Probing Charge Carrier Transport and Recombination Pathways in Monolayer MoS2/WS2 Heterojunction Photoelectrodes

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Supporting Information

ABSTRACT: Monolayer heterojunctions such as MoS2/WS2 are attractive for solar energy conversion applications because the interfacial electric field spatially separates charge carriers in less than 100 fs. Photoelectrochemical cells represent an intriguing platform to collect the spatially separated carriers. However, the recombination, transport, and interfacial charge transfer processes that take place following the ultrafast charge separation step have not been investigated. Here we demonstrate novel charge recombination and transport pathways in monolayer MoS2/WS2 photoelectrochemical cells by spatially resolving the net collection of carriers (i.e., the photocurrent) at the single nanosheet level. We discovered an excitation-wavelength-dependent recombination pathway that depends on the heterojunction stacking configuration and the carrier generation profile in the heterostructure. Photocurrent mapping measurements revealed that charge transport occurs parallel to the layers over micrometer-scale distances even though the indium tin oxide electrode and liquid electrolyte provide efficient charge extraction pathways via intimate electron- and hole-selective contacts. Our results reveal how composition heterogeneity influences the performance of bulk heterojunction electrodes made from randomly oriented nanosheets and provide critical insight into the design of efficient heterojunction photoelectrodes for solar energy conversion applications.

KEYWORDS: Monolayer photoelectrochemistry, transition metal dichalcogenides (TMDs), heterojunction, photoelectrochemical cell, photocurrent microscopy

Transition metal dichalcogenides (TMDs) with the chemical formula MX2, where M = Mo or W and X = S or Se, are layered materials that are held together by weak van der Waals interactions. The lack of covalent bonding between layers relaxes the lattice matching requirement for the layer-by-layer assembly of TMD heterojunctions.1,2 This layer-by-layer stacking approach has been used to fabricate TMD heterojunction devices with tailored functional properties such as field-effect transistors,3,4 light-emitting diodes,5,6 photodetectors,7,8 and photovoltaics.7,8

TMD heterojunctions such as MoS2/WS2 are particularly interesting for solar energy conversion applications. The physical coupling of TMDs with different electronic properties creates a driving force for charge separation at the heterojunction interface and facilitates charge transport to electrical contacts.1,4,11 Charge transport is typically studied in solid-state device geometries, where the TMDs are stacked on top of each other and electrical contacts are deposited on the perimeter edges of the individual TMDs.4,11 In this geometry, photogenerated carriers within the heterojunction region, or those carriers that can diffuse to the heterojunction region, may be separated efficiently. For MoS2/WS2 heterojunctions, this interlayer charge separation step produces electrons in MoS2 and holes in WS2. Following the interlayer charge separation step, electrons and holes must traverse long distances to reach electrical contacts. Charge transport takes place parallel to the layers across micron-scale distances instead of perpendicular to the layers across six atoms. Thus, solid-state devices with edge-on electrical contacts do not transport charge carriers across the atomically thin layers even though all carriers are produced at a charge-collecting interface. The long transport distances promote interlayer electron–hole recombination that ultimately limits the collection efficiency of photogenerated carriers.10,13 It has been suggested that implementing perpendicular carrier transport pathways via the top and bottom carrier-selective contacts could improve heterojunction photoelectrode efficiency.14
Photoelectrochemical cells represent an alternative device geometry to study the underlying solar energy conversion processes in ultrathin materials. In the liquid junction geometry, the TMD heterojunction is deposited on a conducting electrode and immersed in a redox electrolyte. The solid electrode and redox electrolyte make intimate electrical contact to the TMD components and enable efficient perpendicular charge separation and transport pathways over large areas. We recently showed that this geometry promotes efficient extraction of photogenerated carriers in model photovoltaic systems, as evidenced by 3.7% external quantum efficiency (EQE) values over 1 cm² photoactive areas, which is competitive with solid-state devices. Electrochemical cells made from monolayer heterojunctions have been used to catalyze the hydrogen evolution reaction under dark conditions. Photoelectrochemical cells made from multi-layer-thick heterojunctions have been explored as water oxidation photoanode, dye-sensitized solar cell counter electrodes, and solar fuels photoelectrodes. Multi-layer-thick TMD films absorb more incident light than monolayer films. However, heterojunction films made from randomly oriented mixtures of different TMD nanosheets exhibit a wide variety of stacking configurations. It is unknown how different TMDs stacking orientations influence charge separation and transport in heterojunction photoelectrodes.

