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Super-resolution imaging of charge carrier recombination and transport in ultrathin liquid junction photovoltaics

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<b>14. ABSTRACT</b> The U.S. Air Force requires on-demand, grid-independent energy solutions to enable warfighters, expand operational effectiveness, and enhance national security. Conventional photovoltaic modules are too bulky for rapid deployment to facilities in resource-scarce locations. One solution is to use photovoltaic devices made of two-dimensional (2D) semiconductor nanosheets, which represent the ultimate miniaturization limit for lightweight and portable photovoltaics. Ultrathin photovoltaic technology could transform the way the Air Force produces energy. However, there is a growing consensus in the electronics research community that surface defect sites limit the solar energy conversion efficiency of ultrathin photovoltaics. The overall objective of this research is to develop a molecular-level understanding of how defect sites impact the overall solar energy conversion efficiency of nanosheet photovoltaics. Our hypothesis is that the presence of surface defects will influence charge carrier recombination and/or transport behavior. The general approach to test this hypothesis is to image directly charge carrier recombination and transport with nanometer spatial resolution in model liquid junction photovoltaics. Specifically, the technical approach for this research is to integrate single-molecule imaging and single-nanosheet photoelectrochemical methods because (1) single-molecule methods visualize, count, and			
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## Final Performance Report for FY 2017-2020

**Overall Project Information:**

**Title:** (YIP) Super-Resolution Imaging of Charge Carrier Recombination and Transport in Ultrathin Liquid Junction Photovoltaics

**Grant #:** FA9550-17-1-0255

**P.I.:** Justin B. Sambur, Colorado State University (CSU)

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**Coworkers:** Dr. Michael Todt, Dr. Li Wang, Allan Isenberg, Russel C. Evans

**Collaborator:** none

**Grant Period:** 04/28/17 – 04/27/20 (3 years)

**Yearly Budget:** \$120,000

**1) Project Overview.**

Overall goal. The overall goal of this project is to understand how defects influence electric fields and interfacial reactivity at 2D/liquid interfaces. Our hypothesis is that local (e.g., chalcogen vacancies) and extended defects (e.g., step edges) modulate the electric field strength perpendicular and parallel to the 2D/liquid interface, enhancing and/or diminishing charge recombination and interfacial charge transfer rates. To test this hypothesis, we developed novel photoelectrochemical imaging techniques to probe charge transport in single 2D semiconductor nanosheets.

Research objectives. To attain the overall project goal, two specific objectives were pursued: 1) image chemical reactivity at 2D semiconductor/electrolyte interfaces and 2) probe the relationship between carrier generation, transport, and reactivity near defect sites. The rationale for the proposed research is that real space imaging of charge transport and chemical reactivity will provide fundamental insight into how perpendicular and parallel electric fields influence photo-induced chemical reactivity in 2D materials, especially near defects. Molecular scale understanding of energy conversion processes will enable new strategies to design functional 2D materials for sensing and optoelectronic applications of interest to the United States Air Force.

Scientific Methods. We developed a “molecular reaction imaging” approach to achieve our overall project goal. This approach uses a diffraction-limited light spot (~300 nm diameter) to generate charge carriers in single semiconductor nanosheets. At the same time, a camera images reaction products as they form on nanosheet surfaces. A potentiostat measures the photocurrent response during the laser pulse, allowing us to quantitatively link image contrast to the total number of reaction products. Combining scanning photocurrent and molecular reaction imaging modalities enables us to measure the contributions of hole and electron surface fluxes directly and selectively to the photoelectrochemical response, thereby providing a direct imaging modality for interfacial charge transport and recombination at defects such as step edges and perimeter edge sites.

Major Activities & Accomplishments: To attain the overall project goal, two specific objectives were pursued: 1) image chemical reactivity at 2D semiconductor/electrolyte interfaces and 2) probe the relationship between carrier generation, transport, and reactivity near defect sites. The rationale for the proposed research is that real space imaging of charge transport and chemical reactivity will provide fundamental insight into how perpendicular and parallel electric fields influence photo-induced chemical reactivity in 2D materials, especially near defects. Molecular scale understanding of energy conversion processes will enable new strategies to design functional 2D materials for sensing and optoelectronic applications of interest to the United States Air Force.

Regarding Objective #1, we published 2 papers that focused on development of chemical imaging methods to study reactivity 2D semiconductor/electrolyte interfaces (ACS Appl. Mater. Interfaces 2018 10, 27780–27786; ACS Energy Lett, 2020, 5, 5, 1474–1486). These papers showed how perimeter and step edge defects within 40-200 nm-thick MoSe<sub>2</sub> and MoS<sub>2</sub> nanoflakes influence charge transport, recombination, and chemical reactivity.

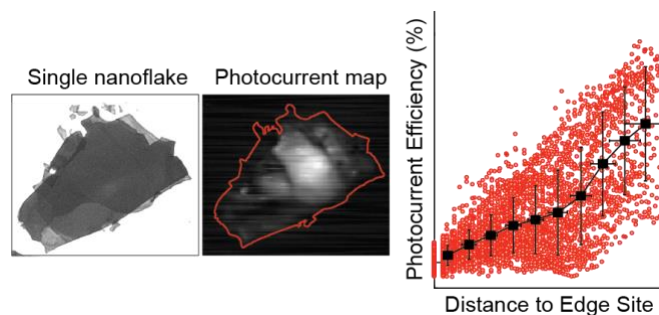
Regarding Objective #2, we published 7 papers that focused on the relationship between carrier generation, transport, recombination and reactivity in monolayer and multi-layer thick semiconductors and heterojunctions. We reported the first photoelectrochemical measurements of pristine, isolated monolayer MoS<sub>2</sub> in the field of photoelectrochemistry (Nano Letters, 2019, 19 (5), 2960–2967). Our study showed that perpendicular electric fields drive exciton dissociation in monolayer MoS<sub>2</sub> photoelectrodes and the intimate contact between the 2D material and liquid electrolyte leads to highly efficient quantum efficiencies for iodide oxidation (44 %). We also leveraged molecular reaction imaging to quantify the electric field strength parallel to the layers in multi-layer thick MoS<sub>2</sub> (ACS Energy Lett, 2020, 5, 5, 1474–1486).

