Hybrid Heterojunctions of Solution-Processed Semiconducting 2D Transition Metal Dichalcogenides

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Supporting Information

ABSTRACT: Exfoliated transition metal dichalcogenides (2D-TMDs) are attractive light-harvesting materials for large-area and inexpensive solar energy conversion given their ability to form highly tolerant heterojunctions. However, the preparation of large-area heterojunctions with these materials remains a challenge toward practical devices, and the details of photogenerated charge carrier harvesting are not well established. In this work, we use all solution-based methods to prepare large-area hybrid heterojunction films consisting of exfoliated semiconducting 2H-MoS2 flakes and a perylene-diimide (PDI) derivative. Hybrid photoelectrodes exhibited a 6-fold improvement in photocurrent compared to that of bare MoS2 or PDI films. Kelvin probe force microscopy, X-ray photoelectron spectroscopy, and transient absorption measurements of the hybrid films indicate the formation of an interfacial dipole at the MoS2/organic interface and suggest that the photogenerated holes transfer from MoS2 to the PDI. Moreover, performing the same analysis on MoSe2-based hybrid devices confirms the importance of proper valence band alignment for efficient charge transfer and photogenerated carrier collection in TMD/organic semiconductor hybrid heterojunctions.

The semiconducting transition metal dichalcogenides (TMDs) have favorable optoelectronic properties for efficient solar energy conversion and, accordingly, have been extensively investigated as promising materials in photoelectrochemical and photovoltaic devices.1 Moreover, recent advances leveraging the van der Waals (vdW) layered crystal structure of TMDs, which affords the ability of the material to be exfoliated into 2D sheets, suggest the possibility of ultrathin flexible and high-performance solar energy conversion devices.2 Indeed, single- or few-layer TMDs exhibit superior light-harvesting characteristics compared to their bulk counterparts and can mitigate the disadvantageous anisotropic electronic properties intrinsic to bulk TMDs.3,4 Using p–n heterojunctions based on only vdW interactions is particularly promising for functional photovoltaic devices as they are exceptionally tolerant to crystal lattice mismatch, affording photogenerated charge separation while enabling low interfacial trap densities.3 Accordingly, promising 2D p–n heterojunctions with various semiconducting TMDs or with other nanstructured semiconductors have been recently demonstrated on the micrometer length scale with single exfoliated TMD flakes.6,7

Considering hybrid TMD/organic semiconductor (OS) heterojunctions, the tunability of the optoelectronic properties and solution-based processability of organic OSs make them attractive candidates for inexpensive large-area photovoltaics. However, demonstration of large-area hybrid TMD/OS heterojunctions for solar energy applications remains unexplored. Moreover, the fundamental requirements for photogenerated charge separation at the hybrid TMD/OS interface have rarely been described.8–10 Thus, developing systems to facilitate the study and optimization of hybrid heterojunctions is an important goal.

In this work, we demonstrate the scalable solution processing of hybrid bilayer heterojunctions based on few-atomic-layer flakes of semiconducting MoS2 or MoSe2 together with an OS. We further scrutinize the nature of the hybrid heterojunction by a number of techniques to establish that the harvesting of photogenerated charge carriers produced by light absorption in
weak noncovalent interactions are present between MoS2 and DHA-PDI.16,17 From direct gap transitions (680 nm), bare MoS2 thin films on the TMD can be greatly enhanced if proper band alignment is present. First, we exfoliated bulk MoS2 powder in N-methylpyrrolidone11 and prepared aggregate-free films using a modified liquid–liquid-based self-assembly method.12 The few-layer flakes range in lateral dimension from ~100 to over ~500 nm and are aligned parallel with the (transparent conducting oxide) substrate surface. A functionalized perylene-diimide (PDI) was chosen as the OS given its good charge transport properties13 and planar π-conjugated core that has been shown to associate with MoS2 via vdW interactions.14 Dihexanoic acid (DHA) and the MoS2 likely result in dihydric acid-PDI hybrid bilayer electrodes.