Several groups have studied charge separation and transport properties of TMD heterojunctions at open circuit and in solid-state devices. Ultrastart spectroscopy measurements of TMDs have shown that the photoinduced interlayer charge transfer takes place on the femtosecond time scale, but the charge transfer mechanism is not entirely understood. Chen et al. reported an interlayer charge transfer mechanism in MoS₂/WS₂ that proceeds via a hot exciton intermediate state. An alternative process is fast interlayer energy transfer, as proposed by Eda and co-workers, where excitons in one TMDs (e.g., WS₂) excite higher-order excitons in the adjacent TMDs (MoSe₂). Ceballos et al. reported a coherent charge transfer mechanism in trilayer TMD heterojunctions where photoexcited electrons in the top MoSe₂ layer transfer through a WS₂ middle layer to a MoS₂ underlayer in about one picosecond. The above mechanisms were largely deduced from ultrastart optical spectroscopy measurements and theoretical calculations of TMD heterojunctions under open-circuit conditions. The relevant environment for optoelectronic and (photo)catalytic devices includes solid- or liquid-phase charge carrier-selective contacts to TMDs. An important open question in the field is to what extent do conformal contacts influence the charge recombination and transport pathways that ultimately lead to current flow in the external circuit.
in photoelectrochemical cells made from TMD heterojunctions.33

Here we investigated charge recombination and transport pathways in Schottky-type liquid junction solar cells made from vertically stacked MoS2/WS2 heterojunctions. We studied TMD heterojunctions in 1 M NaI electrolyte because hole-induced iodide oxidation by TMDs is one of the most efficient and chemically stable photoelectrochemical reactions.33,36 Spatially resolved photocurrent measurements of different TMDs stacking configurations (ITO/MoS2/WS2 versus ITO/WS2/MoS2) under different illumination conditions revealed novel charge recombination and transport pathways in the monolayer heterojunction photoelectrodes. The ITO/MoS2/WS2 system exhibited a significant photocurrent enhancement effect under both 532 and 635 nm illumination. On the other hand, we observed excitation-wavelength-dependent charge separation and recombination pathways in the ITO/WS2/MoS2 system. Under 532 nm illumination that excites both TMDs, electrons in MoS2 recombine with holes in WS2. This interlayer recombination pathway is suppressed under MoS2-selective (635 nm) conditions. Lastly, photocurrent mapping data and charge transport simulations showed that charge transport occurs parallel to the TMD layers via a diffusion mechanism even though the ITO electrode and liquid electrolyte provide facile perpendicular charge transport pathways.

Results and Discussion. Optical Characterization of Monolayer Heterojunctions. Monolayer MoS2 and WS2 samples were grown on sapphire substrates via a chemical vapor deposition process and transferred to indium doped tin oxide (ITO) substrates using poly(methyl methacrylate) (PMMA) stamps.37 Two stacking configurations were prepared (ITO/MoS2/WS2 and ITO/WS2/MoS2) and annealed in a vacuum (ca. 10−3 mbar) at 120 °C for 6 h to remove polymer residue from the mechanical transfer process and improve the interlayer coupling between the monolayers. To minimize the influence of sample-to-sample heterogeneity, the heterojunctions were prepared from monolayers that were synthesized in the same batch and postannealed in a side-by-side fashion.

Raman and photoluminescence (PL) spectroscopy measurements were used to probe the interlayer charge transfer in the monolayer heterojunction under open-circuit conditions. Figure 1a,g shows representative bright-field optical transmission images of the ITO/MoS2/WS2 and ITO/WS2/MoS2 samples, respectively. Figure 1b shows Raman spectra that were measured from the focused laser positions in Figure 1a. The Raman spectra acquired from the isolated monolayer materials exhibit the characteristic out-of-plane (A′) and in-plane (E′) modes of MoS2 and WS2. The 19 and 65 cm−1 splitting between the A′ and E′ peaks indicates that the triangles are monolayer-thick MoS2 and WS2, respectively.38,39 The large 20–30 µm triangles in Figure 1a,g are WS2 monolayers, whereas the smaller 10 µm triangles are MoS2 monolayers. MoS2 absorbs more photons than WS2 under white light illumination conditions, and therefore, the MoS2 triangles exhibit dark contrast in transmission images. Raman spectra measured from the heterojunction region, corresponding to the sample region in Figure 1a,g, where the dark and light triangles spatially overlap, show no significant peak shifts for either stacking configuration.

The PL spectra measured from both heterojunction stacking configurations exhibit significant intensity changes compared to the isolated materials. Isolated WS2 exhibits an intense PL peak at around 640 nm, whereas MoS2 exhibits a comparatively weaker PL peak at 684 nm and a smaller shoulder peak at 628 nm (Figure 1c,(i)), in agreement with literature.39 The PL peaks at 640 nm (1.94 eV) and 684 nm (1.81 eV) correspond to the A exciton transition of the direct band gap monolayer WS2 and MoS2, respectively; the small shoulder peak in the MoS2 spectrum corresponds to the indirect B exciton transition.39 The PL spectrum from the photoexcited heterojunction region resembles that of the higher band gap WS2. The weak MoS2 PL peak at 684 nm is difficult to detect beneath the more intense WS2 spectrum. Importantly, the PL intensity from the heterojunction region is an order of magnitude lower than that of isolated WS2. The PL quenching behavior indicates interlayer charge transfer in the heterojunction region.39