Potential Impacts. Ultrathin 2D materials have the potential to transform electro-optical capabilities of the US Air Force, including lightweight and flexible power generation devices. The research project will lead to a deeper understand of how electrons move through ultrathin semiconductors, and how electric fields drive charge movement and reactivity at different surface sites. The potential impact of the proposed research is that it will enable new design strategies for ultrathin photovoltaics, light emitting diodes, photodetectors, transistors, and wearable electronics because these devices share the same basic operating principles with liquid junction photoelectrochemical cells. In line with the Air Force mission to foster an energy aware culture, this research will educate graduate students and postdocs on the global energy problem and provide them with interdisciplinary skills for energy– and/or STEM–related careers.

## 2) Detailed Performance Report and Accomplishments for the Project Period 04/28/17 – 04/27/20.

- a) Todt, M.A., Isenberg, A., Miller, E.M., Nanayakkara, S.U., Sambur, J.B.; “Single nanoflake photoelectrochemistry reveals champion and spectator nanoflakes in exfoliated MoSe<sub>2</sub> films” *J. Phys. Chem. C.*, 2018, 122 (12), pp 6539–6545.  
[<https://pubs.acs.org/doi/abs/10.1021/jacs.7b06173>]

Background and Motivation: This work focused on answering the following fundamental question: *How do the physical properties of individual semiconductor nanoflakes (e.g., thickness, area) and types of surface defect sites (interior step edge sites versus perimeter edge sites) influence charge carrier recombination and surface reactivity?* We developed a single-nanoflake photoelectrochemical approach to study how the individual properties of nanoflakes influenced photo-induced charge carrier collection efficiency. We exfoliated bulk MoSe<sub>2</sub> samples and dry-transferred nanoflakes to ITO electrodes. Our spatially resolved measurements showed that 7% of nanoflakes are highly active “champions” whose photocurrent efficiency exceeds that of the bulk crystal. However, 66% of nanoflakes are inactive “spectators”, which are mostly responsible for overall lower photocurrent of nanoflake thin films compared to the parent bulk crystal. The photocurrent collection efficiency increases with nanoflake area and decreases more at perimeter edges than at interior step edges. These observations, which are hidden in ensemble-level measurements, reveal the underlying performance issues of exfoliated TMD electrodes for photo-electrochemical energy conversion applications.



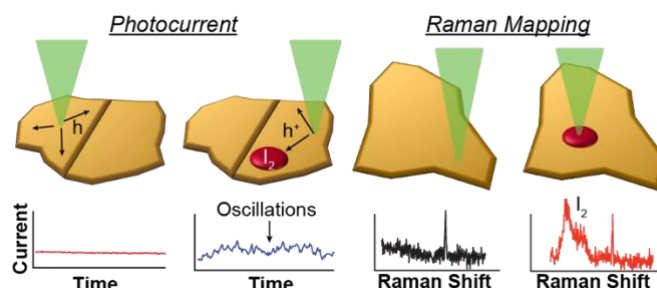
**Figure 1.** Single-nanoflake photoelectrochemistry. Scanning photoelectrochemical microscopy is used to map the photocurrent efficiency as a function of charge carrier generation location. By analyzing the carrier collection efficiency versus distance to the nearest edge sites, we discovered that charge carriers are preferentially transport to and recombine at perimeter edge sites.

*Impact:* This work showed that nanoflake thin films can achieve energy conversion efficiencies similar to bulk crystals. However, the energy conversion efficiency is limited by edge sites, especially the perimeter edge sites at the triple boundary between the 2D semiconductor/electrolyte/ITO substrate. These findings open up opportunities to model carrier generation, transport, and reactivity at this unique triple boundary.

- b) Isenberg, A. E., Todt, M. A., Wang, L. & Sambur, J. B. “Role of Photogenerated Iodine on the Energy-Conversion Properties of MoSe<sub>2</sub> Nanoflake Liquid Junction Photovoltaics” *ACS Appl. Mater. Interfaces* 2018 10, 27780–27786. [<https://pubs.acs.org/doi/10.1021/acsami.8b07617>]
- Article selected for Supplemental Journal Cover.

**Background and Motivation:** One limiting factor of MoSe<sub>2</sub>-nanoflake|I<sup>-</sup>/I<sub>2</sub>|Pt liquid junction solar cells is that reaction products (i.e., I<sub>2</sub> and I<sub>3</sub><sup>-</sup>) accumulate on the electrode surface and decrease the energy conversion efficiency. The products strongly adsorb to the electrode surface and block I<sup>-</sup> from diffusing to and reacting with photogenerated holes at the solid/liquid interface. This manuscript addressed the following *major knowledge gaps*: (1) Do surface reaction products accumulate on specific surface motifs (e.g., basal planes, interior step edges, and perimeter edge sites)? (2) How do surface reaction products influence the local energy conversion properties such as the photocurrent collection efficiency and open circuit voltage?

**Results and Significance:** We used a single-nanoflake photoelectrochemical and Raman microscopy approach to probe how photogenerated I<sub>2</sub>/I<sub>3</sub><sup>-</sup> products impact the photocurrent collection efficiency and onset potential in MoSe<sub>2</sub>-nanoflake|I<sup>-</sup>/I<sub>2</sub>|Pt photoelectrochemical solar cells. We quantified the critical incident light intensity for I<sub>2</sub> formation on 50 diffraction-limited spots on 18 MoSe<sub>2</sub> nanoflakes. We observed a strong negative correlation between the maximum photocurrent efficiency of the spot and the critical incident light intensity for iodine formation—the highest efficiency sites are the first to be limited by I<sub>2</sub> formation. Iodine formation does not preferentially occur on specific surface motifs. Instead, Raman micro-spectroscopy showed that I<sub>2</sub> products accumulate at sites have the most negative photocurrent onset potential. The negative shift in onset potential could be attributed to variations in surface reaction kinetics or doping density across the nanoflake. Our results revealed hidden correlations between surface chemistry and critical energy conversion properties in liquid junction photovoltaics.