The incident photon-to-current efficiency (IPCE) spectrum of the MoS2 electrode measured at +0.1 V vs Ag/Ag⁺ for the MoS2 and DHA-PDI electrodes, respectively, averaging over five replicate electrodes. Remarkably, the hybrid MoS2/DHA-PDI electrodes gave several times higher $J_{ph}$ (2.60 ± 0.29 mA cm⁻² at +0.1 V vs Ag/Ag⁺). We note that no significant decay in photocurrent was observed for the hybrid heterojunction electrode during chronoamperometry under intermittent illumination for the minutes times scale (see Figure S6); thus, photocorrosion reactions can be excluded as an origin of the increased photocurrent. This conclusion is further supported by the number of the Mo atoms and PDI molecules present in the electrode, which is 2–3 orders of magnitude smaller than the number of photogenerated electrons collected during the chronoamperometry measurements.

The incident photon-to-current efficiency (IPCE) spectrum of the MoS2 electrode measured at +0.1 V vs Ag/Ag⁺ (Figure 1e) exhibits the same shape as the thin-film absorption and shows that less than ~2% of the incident photons can be converted to photocurrent, corresponding to ~7% absorbed photon-to-current efficiency (APCE) at 670 nm. For the hybrid electrode, the IPCE spectrum shows a similar shape and

Figure 1. (a) Morphology of the MoS2/DHA-PDI hybrid bilayer film shown by TEM. (b) photograph of the hybrid and control film deposited on F:SnO2-coated glass substrates. (c) UV–vis absorbance spectra. (d) $J$–$V$ curves measured with an $\Gamma$/$I$⁻ redox couple under intermittent (1 sun) illumination and IPCE spectra measured at (e) +0.1 and (f) −0.35 V vs Ag/Ag⁺ of solution-processed DHA-PDI, MoS2, and MoS2/DHA-PDI hybrid bilayer electrodes.
dramatic enhancement over the whole MoS$_2$ absorption region compared to the bare MoS$_2$. The APCE at 670 nm of $\sim$37% in the hybrid film indicates significantly improved hole extraction from the MoS$_2$ to the redox couple via the DHA-PDI overlayer. The absence of a clear contribution from DHA-PDI absorption in the IPCE of the hybrid bilayer is likely caused by its relatively small light absorption, as seen in the UV−vis spectrum.

Further insight into enhanced charge carrier extraction in the hybrid film was gained from the IPCE spectra measured at $-0.35$ V vs Ag/Ag$^+$. At this potential, only a weak driving force is provided for charge separation. Therefore, without DHA-PDI, photogenerated charge carriers in the bare MoS$_2$ electrode recombine before being extracted, leading to the absence of sustained $J_{ph}$ (see the inset of Figure 1d) and an IPCE below the signal-to-noise detection limit. In the hybrid electrode, we observed an IPCE that originates from photon absorption by MoS$_2$. This suggests that DHA-PDI promotes charge extraction from MoS$_2$ in the hybrid heterojunction. We note that the shape of the hybrid electrode IPCE at $-0.35$ V is slightly different from the IPCE at +0.1 V due to the enhanced relative contribution from DHA-PDI with direct contact to the substrate.

The enhancement in photoactivity with the hybrid film was confirmed using two-electrode photovoltaic cells (Figure S7). At 1 sun illumination, short-circuit current density remarkably increased from 0.1 (MoS$_2$ only) to 0.7 mA cm$^{-2}$ for the hybrid cell, following the same trend of three-electrode photoelectrochemical results. A clear improvement in open-circuit voltage (from 25 to 80 mV) was also observed. We note that the small $V_{OC}$ could reasonably be improved by choosing a redox couple with a more positive oxidation potential, including blocking layers and optimizing the flake size and thickness. However, the drastic increase in photocurrent afforded by the hybrid film is remarkable given previously reported photoperformance of solution-processed TMD semiconductors. 

