Engineering Chemically Exfoliated Large-Area Two-Dimensional MoS$_2$ Nanolayers with Porphyrins for Improved Light Harvesting


Molybdenum disulfide (MoS$_2$) is a promising candidate for electronic and optoelectronic applications. However, its application in light harvesting has been limited in part due to crystal defects, often related to small crystallite sizes, which diminish charge separation and transfer. Here we demonstrate a surface-engineering strategy for 2D MoS$_2$ to improve its photoelectrochemical properties. Chemically exfoliated large-area MoS$_2$ thin films were interfaced with eight molecules from three porphyrin families: zinc(II)-, gallium(III)-, iron(III)-centered, and metal-free protoporphyrin IX (ZnP, GaP, FeP, H$_2$P); metal-free and zinc(II) tetrapropylporphyrin (H$_2$TPP, ZnTPP); and metal-free and zinc(II) tetraphenylporphyrin (H$_2$T$_4$, ZnT$_4$); and metal-free and zinc(II) tetraphenylporphyrin (H$_2$T$_4$, ZnT$_4$); and metal-free and zinc(II) tetraphenylporphyrin (H$_2$T$_4$, ZnT$_4$); and metal-free and zinc(II) tetraphenylporphyrin (H$_2$T$_4$, ZnT$_4$); and metal-free and zinc(II) tetraphenylporphyrin (H$_2$T$_4$, ZnT$_4$); and metal-free and zinc(II) tetraphenylporphyrin (H$_2$T$_4$, ZnT$_4$). We found that the photocurrents from MoS$_2$ films under visible-light illumination are strongly dependent on the interfacial molecules and that the photocurrent enhancement is closely correlated with the highest occupied molecular orbital (HOMO) levels of the porphyrins, which suppress the recombination of electron–hole pairs in the photoexcited MoS$_2$ films. A maximum tenfold increase was observed for MoS$_2$ functionalized with ZnP compared with pristine MoS$_2$ films, whereas ZnT$_4$-functionalized MoS$_2$ demonstrated small increases in photocurrent. The application of bias voltage on MoS$_2$ films can further promote photocurrent enhancements and control current directions. Our results suggest a facile route to render 2D MoS$_2$ films useful for potential high-performance light-harvesting applications.

1. Introduction

Layered transition-metal dichalcogenide (TMDC) materials have received much attention, due to the accessibility of atomically thin layers and unique layer-number-dependent physical properties.[1] For example, molybdenum disulfide (MoS$_2$) transitions from an indirect bandgap semiconductor in the bulk phase to a direct bandgap semiconductor as monolayer sheets, with strong photoluminescence (PL) centered at around 1.88 eV.[1a] This atomically thin semiconductor demonstrates a high in-plane carrier mobility and on/off ratio,[2] which are critical in nanoelectronics and optoelectronics.[1a,2]

MoS$_2$ also has been explored as a promising photoelectrode material in photoelectrochemical (PEC) cells.[3] Their good stability against photo-damage[4] and wide range of visible absorption render MoS$_2$ useful as photoanodes.[5] Given the cost-effectiveness and excellent electrocatalytic properties of MoS$_2$, it has been explored as an additive agent for counter electrodes in dye-sensitized solar cells (DSSCs).[6] An atomically thin layer of MoS$_2$ coated on the counter electrode considerably enhanced the overall performance of DSSCs.[7] MoS$_2$ may also be exploited as a catalyst for the hydrogen-evolution reaction (HER),[8] in which sulfur vacancies from optimized 2H-MoS$_2$ monolayers can serve as catalytic sites.[9]