Raman and PL mapping experiments further confirm that interlayer charge transfer occurs in both heterojunction stacking configurations under open-circuit conditions. Figure 1d–f (ITO/MoS2/WS2) and Figure 1j–l (ITO/WS2/MoS2) show the spatial distribution of the MoS2 and WS2 A′, Raman peak intensities and the integrated PL peak intensities. The out-of-plane A′ mode of WS2 increases significantly (Figure 1e,k) in the heterojunction region, while the MoS2 A′ intensity decreases slightly (Figure 1d,j) for both stacking configurations. Previous calculations of MoS2/WS2 heterojunctions showed that those peak intensity changes indicate that photoinduced interlayer charge transfer takes place between the physically coupled TMDs.41,42 The peak intensity of the in-plane E′ modes of MoS2 and WS2 show no significant intensity changes in both stacking configurations (Figure S1), presumably because the in-plane Raman modes of monolayer heterojunctions are typically less susceptible to changes in interlayer coupling.43,44 On the other hand, the out-of-plane Raman modes are sensitive to the physical coupling between layers, and photoinduced interlayer photoexcited charge transfer occurs in strongly coupled MoS2/WS2 heterojunctions.41,42 In summary, the PL spectra and spatially resolved Raman measurements indicate that interlayer charge transfer occurs for both monolayer heterojunction stacking configurations.

Probing Carrier Collection Efficiencies in Monolayer MoS2/WS2 Heterojunctions. Having established that interlayer charge transfer occurs in both heterojunction stacking configurations under open-circuit conditions, we probed the carrier collection efficiency of both heterojunctions using photocurrent microscopy measurements in ITO/TMDs/I−, I3−/Pt photoelectrochemical cells. In a typical experiment, the electrochemical cell is mounted on the same inverted microscope that was used for Raman and PL microspectroscopy measurements. The sample stage moves the cell in 1 μm increments, while a tightly focused laser spot excites a 1 μm2 area of the heterojunction working electrode. Supra-band gap illumination generates electron–hole pairs in the TMDs, and a potentiostat measures the photoinduced current response due to iodide oxidation. The charge transport pathways are as follows (Figure S2). Photogenerated holes are transported to the TMDs/electrolyte interface and oxidize I− to I3−, which rapidly reacts with I− to form I3−. Photogenerated electrons are transported to the TMDs/ITO contact and extracted to the external circuit. Photoelectrochemical microscopy measurements report on the net flow of charge through the entire nanosheet upon photoexciting a microscopic location within a
Figure 2. Scanning photoelectrochemical microscopy of monolayer heterojunctions under 532 nm excitation. (a) Optical transmission images and (b) photocurrent maps of ITO/MoS₂/WS₂ electrodes. Photocurrent maps were measured in 1 M NaI electrolyte at +0.5 V versus an Ag/AgI reference electrode using a 1.2 μm diameter and 532 nm laser spot (13.5 kW/cm²). (c) EQE distributions from the photocurrent map in panel b. The distributions were determined using the detailed photocurrent mapping analyses procedures that are described in the Supporting Information, Note 1. (d) Average EQE values from the distributions in panel c, where the error bars represent the standard error of the mean. Panels e–h are the same as that for panels a–d, but for the ITO/WS₂/MoS₂ stacking orientation.

Figure 2 shows representative optical transmission images and photocurrent maps of ITO/MoS₂/WS₂ and ITO/WS₂/MoS₂ electrodes at +0.5 V vs Ag/AgI and under 532 nm illumination conditions. The +0.5 V applied potential was chosen for photocurrent mapping experiments because (1) it is the most positive anodic bias that can be applied to the TMDs electrode without producing dark anodic currents due to iodide oxidation, and (2) it minimizes photocurrent transient effects that could influence the lock-in detected current; these lock-in detected currents represent the steady-state photocurrent response (Figure S3). Qualitative comparison of the transmission and photocurrent images in Figure 2a,b indicates that the largest photocurrents (bright pixels) stem from photoexcited ITO/MoS₂/WS₂ regions.