![Figure 2. Surface potential measurements. (a) False-colored topography image of MoS$_2$ nanoflakes deposited on bare glass (shaded green) and on a DHA-PDI thin film (shaded purple). The KPFM surface potential maps are given in panel (b) for the dark condition and panel (c) for the illuminated condition, as described in the main text. The average measured surface potential over the flakes for each condition is shown in (d).](http://doc.rero.ch)

![Figure 3. XPS Mo core level (a) and valence band spectra (b) of the MoS$_2$ and MoS$_2$/DHA-PDI hybrid thin films. Transient absorption (TA) spectra (c) of MoS$_2$ and MoS$_2$/DHA-PDI films recorded at different pump−probe delays; (d) temporal evolution of the normalized absorption change obtained for probe photon energies in resonance with excitonic A (674 nm) and B (611 nm) transitions.](http://doc.rero.ch)
One possible explanation for the enhancement of $J_{ph}$ could be the simple suppression of recombination due to the passivation of charge trapping sites on the MoS$_2$. Indeed, the carboxylic functionality is well-known to associate with surface species of many oxides and chalcogenides. This possibility can be addressed by exposing the bare MoS$_2$ film to hexanoic acid, which yielded no improvement (see Figure S8), suggesting that the carboxylic acid functionality does not effectively passivate recombination. Similarly, other possibilities, such as Cl$^-$ ion adsorption$^{24,25}$ or etching$^{25}$ induced by HCl used in the DHA-PDI coating process were excluded by control experiments (Figure S8).

We next employed scanning Kelvin probe force microscopy (KPFM, Figure 2) to map the surface potential of individual MoS$_2$ flakes in contact with either bare glass (green-colored flakes in Figure 2a) or DHA-PDI (purple-colored flakes) during the same scan, afforded by a specially prepared film (see the Supporting Information for a full experimental description). KPFM results acquired in air under dark and illuminated (ca. 0.1 sun) conditions are shown in Figure 2b–d. In the dark, the MoS$_2$ flakes can be clearly distinguished as they show a lower surface potential compared to that for DHA-PDI or the substrate. Under illumination, the surface potential of the MoS$_2$ on DHA-PDI decreases by 40 mV on average, while the MoS$_2$ flakes on bare glass remain approximately constant. For further comparison, a surface potential difference map (subtracting light and dark results) is shown in the Supporting Information (Figure S9).

If only defect passivation occurred at the DHA-PDI/MoS$_2$ interface, no change would be expected in the surface potential difference at these measurement conditions (i.e., in the absence of a built-in potential from conductive contacts or redox species). Instead, the observed surface potential difference between the dark and light conditions implies the accumulation of negative charges$^{24,25}$ in the 2D MoS$_2$ flakes when in contact with DHA-PDI and under illumination. This charging of the 2D flakes is consistent with either the photogenerated charge redistribution in the MoS$_2$ flakes (caused by a dipole induced at the DHA-PDI/MoS$_2$ interface and the resultant electric field that would drive photogenerated holes to the MoS$_2$/PDI interface and electrons away from the interface) or from the direct photogenerated hole transfer from MoS$_2$ flakes to the OS (leading to an accumulation of photogenerated electrons in the MoS$_2$).

To gain further insight into the MoS$_2$/DHA-PDI interface and the possible presence of an interfacial dipole, X-ray photoelectron spectroscopy (XPS) was used, and the spectra for the Mo core level and valence band are shown in Figure 3a,b. First, we note that no signal consistent with Mo=O coupling (binding energy higher than 234 eV) was observed before or after DHA-PDI deposition, consistent with the absence of covalent bonding between MoS$_2$ and DHA-PDI via carboxylic group anchoring or the oxidation of MoS$_2$. The Mo 3d peaks are found to uniformly shift 0.4 eV to lower binding energy when the DHA-PDI overlayer is present, which can be attributed to a Fermi level shift caused by chemical doping from an overlayer or to the formation of a built-in potential via interfacial dipole creation.$^{26,27}$ The absence of a clear shift in Raman spectra (Figure S5) after DHA-PDI coating indicates that any chemical doping effect is very weak. Moreover, in Figure 3b, the valence band spectra with organic coating shows a shift from 1.41 to 1.02 eV, equivalent to that observed in the core level spectrum. The consistent shift of 0.4 eV, which can be further confirmed by the S 2p spectra (see Figure S10), clearly indicates the formation of an interfacial dipole, likely a result of an equilibration of the Fermi level of the inorganic with the polaron level of the OS, as described previously in a similar hybrid system.$^{28}$ In our case, an electric field in the MoS$_2$, which would drive free holes toward the interface with the DHA-PDI layer, is reasonably present, consistent with the KPFM results.

