Toward a Complete Understanding of MXene Photodetection

Introduction and Preliminary Results: Discovered at Drexel University in 2011, MXenes are a novel class of 2D materials that comprise metal carbides and nitrides. Due to their excellent electronic, optical, thermal, and mechanical properties, MXenes have great promise for applications in several technologies including additives in solar cells and electronic contacts for semiconductors [1]. Compared to other 2D materials, MXenes offer an optimal combination of high electronic conductivity, low cost, and facile synthesis methods. Furthermore, their tunable optoelectronic properties, such as work function and optical absorption, enable MXenes to improve emerging photovoltaic materials such as perovskites and inorganic semiconductors. To realize the full potential of MXene photodetectors, an improved fundamental understanding of their electronic and optical properties is needed.

During my master's thesis, I refined methods for photodetection analysis of MXene thin films. While it laid the groundwork for the optoelectronic study of MXenes, the underlying factors that drive MXene response to light (photoresponse), such as the impacts of the electrode and substrate type, are not well-understood. While MXenes have proven successful as additives and electrodes, I aimed to bring them to the mainstream as active materials. My work focused on the photoactive capabilities of Ti_3C_2, which has already succeeded as a transparent photodetector electrode [2]. Although Ti_3C_2 is the most commonly studied MXene, its response to chopped illumination with visible light had not yet been reported.

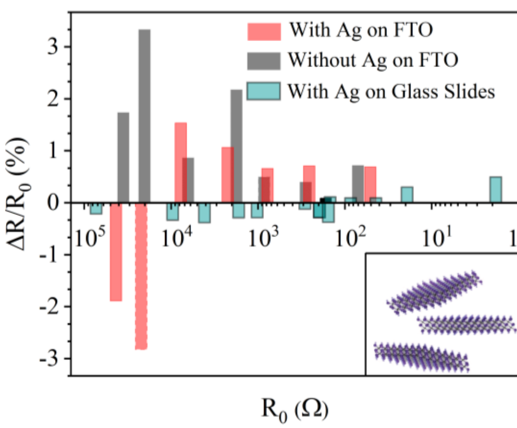

Figure 1: Ti_3C_2 films exhibit consistent negative photoconductivity when deposited on patterned fluorine-doped tin oxide (FTO) substrates without the use of silver paste contacts (black). However, thin films with high R_0 switch from negative to positive photoconductivity upon illumination with the application of metal contacts (red) and experience suppressed photoresponse when deposited on glass slides (green). Schematic of MXenes shown in inset [2].

Figure 1 compares the average change in resistance (*R*) upon illumination for films with different initial resistance values (corresponding to thickness) and with different contact methods. Here, the application of silver paste as an electrical contact causes Ti_3C_2 to deviate from innate behavior upon illumination, while a change to a thinner substrate (glass slides) suppresses the magnitude of the photoresponse. Ti_3C_2 is a well-known metallic and photothermal material with innate negative photoconductivity, leading to an expected increase in *R* upon illumination or heating; these observations that contradict expected behavior call into question the role of silver-MXene interactions, carrier dynamics, and heat transfer in determining the material's photoresponse. I hypothesize that the photovoltaic (PVE) and the photothermoelectric (PTE) effect each play into the photocurrent generated by MXenes, giving them the power to serve multiple applications, from thermal imaging to photovoltaic electrodes.

Research Plan: I aim to both experimentally and computationally study heat and charge transport in MXene photodetectors to guide their design in imaging and energy generation applications. I will begin my examination with Mo-based MXenes, a lesser-studied subset of MXenes with potential as a photoactive material. Previous empirical studies question computational results showing Mo_2TiC_2 has semiconductor-like properties [3]. This work will seek to confirm these analyses by isolating contributions to light-matter interactions for Mo-based MXenes. Furthermore, over 30 different MXenes have been reported to date [1]. This proposal outlines just the beginning of our exploration into MXene photodetection capabilities in response to visible light, as the methods listed can be applied to other photoactive MXenes as well.