To quantitatively compare the photocurrent response from isolated MoS₂ and WS₂ to that of MoS₂/WS₂, we assign every pixel in the photocurrent map to photoexcited ITO, MoS₂, WS₂, or MoS₂/WS₂ regions using an image overlay procedure that is described in Figure S4 and Note 1. Figure 2c shows the distribution of external quantum efficiency (EQE) values, respectively, from photoexcited MoS₂, WS₂ and MoS₂/WS₂ regions of the sample in Figure 2a. The monochromatic external quantum efficiency is calculated according to EQE = \( i/qI_{\text{inc}} \) where \( i \) is the photocurrent, \( q \) is the elementary charge, and \( I_{\text{inc}} \) is the incident 532 nm laser power (s⁻¹). The broad distribution of EQE values among the different regions are presumably due to heterogeneity among the nanosheets. Figure 2d shows that, on average, the ITO/MoS₂/WS₂ heterojunction region exhibits a significant synergistic enhancement effect over the isolated MoS₂ and WS₂ areas. Specifically, the EQE of ITO/MoS₂/WS₂ (0.8%) exceeds the sum of MoS₂ and WS₂ (0.4%). The enhancement behavior in Figure 2a–d was observed for different areas from the same cell as well as other cells (Figures S5 and S6), indicating that the synergistic enhancement effect is general for these ITO/MoS₂/WS₂ heterojunctions.

We attribute the photocurrent enhancement effect for ITO/MoS₂/WS₂ to an increase in the charge separation efficiency. This can be rationalized as follows: a general expression for photocurrent density of a photoelectrochemical cell, \( J_{\text{PEC}} = I_{\text{abs}} \times \eta_{\text{sep}} \times \eta_{\text{cat}} \) where \( I_{\text{abs}} \), \( \eta_{\text{sep}} \), and \( \eta_{\text{cat}} \) are the absorbed photon flux, the efficiencies of charge separation, and interfacial charge transfer to redox species in the electrolyte, respectively. The increase in EQE for ITO/MoS₂/WS₂ is likely not due to an increase in \( \eta_{\text{cat}} \) because the catalytic properties likely do not change for the physically coupled TMDs, and we performed control measurements on the same batch of nanosheets that are located just microns apart. In addition, light absorption enhancement in the heterojunction also cannot account for the EQE enhancement because the absorption spectrum of the heterojunction is approximately the sum of the individual monolayers, and we observed that the EQE of ITO/MoS₂/WS₂ exceeds the sum of the monolayers by a factor of 2 (Note 2 and Figures S7 and S8). Thus, we attribute the increase in EQE to an increase in \( \eta_{\text{sep}} \) as a result of the conduction band level offset between WS₂ and MoS₂, as will be discussed below.

On the contrary, the ITO/WS₂/MoS₂ stacking orientation showed a significant photocurrent quenching effect under 532 nm laser illumination. The photocurrent map in Figure 2f shows that photoexcited heterojunction regions produce low photocurrents (dark pixels), which indicates that photoexcited carriers in the heterojunction mostly recombine and do not participate in the iodide oxidation reaction. We note that the photocurrent response from the ITO/WS₂/MoS₂ regions is not completely suppressed and is larger than that of bare ITO regions. Photocurrent maps from other electrochemical cells and sample regions show the same quenching behavior (Figure S9). The EQE distribution of the ITO/WS₂/MoS₂ is broad and exhibits two populations that overlap with ITO/MoS₂ and ITO/WS₂ (Figure 2g). Quantitative analysis of the ITO/WS₂/
MoS₂ photocurrent map indicates that ITO/MoS₂/WS₂ does not exceed the sum of the isolated TMD components (Figure 2h). Similarly, the photocurrent quenching effect is likely not due to a small $\eta_{\text{int}}$ (i.e., local differences in catalytic properties) because we performed control experiments on isolated materials and confirmed that both materials oxidize iodide. Instead, the photocurrent quenching effect should likely arise from the small $\eta_{\text{sep}}$ as a result of physically coupling individual TMD components in the ITO/WS₂/MoS₂ stacking configuration.

Probing Charge Carrier Transport and Recombination Pathways in Two Heterojunctions. To understand the relationship between carrier generation, recombination, and transport in these MoS₂/WS₂ stacking configurations, we studied the photocurrent response under both 532 nm (green) and 635 nm (red) excitation conditions. The red laser preferably excites the low band gap MoS₂ material, whereas the green laser excites both materials (Figure S7). Figure 3b,h shows zoomed-in photocurrent maps of the ITO/MoS₂/WS₂ and ITO/WS₂/MoS₂ stacking configurations under 532 nm excitation (Figure S10 shows the whole photocurrent maps). We observed the same photocurrent enhancement and quenching behavior as shown in Figure 2. Then, we measured photocurrent maps of the same regions under 635 nm excitation (Figure 3c). The ITO/MoS₂/WS₂ sample showed the same photocurrent enhancement effect under 635 nm excitation (Figure 3c), indicating that photogenerated carriers in the MoS₂ are efficiently extracted from the bottom layer in the heterojunction. The line profiles in Figure 3d quantify the...
photocurrent responses under different illumination conditions.