The presence of an interfacial dipole that could promote charge separation in MoS$_2$ does not preclude the presence of charge transfer from the MoS$_2$ to DHA-PDI. To gain further insight into the charge carrier dynamics in this system, the bare and hybrid films were measured by femtosecond transient absorption (TA) spectroscopy. The absorption change upon pumping at 600 nm was probed at different times up to 1 ns after photoexcitation. The resulting TA spectra for selected time delays are shown in Figure 3c. The complete results and detailed interpretation of the TA spectra are described in the Supporting Information (section 5, Figures S13 and S14). In brief, similar to a previous report,$^{27}$ we observe for both MoS$_2$ and MoS$_2$/DHA-PDI films negative photobleaching bands from the excitonic states B and A of MoS$_2$ at 0.1 ps (centered at 611 and 674 nm, respectively), which decay rapidly (in 300 ps) together with blue shifts to 589 and 647 nm, respectively, owing to the formation of free charge carriers at the direct band edges.$^{29}$ The presence of free carriers at the direct band edges results in positive photoinduced absorption signatures at long times, which decay with identical time constants as the corresponding photobleaching signature of free charges. As noted in previous work, the photoinduced absorption signatures coincide with wavelengths of the excitonic transitions, allowing quantification of both exciton (short time) and free charge carrier concentration (longer time) using the signal at 674 nm.

Comparing the TA spectra of the MoS$_2$ and MoS$_2$/DHA-PDI films measured with equivalent pump fluence ($\sim$1 μJ cm$^{-2}$), the identical features noted at all time delays (Figure 3c) indicate that the TA signatures of MoS$_2$ were not significantly perturbed by DHA-PDI (the TA signals for DHA-PDI at the pump wavelength are significantly smaller, see Figure S15). Therefore, a similar number of absorbed photons and initial excitations was generated in both films. However, the TA signal of the hybrid film consists of a smaller amplitude of the photobleaching signals from the excitonic states recorded at early time delays ($t = 0.1$ ps) and a higher amplitude of the free charge signatures at $t = 300$ ps compared to those of the MoS$_2$ bare film. The presence of additional long-lived free carriers at the direct band edges in the hybrid film was confirmed by the normalized temporal evolution of the TA signals probed at 674 and 611 nm (Figure 3d). Further TA measurements with different initial carrier densities (see Figure S16 with increasing excitation fluence to 2 μJ cm$^{-2}$) or with higher pump photon energy (3 eV) followed the same trend.

The greater free charge carrier concentration in the direct bands in the MoS$_2$/DHA-PDI film implied by the TA results can be rationalized by an increased photogenerated charge carrier separation, which reduces recombination in the PEC measurement. However, this effect could be due to either the interfacial dipole-induced charge separation or hole transfer from the MoS$_2$ to the organic due to exciton splitting at the hybrid junction. We note that because the dynamics of the exciton decay on the few-picosecond time scale are very similar in both case (see Figure S17), the smaller initial concentration of excitons observed after 0.1 ps in the hybrid films could...
possibly suggest that the additional free charge generation in MoS\(_2\) in the presence of DHA-PDI occurs faster than our experimental time resolution (<100 fs). Unfortunately, further insight into the possibility of ultrafast charge transfer to organic was not possible due to the weak TA signal from DHA-PDI, which overlaps with the signal from MoS\(_2\). Lastly, other possible explanations for the smaller initial exciton concentration in the hybrid film, such as excitation (resonance) energy transfer from the MoS\(_2\) to the PDI, can be excluded based on the energy levels.

Because the TA results cannot unambiguously corroborate photogenerated hole transfer from the MoS\(_2\) to the PDI, we next hypothesized that interfacial hole transfer would depend on the relative valence band positions of the TMD. To investigate this factor, we fabricated a bilayer film based on the selenium TMD (i.e., MoSe\(_2\)/DHA-PDI), given that the valence band edge level of MoSe\(_2\) is \(\sim 0.5\) V higher in energy than that in MoS\(_2\).\(^{30,31}\) Due to the similar crystal structures of MoS\(_2\) and MoSe\(_2\), the fabrication of MoSe\(_2\) and MoSe\(_2\)/DHA-PDI bilayer films by the same experimental methods and obtaining comparable morphology and similar flake size and thickness (ca. 10 nm) were possible.