Objective 1 – Understand the impacts of device architecture: In varying the deposited film thickness, contact geometry, and substrate type, I will evaluate their individual influences on photodetector properties (responsivity, noise, stability) in response to chopped illumination with visible light. Using thermally conductive substrates, such as sapphire, the impact of thermal effects can be mitigated. I expect strongly absorbing films, non-metal electrical contacts, and thin, thermally conductive substrates to produce the strongest photoresponse for Mo-based MXenes. Upon gaining this phenomenological data, I will then study charge carrier dynamics to understand the light-matter interactions for each MXene device. Under the guidance and expertise of Prof. R.J. Holmes, I will probe exciton diffusion at the interface of the photoabsorbing MXene and the electrical contact *via* an external quantum efficiency measurement method curated in his group [4]. This broadly applicable method provides additional understanding of carrier dynamics upon photoexcitation and will guide selection of device architecture for improved performance.

Objective 2 – Model optical and thermal transport kinetics: Through computational efforts to model contributions from the PTE and the PVE, I will confirm the dominant effect that determines the photoresponse. Should combined contributions dictate the photoresponse, I aim to create a secondary model system specific to MXenes. By compiling a model from literature for both heat and carrier transport, I will determine optimal film thicknesses, contact geometry, and substrate types for devices that rely on either the PVE or the PTE, creating two reliable device architectures with improved responsivity. Moreover, simulating the photodetector architectures created in Objective 1 using COMSOL will push them to their thermal and electronic limits, granting insight into widespread implementation of MXene photodetectors.

Objective 3 – Create devices and optimize performance: Equipped with the knowledge of optimal device architecture and film deposition, I will build Mo-based photodetectors and investigate industrially relevant issues, such as stability, lifetime, and performance of larger area devices. Given the inevitable obstacles in scaling up a device, I must tailor the device parameters found in Objective 1 to suit applications that would benefit from either the PVE or the PTE, such as energy generation or thermal imaging, respectively. I envision my contributions will spur the development of MXene-based photodetectors that suit multiple purposes simply by changing the device architecture.

Intellectual Merit: My well-rounded background in chemical engineering and materials science and engineering allows me to understand not only why MXenes behave the way they do, but also how we can implement these materials in devices. I will utilize the wealth of knowledge from multiple energy transport experts, including Prof. Holmes, as well as state-of-the-art facilities for nanotechnology research at UMN to ensure the success of this project. The proposed research will provide an improved fundamental understanding of the factors that influence MXene photodetection, an emerging field of interest with limited literature available. Upon gaining this understanding, we can continue to use MXenes in optoelectronic applications, reducing the cost to produce photodetectors and allowing for widespread implementation of more conductive, easily synthesized materials.

Broader Impacts: My work aims to inspire other researchers to consider implementing MXenes in their devices, bringing the field closer to a reliable, reproducible method for renewable energy generation. Through my research on nanomaterials in energy applications, I aspire to make clean energy commonplace, expanding on my dreams of a sustainable future arising from wanting to develop accessible biodegradable plastics in high school. I also aim to continue my impactful record of mentorship and community outreach. Leaning on my extensive outreach experience described in the accompanying personal statement, I plan to create an interactive lesson on current and novel photodetectors and sensors through Science for All, a student-run group created to support and promote STEM fields to local, underserved middle schools in the urban Twin Cities. Prof. Holmes also has the laboratory facilities to package photodetectors, allowing me to bring samples to the classroom. Lastly, through the Undergraduate Research Mentorship Program (UROP), I will seek and recruit undergraduate students from underrepresented groups for this project, serving as a research and personal mentor to guide them through their technical careers and encourage them to continue their STEM education.

References: [1] L. Zhao, et al. Tungsten, 2 (2020): 176 – 193 [2] K. Montazeri, et al. Adv. Mater., 31.43 (2019): 1 – 9. [3] G. Li, et al. Proc. SPIE 11279, 112791U (2020): 66 – 84. [4] T. Zhang, et al. Nat. Commun., 10.1 (2019): 3489 – 3495.