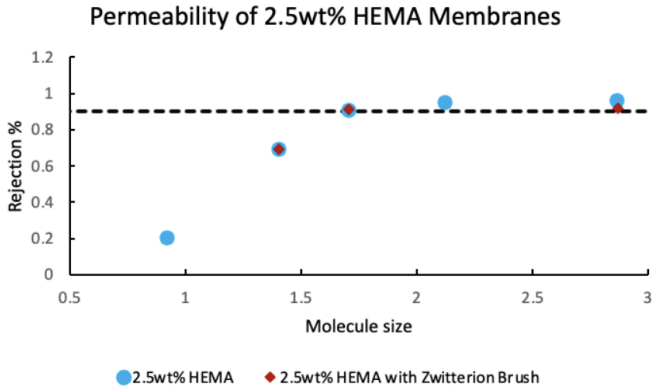

Figure 2. It is highly likely that there is no change in the physical membrane as a result of polymerization.

The next steps in this research are to determine the extent to which this zwitterionic brush can reduce fouling on the surface of the membrane by examining how permeability through the membrane interacts with time. If fouling occurs, the permeability will decrease with time, whereas if the zwitterionic brush is successful, this trend should not occur at all, or at least not as drastically.