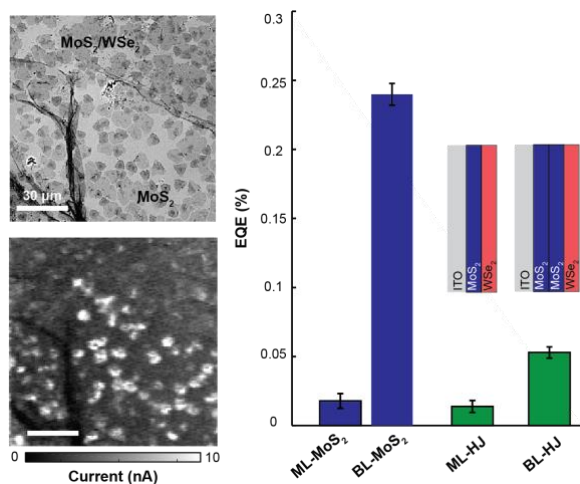
**Figure 2.** Correlated single-nanoflake photoelectrochemistry and Raman micro-spectroscopy reveals the role of photogenerated oxidation products on the charge carrier collection efficiency in nanoflake liquid junction photovoltaics.

- c) Wang, L., Sambur, J. B., “Efficient Ultrathin Liquid Junction Photovoltaics Based on Transition Metal Dichalcogenides” *Nano Letters*, **2019**, 19 (5), 2960–2967.  
[<https://pubs.acs.org/doi/10.1021/acs.nanolett.9b00070>]

- *This study represents the first photoelectrochemical measurements of isolated monolayer photoelectrodes in the field of photoelectrochemistry.*

**Background and motivation:** Ultrathin photovoltaics made of MoS<sub>2</sub> or WSe<sub>2</sub> have the potential to convert solar energy to electricity with high efficiency because all photo-generated carriers are produced at a charge-collecting interface. However, solid-state monolayer photovoltaic devices typically require that charge carriers travel parallel to, instead of perpendicular to, the three atom-thick material towards charge-collecting contacts. Parallel charge transport across long distances decreases energy conversion efficiency because randomly distributed defects induced electron-hole recombination. Here we demonstrate proof-of-concept monolayer and bilayer TMD|I<sup>-</sup>,I<sub>3</sub><sup>-</sup>|Pt photoelectrochemical solar cells that use a conformal liquid electrolyte junction for efficient perpendicular charge transport over significantly larger active areas than solid state systems. Using a novel high-throughput correlated laser reflection/photocurrent mapping, we made breakthrough discoveries regarding ultrathin photovoltaic systems with perpendicular charge transport pathways, which address key knowledge gaps in the field, as summarized below.

**Results and Significance.** Our work includes a number of first-of-the-kind measurements and discoveries. It reports the first application of photoelectrochemical cells in the field of monolayer photovoltaics. The liquid junction approach enables perpendicular charge transport across centimeter-square materials, beyond previous studies of micrometer-square solid-state monolayer MoS<sub>2</sub>/WSe<sub>2</sub> photovoltaics. Efficient perpendicular charge transport is evidenced by high peak internal quantum efficiencies (IQE) of 44.2, 9.1, and 10.5% for 0.4 mm<sup>2</sup> MoS<sub>2</sub>, WSe<sub>2</sub>, and MoS<sub>2</sub>/WSe<sub>2</sub> domains in a predominantly monolayer MoS<sub>2</sub>/WSe<sub>2</sub> film (Figure 3). The monochromatic energy conversion efficiencies are competitive with state-of-the-art solid-state monolayer heterojunction photovoltaics. It reports a new photocurrent mapping approach to determine structure/function relationships in ultrathin photovoltaics. Correlated Raman and scanning photoelectrochemical microscopy measurements revealed a non-linear scaling relation between IQE and layer thickness for MoS<sub>2</sub>, WSe<sub>2</sub>, and MoS<sub>2</sub>/MoS<sub>2</sub>/WSe<sub>2</sub>. Specifically, the monochromatic energy conversion efficiency of bilayer MoS<sub>2</sub> is an order of magnitude greater than monolayer MoS<sub>2</sub> and MoS<sub>2</sub>/MoS<sub>2</sub>/WSe<sub>2</sub> exceeds MoS<sub>2</sub>/WSe<sub>2</sub> by a factor of four. The non-linear enhancement in bilayer MoS<sub>2</sub> is likely due to the high probability of free carrier generation in MoS<sub>2</sub> bilayers and the large exciton binding energy in monolayer MoS<sub>2</sub>. The structure/function relationships are hidden in ensemble-level photoelectrochemical measurements.



**Figure 3.** (left) Optical transmission images and photocurrent maps of a MoS<sub>2</sub>/WSe<sub>2</sub> heterojunction photoelectrode. (right) Average photocurrent of ML and BL MoS<sub>2</sub> relative to heterojunction regions.

**Impact:** On the *technological* side, we envision a widespread use of the novel scanning photocurrent/laser reflection mapping technique developed in this study. The method can be broadly applied to 2D perovskites, QD solids, and plasmonic materials that are widely studied for catalysis and energy conversion applications. On the *scientific* side, our study shows that the liquid junction approach represents a simple and rapid strategy to screen ultrathin TMD materials combinations, tune interfacial energetics, and make conformal electrical contacts in photoelectrochemical energy conversion systems for electricity or solar fuels production. Our results demonstrate a critical need to develop nanostructured or plasmonic electrode architectures that enhance overall light absorption and therefore overall power conversion efficiency. Our discovery of non-linear energy conversion efficiency with layer thickness represents an intriguing opportunity to optimize performance via interface and materials

engineering.