Similar to the MoS\(_2\)/DHA-PDI film, the XPS spectra of the MoSe\(_2\)/DHA-PDI bilayer thin film (Figure 4a,b) show an equivalent shift of 0.3 eV for both the Mo 3d core level and valence band level compared to bare MoSe\(_2\), indicating the presence of an interfacial dipole. The \(J\)–\(V\) curves (Figure 4c) from the photoelectrochemical measurements show similar photocurrent for the bare MoSe\(_2\) compared to that for MoS\(_2\). A higher dark current is likely a result of higher catalytic activity of defects and edge sites on MoSe\(_2\) flakes.\(^{32}\) However, the PEC behavior in the MoSe\(_2\)/DHA-PDI hybrid photoelectrodes was in stark contrast to that of the MoS\(_2\)-based hybrid electrodes. The photocurrent increased only slightly from 0.21 ± 0.03 (MoSe\(_2\) only) to 0.37 ± 0.09 mA cm\(^{-2}\) (MoSe\(_2\)/DHA-PDI) at +0.1 V vs Ag/Ag\(^+\) (average over five electrodes). Moreover, the TA spectra for the B exciton of the MoSe\(_2\) and hybrid bilayer films (Figure 4d) does not indicate significant change in the TA spectra at 0.1 ps (mainly excitonic transitions) or at 300 ps (long-lived free carriers). In addition, the normalized temporal decay of the B exciton (Figure 4d inset) is identical for the bare and hybrid films. These TA results are consistent with the insignificant photocurrent increase observed for the hybrid electrodes in the photoelectrochemical measurements.

Overall, the results with MoSe\(_2\) help to complete a clear picture of the important factors leading to the enhanced photocurrent in the MoS\(_2\)/DHA-PDI films. From the XPS spectra for MoS\(_2\) and MoSe\(_2\), DHA-PDI coating on both TMDs creates an interfacial dipole, thus implying band bending in the TMD at the hybrid interface. Such band bending potentially provides a driving force for charge separation within the TMD layer. However, the effect of the dipole-induced band bending on the photocurrent is likely limited, given the insignificant photoactivity improvement observed for the MoSe\(_2\)/DHA-PDI hybrid electrode despite the similar magnitude of band bending shown by XPS (0.4 and 0.3 eV for MoS\(_2\) and MoSe\(_2\), respectively). Because the improvement in \(J_{ph}\) is considerably smaller than that using MoS\(_2\), we can also conclusively eliminate the possibility that the observed improvement of the MoS\(_2\) hybrid electrodes was only a result of defect passivation or surface polarization. Instead, the distinct photoelectrochemical performance can be attributed to a difference in band alignment. Indeed, the red-shifted excitonic energy in the UV–vis spectrum (Figure S11) of MoSe\(_2\) compared to that of MoS\(_2\) suggests a narrower direct band...
defect-poor planar surface of solvent-assisted exfoliated TMDs. The density of the edge sites for MoS$_2$ and MoSe$_2$ is likely similar. Given that of MoS$_2$ (see Figure S12, Supporting Information). Indeed, the identical excited-state dynamics in MoSe$_2$ with and without an overlayer shown by the TA measurement support the conclusion that the DHA-PDI plays a role. The density and energy of surface states at the edges are however important to consider. Indeed, the edge sites, where transition metal atoms are exposed, are known to be trap sites that cause severe recombination in TMDs. We cannot exclude hole transfer from the indirect valence band given by the decreased dark current of the MoSe$_2$ hybrid electrode, or (3) the interfacial dipole created at the MoSe$_2$/DHA-PDI interface providing a slight advantage for charge extraction directly from the MoSe$_2$ to the electrolyte. On the other hand, type-II heterojunction formation with MoS$_2$ and DHA-PDI is likely afforded by the deeper-lying valence band of MoS$_2$. Such a junction would favor the transfer of photogenerated holes in MoS$_2$ to DHA-PDI, reducing charge carrier recombination and resulting in increased $J_{ph}$. We note that, while we observed hole transfer from the direct excited states, we cannot exclude hole transfer from the indirect valence band states (as illustrated in Figure 5a).