We observed a synergistic enhancement effect when MoS₂ and WS₂ are physically coupled, but only MoS₂ is photoexcited. Figure 3a,c shows that under MoS₂-selective excitation conditions, photoexcited MoS₂ in the ITO/MoS₂/WS₂ region produces a larger photocurrent than isolated MoS₂. The EQE of ITO/MoS₂/WS₂ is about 2.5 times larger than that of ITO/MoS₂ under 635 nm excitation conditions (Figure S11). Photogenerated carriers in MoS₂ are more efficiently separated if those carriers are produced in the heterojunction region than in the isolated region. In other words, η_{sep} is larger for photogenerated carriers in ITO/MoS₂/WS₂ than for ITO/MoS₂. We attribute the enhanced separation efficiency to a built-in electric field that promotes rapid hole transfer from the bottom MoS₂ layer to the top WS₂ layer.

Interestingly, we did not observe a significant photocurrent quenching effect for the ITO/WS₂/MoS₂ samples under 635 nm excitation conditions even though the same triangle exhibits a photocurrent quenching effect under 532 nm laser conditions (Figure 3i versus h). The line profiles in Figure 3j show that the photocurrent response in the heterojunction region under the 635 nm illumination condition increases compared to the 532 nm illumination condition. This observation does not depend on the order of the experiments; the results hold true whether the 532 nm map was performed before or after the 635 nm mapping experiment (Figure S10 versus Figure S12). We also note that the incident photons per second are equal in both experiments, and therefore the observation is not due to differences in carrier generation. In the ITO/WS₂/MoS₂ stacking configuration under MoS₂-selective illumination conditions, photogenerated electrons are transferred from the MoS₂ top layer to the ITO electrode through the WS₂ bottom layer. Ceballos et al. reported a similar anomalous charge transport pathway in trilayer TMDs, where charge carriers flowed from a top MoSe₂ monolayer to a bottom MoS₂ monolayer without populating the middle WS₂ monolayer.

We propose the following charge generation, recombination, and transport schemes to explain the photocurrent mapping data for both heterojunction configurations under green and red excitation conditions. Theoretical studies have shown that monolayer MoS₂ and WS₂ form a type-II energy band alignment where the conduction band minimum (CBM) of WS₂ is 0.35 eV above (or more negative on the electrochemical scale) the CBM of MoS₂, and the valence band maximum (VBM) of WS₂ is 0.39 eV above that of MoS₂. The type-II band alignment promotes electron transfer from WS₂ to MoS₂ and hole transfer from MoS₂ to WS₂. For the ITO/MoS₂/WS₂ configuration, the type-II energy level alignment promotes electron and hole transport to the ITO and electrolyte contacts, respectively (Figure 3e). The charge transport pathway of photogenerated carriers in MoS₂ does not depend on the excitation wavelength (Figure 3f). The overall charge separation and transport efficiency of carriers in MoS₂ is enhanced significantly if those carriers are produced in the heterojunction region instead of an isolated MoS₂ region. The photocurrent enhancement effect for the ITO/MoS₂/WS₂ stacking configuration can be attributed to a rapid interlayer charge separation that produces spatially separated electrons and holes near hole-selective and electron-selective contacts.

For the ITO/WS₂/MoS₂ stacking configuration, the charge recombination and transport pathways critically depend on carrier generation in the TMDs. We observed a large photocurrent response upon exciting the heterojunction region with 635 nm light during a small photocurrent response when both TMDs were excited simultaneously with 532 nm light. Thus, charge carrier generation in both materials induces a recombination pathway that is not present under MoS₂-selective carrier generation conditions. This result suggests that electrons in the conduction band of MoS₂ recombine with holes in the valence band of WS₂ as shown in Figure 3k. In this scenario, green light generates excitons in both materials (vertical black arrows in Figure 3k). Next, interlayer charge transfer occurs on an ultrafast time scale (~50 fs). Photogenerated electrons in the low-lying conduction band of MoS₂ recombine with valence band holes in WS₂ (pink arrow in Figure 3k). Photogenerated electrons in the low-lying conduction band of MoS₂ recombine with valence band holes in WS₂ (pink arrow in Figure 3k) likely because (1) the spatially separated electrons and holes are not located near their respective carrier-selective contacts (i.e., ITO and electrolyte), and (2) the type-II energy level alignment imposes a potential energy barrier for electrons and holes to transfer into the ITO and electrolyte contacts, respectively. Alternatively, it is also possible that photogenerated holes in the top MoS₂ layer rapidly oxidize iodide to I₂ or I₃⁻. Since there is an energy barrier for photogenerated electrons in MoS₂ to transfer to the bottom WS₂ layer, the photogenerated electrons could react with the surface adsorbed oxidized products (I₂ or I₃⁻), leading to the photocurrent quenching behavior. Regardless of the underlying mechanism, a photogenerated hole population in the WS₂ bottom layer is apparently necessary to activate the interlayer recombination channel. Lee et al. proposed a similar interlayer charge recombination process to explain electron–hole recombination in solid-state MoS₂/WS₂ heterojunctions with lateral electrical contacts. The authors proposed that interlayer charge recombination occurs through either a Shockley–Read–Hall or Langevin mechanism or a combination of both.