- d) Wang, L; Schmid, M; Tahir, M; Chen, H; Sambur, J.B.; “Laser Annealing Improves Photoelectrochemical Activity of Ultrathin MoSe<sub>2</sub> Photoelectrodes” *ACS Appl. Mater. Interfaces*, **2019**, 11 (21), 19207-19217. [https://pubs.acs.org/doi/10.1021/acsami.9b04785]

**Background and Motivation:** The 2D materials community is striving to understand light-matter interactions in ultrathin semiconductors. Recent studies have shown that high intensity illumination (so-called laser annealing) can influence the physical, electronic, and optical properties of ultrathin transition metal dichalcogenides (TMDs) such as MoS<sub>2</sub>, MoSe<sub>2</sub>, WS<sub>2</sub>, and WSe<sub>2</sub>. A handful of studies have shown that laser annealing can influence the functional properties of TMD-based photodetectors. Yet, no studies exist regarding the possibility of using laser annealing to tune catalytic properties of ultrathin TMDs. Here we show for the first time that laser annealing increases the photoelectrochemical activity and solar energy conversion efficiency of liquid junction photovoltaics based on few layer MoSe<sub>2</sub>. We used a novel high-throughput photocurrent mapping technique to understand how laser annealing “activates” MoSe<sub>2</sub>.

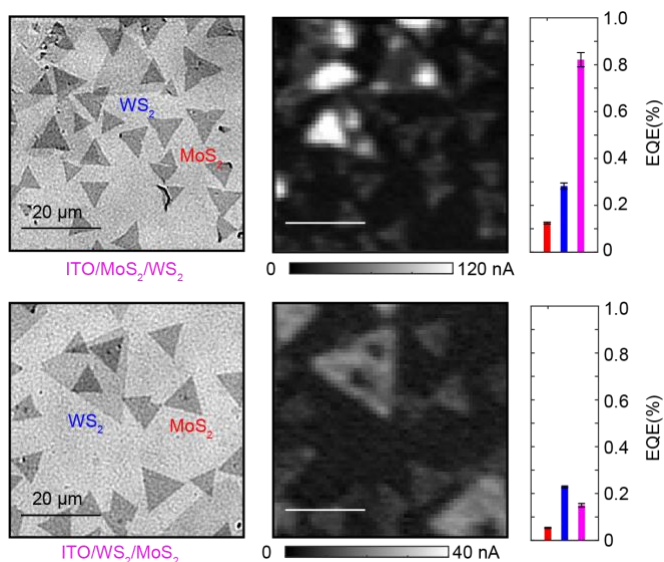
**Results and significance:** Scanning photoelectrochemical microscopy measurements revealed that pristine bilayer (2L)-MoSe<sub>2</sub>, trilayer (3L)-MoSe<sub>2</sub>, and multilayer-thick nanosheets are initially inactive for iodide oxidation. The light treatment activates 2L-MoSe<sub>2</sub> and 3L-MoSe<sub>2</sub> materials, and the activation process initiates at the edge sites. The photocurrent enhancement is more significant for 2L-MoSe<sub>2</sub> than for 1L-MoSe<sub>2</sub>. Multilayer-thick MoSe<sub>2</sub> remains inactive for iodide oxidation even after the laser treatment. Our microscopy measurements revealed that the laser-induced enhancement effect depends critically on MoSe<sub>2</sub> layer thickness. X-ray photoelectron spectroscopy measurements showed that the laser treatment oxidizes Mo(IV) species that are initially associated with Se vacancies. Ambient oxygen fills the Se vacancies and removes trap states, thereby increasing the overall photogenerated carrier collection efficiency. To the best of our knowledge, this work represents the first report on using laser to enhance the photoelectrocatalytic properties of few-layer-thick TMDs. The simple and rapid laser annealing procedure is a promising strategy to tune the reactivity of TMD-based photoelectrochemical cells for electricity and chemical fuel production.

- e) Wang, L; Schmid, M; Sambur, J.B.; “Single nanoparticle photoelectrochemistry: what is next?” *J Chem Phys*, **2019**, 151, 180901. (Invited perspective article). [https://aip.scitation.org/doi/10.1063/1.5124710]

**Summary:** Our current understanding of charge carrier generation, separation, transport, and interfacial charge transfer at heterogeneous nanoscale interfaces is derived mainly from ensemble-average measurements of nanoparticle electrodes that report on the average behavior of trillions of nanoparticles. Ensemble-average measurements conceal how nanoparticle heterogeneity (e.g., differences in particle size, shape, and surface structure) contributes to the overall photoelectrochemical response. This perspective article focuses on the emerging area of single particle photoelectrochemistry, which has opened up an exciting new frontier: direct investigations of photodriven reactions on individual nanomaterials, with the ability to elucidate the role of particle-dependent properties on the photoelectrochemical behavior. This article (1) reviews the basic principles of photoelectrochemical cells, (2) points out the potential advantages and differences between bulk and nanoelectrodes, (3) introduced approaches to single nanoparticle photoelectrochemistry and highlight key findings, and (4) provides our perspective on future research directions.

- f) Wang, L; Tahir, M; Chen, H; **Sambur, J.B.**; “Probing charge carrier transport and recombination pathways in monolayer MoS<sub>2</sub>/WS<sub>2</sub> heterojunction photoelectrodes” *Nano Lett.* **2019**, *19* (12), 9084-9094. [https://pubs.acs.org/doi/pdf/10.1021/acs.nanolett.9b04209]

**Background and motivation:** Monolayer heterojunctions such as MoS<sub>2</sub>/WS<sub>2</sub> are attractive electrode materials for photoelectrochemical energy conversion applications because light excitation produces carriers at a charge-separating interface, making the carriers easily accessible for charge collection. However, very little is known about the fundamental solar energy conversion processes of isolated *and* physically coupled semiconductor monolayer photoelectrodes. Here we present the first detailed studies that focus on the photoelectrochemical properties of monolayer MoS<sub>2</sub> and WS<sub>2</sub>, and how those properties change as the isolated materials are physically coupled to form a monolayer heterojunction photoelectrode. We used a single-nanosheet photocurrent microscopy approach to make breakthrough discoveries regarding individual steps in the solar energy conversion process (charge generation, separation, transport, and recombination), as summarized below.