Despite the advantages of MoS$_2$, there are several challenges in utilizing MoS$_2$ in PEC or other solar-energy harvesting applications. Large-area two-dimensional (2D) MoS$_2$ films are desirable, but their preparation is challenging. Chhowalla and co-workers addressed this issue recently, to considerable extent, by introducing Li-ion intercalation followed by forced hydration.[7] The exfoliated MoS$_2$ flakes in aqueous solution were then deposited on a membrane that was transferred to indium tin oxide (ITO)-coated glasses to form active working electrodes after appropriate thermal annealing.[4b,8] This approach shows the potential to create large-area 2D materials in a cost-effective manner.[9]

Although large-area fabrication is now possible, several other issues still remain to be addressed, such as nonradiative recombination and suppression of charge transfer due to the small crystallites and crystal defects.[4b,10] To overcome these
issues, the environmental sensitivity of MoS$_2$ may be exploited. Several recent studies reported that the surface functionalization of MoS$_2$ can dramatically modulate the optoelectronic, electrochemical, and catalytic properties.$^{[6,10]}$ For example, molecular oxygen or p-type doping chemicals (e.g., 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane or F4TCNQ) can withdraw electrons from n-type semiconducting MoS$_2$. This can lead to suppression of nonradiative recombination and, therefore, a drastic enhancement in the PL emission quantum yield.$^{[10-12]}$ Thus, the MoS$_2$ surface could be engineered to improve its physical properties to promote charge separation and transfer. Conversely, the environmental sensitivity of MoS$_2$ nanolayers requires surface protection and treatments, which may otherwise result in unwanted or poor performance when the materials are integrated into devices.

Herein, we demonstrate interfacial molecular engineering of large-area 2D MoS$_2$ films to enhance their photoelectrochemical properties (see Figure 1a). This study aims to develop a facile method for engineering MoS$_2$ nanolayers with porphyrin molecules to improve light-harvesting characteristics and to elucidate the underlying mechanisms. In particular, eight molecules from three porphyrin families were examined: zinc(II)-, iron(III)-, gallium(III)-centered, and metal-free protoporphyrin IX (ZnPP, FePP, GaPP, H$_2$PP); metal-free and zinc(II)-centered tetra(N-methyl-4-pyridyl)porphyrins (H$_2$TPP, ZnTPP). These porphyrin molecules were physically adsorbed onto large-area ($\approx 1$ cm$^2$) 2D MoS$_2$ films that had an average thickness of 2.8 nm. The functionalized MoS$_2$ films were then examined by using atomic force microscopy (AFM), micro-Raman spectroscopy, and photoelectrochemistry.

We observed that the currents generated under light illumination closely follow the absorption signature of MoS$_2$, which indicated that the photocurrent originates from thin layers of MoS$_2$ and that the current is an order of magnitude greater than in the bulk phase. We found that the photocurrent is greatly dependent upon the porphyrin molecules at the interface. For example, ZnPP demonstrated a maximum tenfold increase in photocurrent, whereas H$_2$T4 and ZnTPP do not alter the MoS$_2$ photocurrent significantly. We conclude that the photocurrent enhancements are closely correlated with the highest occupied molecular orbital (HOMO) levels of the interfacial porphyrin molecules. Higher photocurrent enhancements were observed for MoS$_2$ films functionalized with porphyrins with a higher HOMO level. The photocurrent can be further engineered by varying the bias voltage such that positive (negative) bias voltage enhancements (suppresses) the photocurrent. These findings could form the basis for atomically thin MoS$_2$ for PEC conversion.

Experimental Section

Materials and Processing Procedures

Crystalline MoS$_2$ powder (0.3 g, Alfa Aesar) was placed into a three-neck flask before sealing and purging with nitrogen. Butyllithium solution (1.6 M) in hexane (3 mL, Sigma–Aldrich) was then injected into the flask by using a syringe pre-wetted with hexane. The intercalation of lithium ions into MoS$_2$ was achieved after 48 h. With positive nitrogen pressure, a second three-neck flask with a glass frit was connected to the previous flask. The glass frit had a medium pore size of 10–15 µm, which should filter all Li$_x$MoS$_2$ flakes. The flakes were collected onto the frit from the solvent by flipping the entire setup. A positive nitrogen pressure was applied to the first flask with the second flask kept under vacuum, so that all liquid passed through and left the Li$_x$MoS$_2$ on the frit. To remove excess butyllithium, the Li$_x$MoS$_2$ was washed with dry hexane (60 mL). Exfoliation was achieved by immersing the Li$_x$MoS$_2$ in water and applying tip-sonication at 5 W for 1 h, which resulted in a dark black mixture. The Li$_x$MoS$_2$ was exfoliated into single- and