Figure 3l shows one possible charge separation and transport pathway for the ITO/WS₂/MoS₂ stacking configuration under 635 nm illumination conditions. In this scenario, electrons transfer from the MoS₂ top layer through the WS₂ bottom layer to the ITO electrode. Holes in MoS₂ transfer to the intimately coupled electrolyte contact. One could have expected a recombination pathway, where ultrafast interlayer hole transfer occurs first from the top MoS₂ layer to the bottom WS₂ layer (not illustrated in Figure 3i), and then interlayer electron–hole recombination occurs as shown in Figure 3k. While this recombination pathway could still take place in the system, our 635 nm photocurrent mapping measurements indicate the photogenerated hole transfer to the iodide electrolyte likely outcompetes interlayer hole transfer (followed by recombination). Finally, we note that the small photocurrent response from isolated WS₂ regions under 635 nm excitation (Figure 3i) is likely due to a minor overlap of the 635 ± 1 nm laser line (Figure S13) with the absorption onset of the WS₂ A-exciton peak (Figure S7). Thus, the 635 nm photocurrent mapping measurements may underestimate the true magnitude of the photocurrent response of the ITO/WS₂/MoS₂ heterojunction under MoS₂-selective conditions because the small photogenerated exciton population in the bottom WS₂ layer could induce the recombination pathway illustrated in Figure 3k. We addressed this issue by photoexciting the sample with 650 nm light from a white light source.
coupled to a monochromator (excitation profile shown in Figure S14), as will be discussed in the current–voltage measurements below.

While the photocurrent quenching result under 532 nm excitation conditions can be rationalized by the mechanism in Figure 3k, it is still surprising that electron–hole recombination occurs despite the fact that (1) there are parallel and perpendicular charge transport pathways for holes to reach the electrolyte, and (2) the applied potential generates a strong internal electric field that drives charge separation. One could have expected electrons and holes to transfer through the potential energy barriers imposed by the ultrathin TMDs, as in Figure 3i. Instead, the strong interlayer electronic coupling promotes ultrafast charge separation, followed by interlayer recombination. Importantly, our photocurrent microscopy approach revealed all of the above relationships between carrier generation, transport, and recombination on heterojunction samples that contained isolated TMDs attached directly to the heterojunction region. Photocurrent measurements of the isolated materials serve as key control experiments that rule out sample heterogeneity or batch-to-batch variations as possible contributing factors to the photocurrent mapping observations.

**Lateral Charge Transport in Monolayer Heterojunctions under 532 nm Excitation.** Spatially resolved photocurrent mapping measurements revealed that charge carriers flow parallel to the TMDs layers even though the ITO electrode and liquid electrolyte provide perpendicular charge transport pathways. We performed the following image analysis procedure to study parallel charge transport pathways. Figure 4b shows a photocurrent map of the ITO/MoS2/WS2 region in Figure 4a. Figure 4c shows the same data as in Figure 4b, but the perimeter edges of the MoS2, WS2, and MoS2/WS2 regions are highlighted with red, blue, and purple pixels, respectively. The detailed structural overlay procedures and additional control experiments are provided in the Supporting Information, Note 3. The bright contrast pixels in Figure 4c extend beyond the heterojunction boundary, and the dark contrast pixels in Figure 4g occur deeper within the heterojunction interior; the photocurrent enhancement and quenching effect extend beyond the physical size of the heterojunction triangle regions.

To quantitatively show how the heterojunction influences parallel charge transport, we extract the photocurrent value for all large WS2 triangles that were physically coupled to a small MoS2 triangle (i.e., blue pixels in Figure S15) and plotted those values versus distance of that WS2 region to the nearest heterojunction edge site (nearest pink pixel in Figure 4c). The detailed image analysis procedure is provided in the Supporting Information, Note 3. Figure 4d shows the photocurrent versus distance to the heterojunction edge (d) profile for the WS2 triangle in Figure 4c. For large d values (>3 μm), photoexcited WS2 produces a 30 nA photocurrent that is independent of d. Then, for d < 3 μm, the photocurrent increases monotonically with decreasing d and eventually exhibits a maximum inside the heterojunction region (−d values). The photocurrent increase at small d values is likely not due to the diffraction-limited resolution of the experiment or a broad laser excitation spot because a line profile analysis of the laser reflection map (Figure S16 and detailed discussion in Note 4) shows a more abrupt transition across the heterojunction edge than the photocurrent profile in Figure 4d. In addition, control experiments of ITO/MoS2 regions also showed an abrupt transition across the MoS2 edge/ITO interface (Figure S16 and Note 4), indicating that the diffraction-limited resolution and light scattering cannot account entirely for the behavior.
observed in Figure 4d. Instead, we conclude that photogenerated carriers in isolated WS$_2$ “feel” the heterojunction edge even though they are spatially separated by about 3 μm.