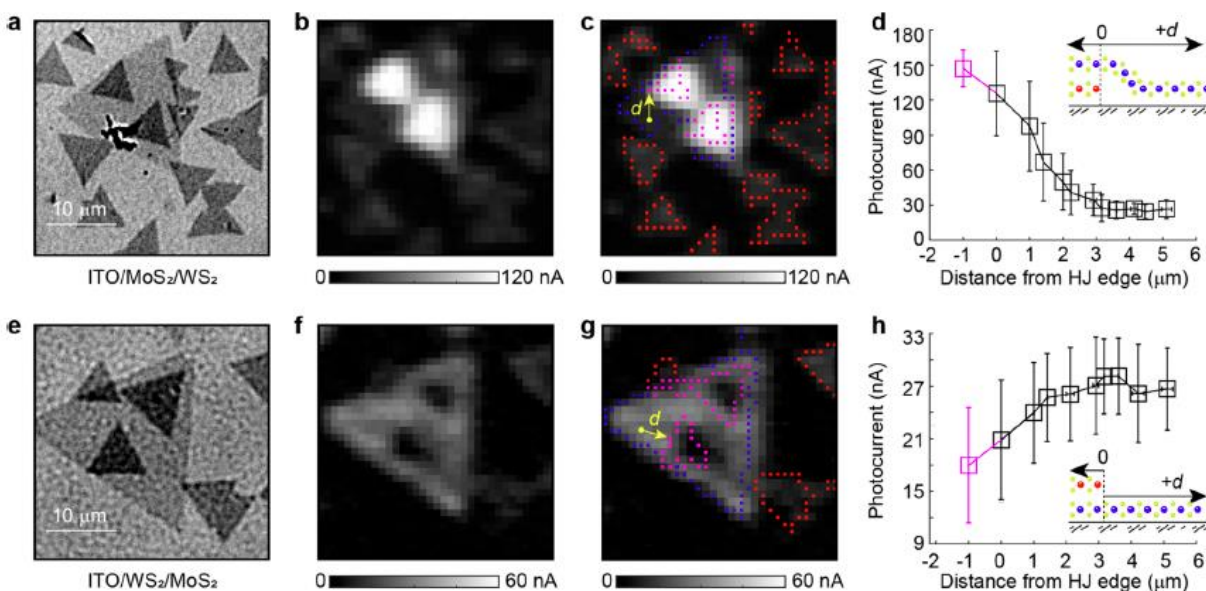


**Figure 4.** Transmission and photoelectrochemical microscopy maps of (top) ITO/MoS<sub>2</sub>/WS<sub>2</sub> and (bottom) ITO/WS<sub>2</sub>/MoS<sub>2</sub> in 1 M NaI. The histograms on the right indicate the average photocurrent response from isolated WS<sub>2</sub> (blue), MoS<sub>2</sub> (red), and the heterojunction (pink).

MoS<sub>2</sub>-selective illumination conditions (635 nm excitation), indicating that (1) electrons transfer to the ITO electrode through the bottom WS<sub>2</sub> layer, and (2) a photogenerated hole population in WS<sub>2</sub> activates the

**Results and Significance:** Our work includes several first-of-the-kind measurements and discoveries. It reports the first demonstration of a synergistic enhancement effect for monolayer heterojunction photoelectrodes in the field of photoelectrochemistry. Spatially resolved photocurrent measurements revealed that the photocurrent efficiency of monolayer ITO/MoS<sub>2</sub>/WS<sub>2</sub> exceeds the sum of ITO/MoS<sub>2</sub> and ITO/WS<sub>2</sub> by a factor of 2 (Figure 4), which could be explained by improved charge separation efficiency of the heterojunction. Interestingly, we observed a photocurrent quenching effect in the ITO/WS<sub>2</sub>/MoS<sub>2</sub> system, which was driven by a novel charge carrier recombination mechanism described below. We also discovered excitation wavelength-dependent charge separation and recombination pathways in the ITO/WS<sub>2</sub>/MoS<sub>2</sub> photoelectrode, where electrons in MoS<sub>2</sub> recombine with holes in WS<sub>2</sub>. This interlayer recombination pathway is suppressed under

recombination channel. Photogenerated carriers in isolated  $\text{WS}_2$  “feel” the heterojunction edge even though they are spatially separated by about 3 microns (Figure 5). In other words, charge carriers flow parallel to the  $\text{WS}_2$  layer to reach the heterojunction edge even though the ITO electrode and liquid electrolyte provide an efficient perpendicular charge transport pathway. Charge transport simulations show that this transport process is driven by carrier diffusion along a concentration gradient from the point of generation (focused laser spot) to the heterojunction edge site, which is likely due to their relatively long exciton lifetime (typically over 100 ps). The Fermi-level of the illuminated heterojunction depends on which material in the heterojunction is photo-excited. We attribute this observation to the fact that the heterojunction energy bands are a superposition of the monolayer energy states and are localized on different monolayers.



**Figure 5. Quantifying charge transport pathways at monolayer heterojunctions.** Photocurrent versus distance measurements at ITO/MoS<sub>2</sub>/WS<sub>2</sub> and ITO/WS<sub>2</sub>/MoS<sub>2</sub> heterojunction edge sites.