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Figure 1. a) Schematic of a MoS$_2$-based photoelectrochemical cell. Chemically exfoliated solution-processed MoS$_2$ flakes were deposited on the ITO substrate and used as the working electrode (WE), with Pt used as the counter electrode (CE); 10 mM ascorbate was used as the electrolyte. Eight molecules from three porphyrin families were examined for their ability to improve the light-harvesting properties of MoS$_2$ in this study: MT$_4$ (tetra(N-methyl-4-pyridyl)porphines; $M = H_2$ and Zn$^{II}$), MTPP (tetraphenylporphyrins; $M = H_2$ and Zn$^{II}$), and MPP (protoporphyrin IX; $M = H_2$, Zn$^{II}$, Fe$^{III}$, and Ga$^{III}$). b) Representative AFM image of a MoS$_2$ film deposited on a silicon wafer and height profiles along the lines of corresponding colors. c) Histogram of the film thickness measured from three random areas of three different MoS$_2$ samples, which indicates that the average thickness of the MoS$_2$ films is $\approx 2.8$ nm.

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few-layers by forced hydration generated by the Li ions interacting with water. The mixture was centrifuged at 5000 rpm for 20 min to remove unexfoliated materials. A stable colloidal green-black suspension was obtained at a concentration of \( \approx 0.3 \text{ mg mL}^{-1} \). The nitrogen-purged solution can be stored in a refrigerator for months.

The deposition of thin MoS\(_2\) films was carried out by using a vacuum filtration process. This process involved the filtration of suspended MoS\(_2\) solution through a polycarbonate membrane (Fisher Scientific) with a pore size of 50 nm. The low-strength vacuum was created by using a water aspirator.\(^{[13]}\) The exfoliated MoS\(_2\) solution was diluted in deionized water (\( \sim 0.03 \text{ mg mL}^{-1} \)) to help achieve uniform deposition. The liquid passed through the pores and MoS\(_2\) flakes were collected on the membrane surface. As the flakes gathered around a pore, the flow rate decreased at that region and accelerated in uncovered area. This process was self-regulating and provided a uniformly deposited MoS\(_2\) film with a controlled thickness by varying the amount of MoS\(_2\) flakes in the suspension.\(^{[14]}\) To transfer the film onto an ITO glass with \( \sim 70–100 \Omega \text{ cm} \) or a silicon wafer, the MoS\(_2\) film on the filter membrane was placed on the substrates, with the MoS\(_2\) film placed against the substrate. By wetting the membrane with water, potential air bubbles could be driven away, which provided better contact between the film and the substrate. The polycarbonate membrane was then completely dissolved in chloroform, which left the MoS\(_2\) film attached to the substrate. By forcing hydration generated by the Li ions interacting with water. The mixture was centrifuged at 5000 rpm for 20 min to remove unexfoliated materials. A stable colloidal green-black suspension was obtained at a concentration of \( \approx 0.3 \text{ mg mL}^{-1} \). The nitrogen-purged solution can be stored in a refrigerator for months.

Porphyrid Functionalization

ZnPP, FePP, GaPP, and H\(_2\)PP powders (Frontier Scientific) were solubilized in dimethyl sulfoxide (DMSO), whereas ZnT4 and H\(_2\)T4 (Frontier Scientific) were dissolved in deionized water for functionalization. The solvent for ZnTPP and H\(_2\)TPP (Sigma–Aldrich) was chloroform. To allow the porphyrins to adsorb physically onto the MoS\(_2\) nanolayers, the MoS\(_2\) films were immersed in 10 \( \mu \text{m} \) porphyrin solutions for 15 min, followed by rinsing with the respective solvents to remove unbound and weakly bound porphyrins.