We performed the same analysis for the ITO/WS$_2$/MoS$_2$ stacking configuration (Figure 4e–h). For large $d$ values (>3 μm), photoexcited WS$_2$ produces a 30 nA photocurrent that is independent of $d$, which is expectedly similar to the isolated material from the other stacking configuration (Figure 4d). The $d$-independent regions of both stacking configurations highlight the fact that the photoexcited WS$_2$ material far from the heterojunction region behaves like isolated WS$_2$ that is not physically coupled to MoS$_2$. However, for $d < 3$ μm, the photocurrent decreases monotonically with decreasing $d$ in the ITO/WS$_2$/MoS$_2$ stacking configuration (Figure 4h). Again, photogenerated carriers in isolated WS$_2$ “feel” the heterojunction edge even though the carriers are generated several microns from the heterojunction region. We observed similar behavior for other regions in both electrochemical cells (Figure S17).

Here we discuss the possible mechanisms of the photocurrent versus distance behavior in Figure 4d,h. One possible mechanism for this parallel charge transport behavior is that carriers move in an electric field due to a drift mechanism. In this scenario, charge carriers are transported in an electric field that forms at the heterojunction edge and extends into the WS$_2$ monolayer. A similar mechanism has been used to explain charge recombination at step edges in bulk TMDs/iodide photoelectrochemical cells. 47,48 Howell et al. reported a similar effect at the edge sites in monolayer/multilayer MoS$_2$-based devices. 49 It is plausible that the drift mechanism occurs over micrometer-scale distances because Kelvin probe force microscopy (KPFM) experiments showed that the width of the parallel electric field region is about 3 μm. 50,51 However, those KPFM measurements were performed in air, and our measurements were performed in concentrated electrolyte solutions. Another possibility is that the charge carriers diffuse along a concentration gradient. In this scenario, the carrier concentration is high at the focused laser spot, and therefore, carriers diffuse from regions of high carrier concentration to low carrier concentration (i.e., toward the heterojunction edge).

To confirm the underlying mechanism of the parallel charge transport processes in these TMD heterojunctions, we performed charge transport simulations based on a simplified one-dimensional model (see Supporting Information, Note 5, for details), following standard practices in the field. Briefly, we solved Poisson’s equation to determine the electric potential in the TMD heterojunction under dark equilibrium conditions. Those calculations showed that the thickness of the electric field region in WS$_2$ at the heterojunction interface is at most 30 nm, due to the strong screening by the 1 M NaI electrolyte and the ITO substrate in contact with the TMD layers. Since the photocurrent decay behavior occurs over a much longer length scale, the lateral electric field at the heterojunction interface likely does not contribute to the photocurrent versus distance behavior in Figure 4d,h. Simulations in the steady state under focused laser illumination show that the parallel charge transport process is driven by carrier diffusion along a concentration gradient from the point of generation (focused laser spot) to the heterojunction edge site. The micron-scale diffusion length is likely due to the relatively long exciton lifetime (typically over 100 ps) in the TMD layers.52

**Current–Voltage Characteristics.** To further confirm the charge carrier pathways proposed in Figure 3, the energetics of the TMDs/liquid electrolyte interface was studied using wavelength-dependent photocurrent versus applied potential (i-E) curves. We determined the photocurrent onset potential ($E_{\text{on}}$) from i-E data because $E_{\text{on}}$ represents the minimum applied potential to separate charge in the photoexcited semiconductors.53 In other words, we assume that $i = 0$ nA when $E = E_{\text{on}}$ because there is no electric field in the TMDs to drive charge separation. At this flatband condition, the applied potential is equal to the energy level difference between the Fermi level of the TMDs ($E_F$) and the electrochemical potential of the liquid electrolyte $E^0$ ($1/e_L$).55 Since the solution potential does not change for the different stacking configurations and illumination conditions, we determine the Fermi level alignment of the isolated and heterojunction TMDs relative to the fixed solution potential.56

Figure 5 shows the i-E curves of the ITO/WS$_2$/MoS$_2$ and ITO/MoS$_2$/WS$_2$ samples under 532 nm (3.0 mW/cm$^2$) and 650 nm (2.4 mW/cm$^2$) illumination, respectively. The illumination spot size was 1.13 mm$^2$. The solid lines represent linear fits to the i-E data.

![Figure 5. Wavelength-dependent photocurrent versus applied potential curves. (a) i-E data under 532 nm (3.0 mW/cm$^2$) and (b) 650 nm (2.4 mW/cm$^2$) illumination, respectively. The illumination spot size was 1.13 mm$^2$. The solid lines represent linear fits to the i-E data.](image-url)
increasing anodic potentials. We attribute the linear $i$-$E$ response to a linear electric potential profile in the TMDs, whose magnitude increases linearly with increasingly anodic potential, in agreement with literature.10,11 We extract $E_{on}$ by fitting the $i$-$E$ response with a linear function and solving for $E$ when $i = 0$ A.