**Impact:** Our work raises important design considerations for emerging heterojunction thin film photoelectrodes based on transition metal dichalcogenides. Bulk heterojunction thin films made from randomly oriented nanosheets exhibit a wide range of local morphologies (e.g., ITO/MoS<sub>2</sub>/WS<sub>2</sub> versus ITO/WS<sub>2</sub>/MoS<sub>2</sub>). Our results reveal how and why different stacking configurations in a heterogeneous film have a tremendous influence on the ensemble-level photocurrent response. We envision that the knowledge gained in these heterojunctions can be used to develop efficient photoelectrocatalytic or solar energy conversion systems based on TMD heterojunctions.

- g) Wang, L.; Nilsson, Z.; Tahir, M.; Chen, H.; Sambur, J.B.; “Influence of the substrate on the optical and photoelectrochemical properties of monolayer MoS<sub>2</sub>” *ACS Appl. Mater. Interfaces*, **2020**, *12*(13), 15034-15042. [<https://pubs.acs.org/doi/10.1021/acsami.9b21230>]

**Background and motivation:** One intriguing research area that has emerged in the solid-state 2D materials community is using substrate engineering to affect the electrical and optical properties of 2D materials. If we can modulate the photophysical properties of monolayer MoS<sub>2</sub> via the substrate, then it may be possible to more efficiently separate photogenerated carriers from ML-MoS<sub>2</sub> before they recombine and use those carriers to drive photocatalytic or photoelectrocatalytic reactions.

**Results and significance:** To test the above hypothesis, we deposited monolayer MoS<sub>2</sub> on an ITO interdigitated array electrode and spatially resolved the PL, Raman, and photoelectrochemical current due to iodide oxidation. We observed the PL intensity of monolayer MoS<sub>2</sub> is an order of magnitude higher in the thin quartz channels of the IDA electrode than in the ITO strip electrode regions. These data suggest

that fast, non-radiative recombination processes take place within photoexcited MoS<sub>2</sub> on ITO substrates. In addition, monolayer MoS<sub>2</sub> absorbs more photons in the quartz region due to constructive/destructive interference effects that take place on the lower refractive index quartz substrate, as evidenced by numerical simulation results. *Both enhanced optical properties could be beneficial for photocatalysis.* Scanning photoelectrochemical microscopy measurements revealed that ML-MoS<sub>2</sub> produced lower photocurrents in the quartz region than in the ITO region. We attribute the low photocurrent response to inefficient electron transport to the ITO electrodes. Thus, the optical and photoelectrochemical properties of these ML-MoS<sub>2</sub> triangles are anti-correlated; we observed no photocurrent enhancement from ML-MoS<sub>2</sub> in the quartz region even though the optical properties are significantly enhanced.

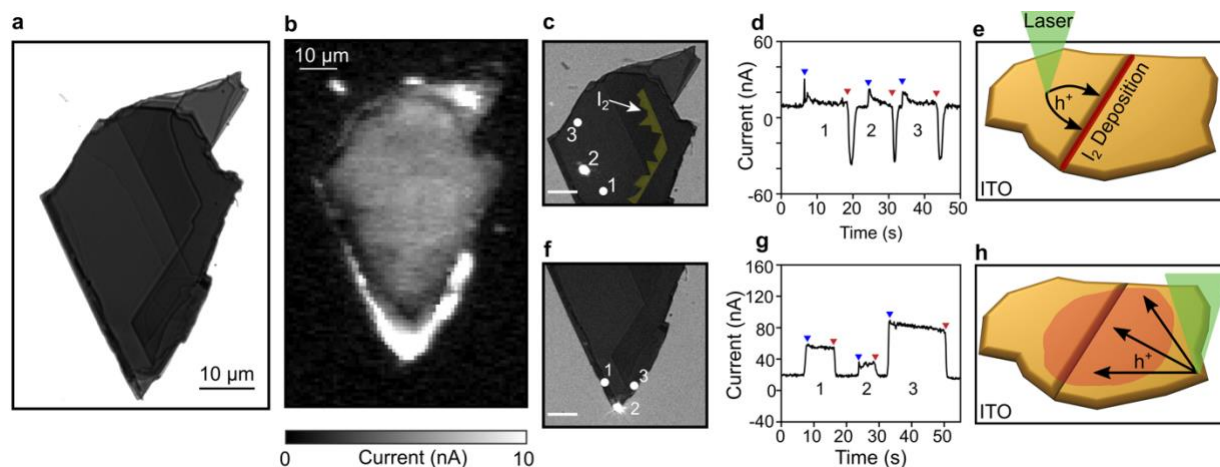
**Impact:** On the technical side, our work introduced an interdigitated array platform to investigate “suspended” 2D materials. Substrate engineering of 2D materials is accelerating at a rapid pace for solid-state optoelectronic devices such as field effect transistors and photodetectors. The results presented herein contribute to the fundamental understanding of substrate effects on monolayer semiconductor properties and the experimental methodology provides a framework to evaluate substrate engineering as a strategy to tune the (photo)electrocatalytic properties of 2D materials.

h) Nilsson, Z.; Van Erdevyk M.; Wang,L; Sambur, J.B.; “Molecular Reaction Imaging of Single-Entity Photoelectrodes” *ACS Energy Lett*, **2020**, 5, 5, 1474–1486. [https://pubs.acs.org/doi/abs/10.1021/acsenerylett.0c00284]

- Our group introduced a novel molecular reaction imaging approach to study the relationship between carrier generation, transport, and interfacial reactivity in nanostructured materials.

This Perspective highlights molecular reaction imaging methods that spatially resolve principal processes in photoelectrochemical cells: (1) reaction intermediate imaging, (2) surface recombination imaging, and (3) charge transport imaging. We discuss opportunities to couple optical microscopy techniques with electron or X-ray microscopy characterization tools to reveal atomic-level structure–property relationships of single-nanoentity photoelectrodes. The atomistic detail of the semiconductor/electrolyte interface may guide the design and synthesis of nanostructured electrodes for direct solar fuels production.