For MoSe$_2$, the higher-lying valence band edge likely results in a barrier for hole transfer at the interface between MoSe$_2$ and DHA-PDI. Indeed, the identical excited-state dynamics in MoSe$_2$ with and without an overlayer shown by the TA measurement support the conclusion that the DHA-PDI overlayer does not promote charge separation in MoSe$_2$. The small increase in $J_{ph}$ observed in the MoSe$_2$/DHA-PDI film can be attributed to the following: (1) light absorption by DHA-PDI and electron injection into the substrates (either directly or through the conduction band of MoSe$_2$), (2) reduced recombination at the exposed substrate/electrolyte interface given by the decreased dark current of the MoSe$_2$ hybrid electrode, or (3) the interfacial dipole created at the MoSe$_2$/DHA-PDI interface providing a slight advantage for charge extraction directly from the MoSe$_2$ to the electrolyte. On the other hand, type-II heterojunction formation with MoS$_2$ and DHA-PDI is likely afforded by the deeper-lying valence band of MoS$_2$. Such a junction would favor the transfer of photogenerated holes in MoS$_2$ to DHA-PDI, reducing charge carrier recombination and resulting in increased $J_{ph}$. We note that, while we observed hole transfer from the direct excited states, we cannot exclude hole transfer from the indirect valence band states (as illustrated in Figure 5a).

In summary, we exclusively use solution-based fabrication to prepare hybrid thin films consisting of 2D semiconducting TMD flakes and a functionalized PDI. Investigations of MoS$_2$- and MoSe$_2$-based hybrid electrodes reveal interfacial dipole formation at the TMD/organic interface; however, this alone is insufficient to afford increased charge extraction from the TMD flakes. On the other hand, our results suggest that proper band alignment at the TMD-based inorganic–organic heterojunction is crucial to afford efficient charge separation and improved photon harvesting. This demonstration, for the first time, presents evidence for efficient charge separation (quantum efficiency up to 37%) from liquid-exfoliated semiconducting 2D MoS$_2$ at a hybrid heterojunction with an OS and suggests possibilities for new applications of semiconducting 2D TMDs in inorganic–organic hybrid systems. While the quantum efficiency of the hybrid films reported here is not far from that of other optimized colloidal nanoparticle/OS hybrid heterojunctions (which typically give quantum efficiency in the 40–50% range), the performance is certainly inferior to single-crystal-based solar energy conversion devices or even optimized bulk heterojunction organic photovoltaics. However, facile preparation of the ultrathin TMD-based devices by solution-based processing shown herein and the known robustness of TMDs make these materials attractive candidates for inexpensive, large-area, and stable solar energy conversion devices. Moreover, the hybrid approach provides advantages such as facile functionalization and energy level tuning of the OSs, which allow alternate routes for device performance optimization and the possibility to employ these heterojunctions in diverse applications. For example, a functional group on the OS could graft a water oxidation catalyst, potentially enabling MoS$_2$ as a light absorber for the solar oxygen evolution reaction. We note that further optimization of the layer thicknesses and study of the defects, edge sites, and the effect of the orientation of the OS at the heterojunction interface will likely lead to insight into the limitations of charge transfer and recombination. These are points of interest for future work to improve the performance of these systems. Overall, the continued development of TMD–organic hybrid heterojunction-based devices, together with our demonstration of the facile solution-based processing, will make these hybrid systems promising for global-scale solar energy conversion.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.6b00707.

Detailed methods regarding electrode fabrication and characterization setup and parameters, PDI derivatives’ synthesis and characterization, additional electron microscopy and morphology analysis of MoS$_2$ and MoSe$_2$.
hybrid electrodes, Raman spectra, two-electrode cells, $J$–$V$ curves for control experiments, additional XPS spectra, UV–vis absorption spectra for MoSe$_2$-based films, additional TA spectra, and detailed TA spectra interpretation (PDF)

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**Notes**

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8