Under 532 nm excitation, the $E_{on}$ for ITO/WS₂ is 0.25 V more negative than that of ITO/MoS₂ (Figure 5a, blue versus red traces). Since $E_{F} = E_{on} + E^0 (1/z_F)$ and the solution potential does not change during these measurements, the more negative $E_{on}$ value for WS₂ indicates that $E_F$ of WS₂ is 0.25 V more negative on the electrochemical scale than MoS₂, which is consistent with literature.58,59 Here we have assumed that the energy difference between the Fermi level and conduction band minimum is the same for both materials.59

The $E_{on}$ value of the ITO/MoS₂/WS₂ configuration under 532 nm illumination conditions lies between isolated ITO/MoS₂ and ITO/WS₂, which is in agreement with theoretical predictions that the Fermi level of the heterojunction is located between that of the isolated TMDs.58 The ITO/WS₂/MoS₂ sample contained a large fraction of exposed WS₂ triangles that contribute to the photocurrent response under these large area excitation conditions, and therefore we were unable to measure the $i$-$E$ response of pure ITO/WS₂/MoS₂ material. $i$-$E$ measurements of ITO/WS₂/MoS₂ samples that contain some isolated WS₂ indicate that $E_{on}$ is between ITO/MoS₂ and ITO/WS₂ under 532 nm illumination conditions, which further indicates that the Fermi level of the heterojunction is located between that of the isolated TMDs (see discussion in Note 6, Supporting Information).

Surprisingly, under 650 nm illumination conditions, the $E_{on}$ of ITO/WS₂/MoS₂ is nearly equivalent to ITO/MoS₂ (0.4 V in Figure 5b). This result supports the charge transport pathway shown in Figure 3l, which shows electron transfer from MoS₂ energy levels to the ITO electrode. The Fermi level of the illuminated heterojunction depends on which TMD in the heterojunction is photoexcited. In this case, the Fermi level of the heterojunction under MoS₂-selective excitation conditions is equivalent to isolated MoS₂, even though the photoexcited MoS₂ in the heterojunction is electronically and physically coupled to WS₂ (and even physically separated from the ITO electrode by WS₂). 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.58 Photoexcited majority carriers reside in conduction band energy states that are MoS₂-like rather than mixed conduction band levels, whose energy level positions are different than the isolated monolayers. This wavelength-dependent Fermi level behavior is independent of the stacking orientation of the heterojunction. The $E_{on}$ value of the ITO/MoS₂/WS₂ configuration under 650 nm illumination conditions is nearly equivalent to that of ITO/MoS₂ (Figure 5b). This observation further suggests that photogenerated carriers reside in MoS₂-like energy levels even though the TMDs are physically coupled. We conclude that $E_{on}$ and, therefore, $E_F$ of the illuminated heterojunction depend on which TMD is photoexcited.

In conclusion, we studied charge recombination and transport pathways as a function of stacking configuration and illumination conditions in MoS₂/WS₂ liquid junction photoelectrochemical cells. Photoluminescence microspectroscopy of ITO/MoS₂/WS₂ and ITO/WS₂/MoS₂ heterojunctions in air indicated efficient interlayer charge transfer, regardless of the heterojunction stacking configuration. Photoelectrochemical measurements of the same samples in iodide electrolytes showed distinct charge recombination and transport behavior. We observed a significant synergistic photocurrent enhancement effect upon exciting ITO/MoS₂/WS₂ electrodes with either 532 or 635 nm illumination. On the other hand, photoexcitation of the ITO/WS₂/MoS₂ sample with 532 nm illumination induces an interlayer recombination process, where electrons in MoS₂ recombine with holes in WS₂. This charge recombination pathway is active when both materials are photoexcited simultaneously and is mostly inactive under 635 nm illumination conditions that selectively excites MoS₂. This charge recombination pathway is significant for the development of bulk heterojunction (BH) TMD photocathodes made from randomly oriented TMD nanosheets.19,60 BH electrodes exhibit random stacking configurations throughout the film, which could give rise to varying recombination pathways that depend on the carrier generation process, as we demonstrated herein. Finally, photogenerated carriers are transported as far as 3 μm along TMDs layers to reach a heterojunction interface. Charge transport simulations show that carriers diffuse along a concentration gradient from the focused laser spot to the heterojunction edge site. 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.

### ASSOCIATED CONTENT

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.9b04209.

- Supporting Information
- Detailed experimental methods; Raman maps; comparison of charge extraction pathways in solid-state and liquid junction devices; ensemble level electrochemical data; detailed photocurrent mapping and image analysis procedures; additional photocurrent maps; absorption spectra; excitation laser profiles; charge transport simulations; detailed $i$-$E$ curve analysis (PDF)

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Notes
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