**Novel molecular reaction imaging method:** To image where photogenerated carriers react at the solid/liquid interface, we acquired bright field transmission image movies during photoelectrochemical measurements. We positioned the laser on either basal plane or perimeter edge locations using the photocurrent map of the nanoflake as a guide (see Figure 6a,b). When the laser illuminated the basal planes (spots 1–3 in Figure 6c), we observed an instantaneous 30 nA photocurrent spike that decayed to a small 3 nA steady-state photocurrent (Figure 6d). At the same time, dark contrast pixels appeared at a step edge that was located 27 μm from the laser spot (indicated by false yellow-colored pixels in Figure 6c for clarity). The dark contrast is due to an increase in optical density as a result of I<sub>2</sub> product accumulation at the step edge, as confirmed by in situ Raman micro-spectroscopy measurements and literature reports. The products persist on the nanoflake surface during the entire illumination period. The products disappear and a large cathodic spike appears upon interruption of the laser illumination (indicated by red triangle in Figure 6d). These results enabled us to calculate the electric field strength within the 2D semiconductor that drives photogenerated holes along the layers to the catalytically active surface sites.



**Figure 6.** Charge transport imaging via bright field optical microscopy. (a) Bright field optical transmission image of a MoS<sub>2</sub> nanoflake. (b) Photocurrent map of the nanoflake in (a). (c) Cropped transmission image of the nanoflake in panel a. The white circles labeled 1, 2, and 3 represent three excitation locations for chopped light photocurrent measurements. The false yellow color pixels indicate the surface iodine layer (indicated by white arrow). (d) Current vs time data from the three excitation locations in (c). (e) Cartoon illustration of the minority carrier transport (black arrows) and iodine deposition process (dark red region at step edge) upon illuminating the basal plane in panel c. (f and g) Same as panels c and d, but for the excitation spots indicated by white circles in panel f. (h) Cartoon illustration of the distribution of hole-induced iodide oxidation reactions across about half of the nanoflake (faint red shaded area) such that iodine deposition does not occur.

**Broad impact and outlook:** An interesting future direction for molecular reaction imaging via bright field microscopy is to study the relationship between charge transport anisotropy and surface morphology on the carrier collection efficiency of 2D nanoentity photoelectrodes. Space charge regions form in the direction parallel to the layers at step/perimeter edges as well as perpendicular to the layers at basal planes. Photogenerated carriers within the space charge region at step edges will preferentially drift toward the edge because the carrier mobility along the layers is much greater than that perpendicular to the layers. This edge effect is expected to influence photogenerated carriers at high step edges because more carriers are produced in the space charge region at the step edge than at the top basal plane surface. However, the fate of photogenerated minority carriers also depends on the edge site reactivity, or whether the edge acts as a recombination or “hot” site. The optical charge transport and reactivity imaging method could play an important role in identifying and characterizing the structure and composition of different types of edges. Optical microscopy can be coupled in a one-to-one fashion with scanning Auger micro-spectroscopy, atomic force microscopy, and scanning tunneling microscopy for high-resolution composition and structural analyses. These findings could guide the development of efficient large-area thin-film nanoflake electrodes that are currently being pursued.

### 3) Synergistic Activities in the AFOSR Molecular Dynamics Program.

We have collaborated with the Cronin research group at the University of Southern California to demonstrate plasmon-enhanced photoelectrochemical activity in Au/WSe<sub>2</sub> monolayers. The Cronin group has expertise in 2D materials growth and heterostructure fabrication. The Sambur group is leveraging this expertise to explore electric fields in new 2D materials configurations.

1. Chen, J.; Bailey, C.S.; Hong, Y.; Wang, L.; Cai, Z.; Shen, L.; Hou, B.; Wang, Y.; Shi, H.; Sambur, J.B.; Ren, W.; Pop, E.; Cronin, S.B.; “Plasmon-Resonant Enhancement of Photocatalysis on Monolayer WSe<sub>2</sub>” *ACS Photonics*, **2019**, 6 (3), pp 787-792.

[<https://pubs.acs.org/doi/10.1021/acsp Photonics.9b00089>]

#### 4) Dissemination of Research Findings.

##### Publications:

14. Nilsson, Z.; Van Erdewyk M.; Wang,L; **Sambur, J.B.**; “Molecular Reaction Imaging of Single-Entity Photoelectrodes” *ACS Energy Lett*, **2020**, 5, 5, 1474–1486. *Invited Perspective Article*.
13. Wang,L; Nilsson, Z.; Tahir, M; Chen, H; **Sambur, J.B.**; “Influence of the substrate on the optical and photoelectrochemical properties of monolayer MoS<sub>2</sub>” *ACS Appl. Mater. Interfaces*, **2020**, 12(13), 15034-15042.
12. Evans, R.C.; Nilsson, Z.; Balch, B.; Wang, L; Neilson, J.R.; Weinberger, C.R.; **Sambur, J.B.**; “Quantifying Capacitive-like and Battery-like Charge Storage Contributions Using Single Nanoparticle Electro-optical Imaging” *ChemElectroChem*, **2020**, 7 (3), 753-760.
11. \*Varra, T; \*Simpson, A; \*Roesler, B.; Nilsson, Z.; Ryan, D; Van Erdewyk M.; Schuttlefield Christus, J.D.; **Sambur, J.B.**; “A homemade smart phone microscope for single particle fluorescence microscopy” *J Chem. Ed.*, **2020**, 97 (2), 471-478.
10. Wang,L; Tahir, M; Chen, H; **Sambur, J.B.**; “Probing charge carrier transport and recombination pathways in monolayer MoS<sub>2</sub>/WS<sub>2</sub> heterojunction photoelectrodes” *Nano Lett.* **2019**, 19 (12), 9084-9094.
9. Evans, R.C.; Nilsson, Z.; **Sambur, J.B.**; “High-throughput single nanoparticle electrochemistry using widefield electro-optical imaging” *Anal Chem* **2019**, 91 (23), 14983-14991.
8. Wang,L; Schmid,M; **Sambur, J.B.**; “Single nanoparticle photoelectrochemistry: what is next?” *J Chem Phys*, **2019**, 151, 180901. *Invited Perspective Article*.
7. Evans, R.C.; \*Ellingworth, A.; Cashen, C.J.; Weinberger, C.R.; **Sambur, J.B.** “Influence of single nanoparticle electrochromic dynamics on the durability and speed of smart windows” *Proc. Natl. Acad. Sci.*, **2019**, 116 (26) 12666-12671.

##### **News Highlights:**

- “Chemists could make ‘smart glass’ smarter by manipulating it at the nanoscale” – CSU Source, Anne Manning. The story was also highlighted by *ScienceDaily* and *Nanowerk News*.
  - “Performance of ‘Smart’ Glass Improved By Manipulating Nano-Materials” – *DesignNews*, 27 June, 2019
6. Wang, L; Schmid, M; Tahir, M; Chen, H; **Sambur, J.B.**; “Laser Annealing Improves Photoelectrochemical Activity of Ultrathin MoSe<sub>2</sub> Photoelectrodes” *ACS Appl. Mater. Interfaces*, **2019**, 11 (21), 19207-19217.
  5. Wang, L.; **Sambur, J.B.**; “Efficient Ultrathin Liquid Junction Photovoltaics Based on Transition Metal Dichalcogenides” *Nano Letters*, **2019**, 19 (5), 2960–2967.
  4. **Sambur, J.B.\***; Shepherd, D.P.; Hesari, M; Van Erdewyk, M.; Choudhary, E.; Chen, P.; "Correlated Single-Molecule Reaction Imaging and Photocurrent Measurements Reveal Underlying Rate Processes in Photoelectrochemical Water Splitting" *J. Electrochem. Soc.*, **2019**. 166 (5), H3286-H3293. *\*corresponding author*.
  3. Chen, J.; Bailey, C.; Hong, Y.; Wang, L.; Cai, Z.; Shen, L.; Hou, B.; Wang, Y.; Shi, H.; **Sambur, J.B.**; Ren, W.; Pop, Eric; Cronin, S. “Plasmon-Resonant Enhancement of Photocatalysis on Monolayer WSe<sub>2</sub>”, *ACS Photonics*. **2019**. 6 (3), pp 787-792.
  2. Isenberg, A. E., Todt, M. A., Wang, L., **Sambur, J. B.**, “The Role of Photogenerated Iodine on the Energy Conversion Properties of MoSe<sub>2</sub> Nanoflake Liquid Junction Photovoltaics” *ACS Appl. Mater. Interfaces.*, **2018**, 10(33), 27780–27786.
  1. Todt, M.A., Isenberg, A., Miller, E.M., Nanayakkara, S.U., **Sambur, J.B.**; “Single nanoflake photoelectrochemistry reveals champion and spectator nanoflakes in exfoliated MoSe<sub>2</sub> films” *J. Phys. Chem. C.*, **2018**, 122 (12), 6539–6545.

Invited Lectures

1. Department of Chemistry, University of New Hampshire, October 2, 2017
2. Department of Physics, Colorado State University, February 12, 2017
3. Department of Chemistry, University of Colorado-Denver, October 4, 2018
4. Department of Chemistry, TU-Darmstadt, March 26, 2019
5. Department of Chemistry, Metro State University, May 3, 2019
6. Department of Chemistry, Temple University, Sept 5, 2019
7. Department of Chemistry, University of Wyoming, Oct 25, 2019
8. Department of Chemistry, University of Oregon, Dec 6, 2019
9. Department of Chemistry, Washington University-St. Louis, Feb 13, 2020
10. Department of Chemistry, Arizona State University, Feb 28, 2020

Contributed Lectures

1. Electrochemical Society Spring National Meeting, Seattle, WA, May 15, 2018
2. Gerischer Symposium, Boulder, CO, August 15, 2018
3. 50<sup>th</sup> Society of Western Analytical Professors Meeting, Tuscon, AZ, Jan. 20, 2019
4. Materials Research Society National Meeting, Phoenix, AZ, April 22, 2019
5. Probing Chemical Reactions by Single-Molecule Spectroscopy  
German Bunsen Society for Physical Chemistry  
Höchst im Odenwald, Germany, Mar 27-29, 2019

Invited Poster Presentations.

1. Air Force Office of Scientific Research Molecular Dynamics Program Review, May 22, 2017  
*Nanoscale Characterization of Ultrathin Photovoltaics*
2. Gordon Research Conference: Electrochemistry, Ventura, CA, January 5, 2018  
*Single Nanosheet Photoelectrochemistry*
3. Gordon Research Conference: Solar Fuels, Ventura, CA, February 2, 2018  
*Single Nanosheet Photoelectrochemistry*
4. Air Force Office of Scientific Research Molecular Dynamics Program Review, May 24, 2018  
*Nanoscale Characterization of Ultrathin Photovoltaics*
5. Air Force Office of Scientific Research Molecular Dynamics Program Review, May 22, 2019  
*Probing Charge Recombination and Transport Pathways in 2D Materials*
6. Gordon Research Conference: Electrochemistry, Ventura, CA, January 8, 2020  
*Nanoscale Imaging of Electrochemical Energy Technologies*

Postdoc Li Wang and Graduate Student R. Colby Evans disseminated research findings at the 2019 Gordon Research Conference on Nanomaterials for Applications in Energy Technology: Challenges and Opportunities at the Nanoscale: Applications, Simulation, Advanced Characterization and Novel Manufacturing.

R. Colby Evans was elected to serve as the next chair of the 2021 Gordon Research Seminar on Nanomaterials for Applications in Energy Technology.

**Honors and Awards**

- 2020 NSF CAREER Award
- 2020 DOE Early Career Award
- 2019 RCSA Scialog Fellow: Advanced Energy Storage