Characterization and Instrumentation

A Perkin–Elmer Lambda 950 UV/Vis/near-IR spectrophotometer was used to record the absorption spectra of the MoS\(_2\) films deposited on ITO/glass slides. The film samples used for PL, Raman, and AFM measurements were deposited onto silicon wafers. PL and Raman spectra were recorded under ambient conditions by using an inVia Renishaw confocal Raman microscope with laser excitation at \( \lambda = 633 \text{ nm} \).

Photoelectrochemical measurements were carried out by using a Princeton 263A galvanostat with a 150 W Xenon lamp. A long-pass filter (\( > 400 \text{ nm} \), Thorlabs) and a short-pass filter (\( < 710 \text{ nm} \), Thorlabs) were used to maintain the irradiation in the entire visible range at 110 mW over the entire film area. A PEC cell was custom-built with the MoS\(_2\)-deposited ITO as the working electrode and a platinum-coated glass as the counter electrode. The reference electrode was short-circuited with the counter electrode. For bias-voltage experiments, a solid silver wire was used as the reference electrode. For the spectrally resolved photocurrent measurements, the MoS\(_2\) films were irradiated by using the same lamp equipped with an Oriel 1/8 m monochromator and a 360 nm blaze grating. The electrolyte in all our PEC measurements was 10 mM ascorbate in deionized water (pH 3).

2. Results and Discussion

2.1. Chemically Exfoliated Solution-Processed MoS\(_2\) Nanolayers

Lithium ion intercalation assisted exfoliation of the MoS\(_2\) crystal powder can produce single- and few-layers flakes with a typical size of several hundred nanometers. After a filtration-based deposition to form films 1 cm in diameter, chemically exfoliated MoS\(_2\) flakes remained in their 1T metallic phase.\(^{[7]}\) As a result, no distinct excitonic features were observed for the MoS\(_2\) films, as shown in the absorption spectrum in Figure 2a.\(^{[7]}\) High-temperature thermal annealing (280 °C) is critical.
in film preparation because it converts MoS$_2$ flakes from the 1T metallic phase to a 2H semiconductor. After annealing, two distinct band structures emerged in the absorption spectrum, which were assigned as A and B interband excitonic transitions at the K point of Brillouin zone.$^{[15]}$ The A and B features are at approximately $\lambda = 660$ (1.88 eV) and 612 nm (2.03 eV), whereas the most dominant absorption appears at $\lambda \approx 430$ nm.$^{[14,16]}$

Figure 2b shows the effect of thermal annealing on the PL spectra of the MoS$_2$ film. PL emission is barely observed before annealing because of the metallic crystal structure in the 1T phase. The high-temperature annealing not only restores the 2H phase from the 1T phase but also reduces crystal defects, which results in significant PL enhancement.$^{[7]}$ Due to the chosen excitation wavelength at $\lambda = 633$ nm, we observed the transition of exciton A only from the thin MoS$_2$ film at approximately $\lambda = 660$ nm.$^{[1b]}$ The sharp peak at $\lambda \approx 654$ nm is the Raman signature of the silicon wafer ($\approx 520 \text{ cm}^{-1}$), whereas the less prominent features from $\lambda = 648$ to 650 nm are the Raman modes of MoS$_2$ (from 380 to 405 cm$^{-1}$).$^{[17]}$

Photocurrent measurements of a MoS$_2$ film before and after thermal annealing, along with bulk MoS$_2$, are shown in Figure 2c. The MoS$_2$ films before and after annealing were prepared from the chemically exfoliated MoS$_2$ flake solution, whereas the bulk MoS$_2$ sample was deposited onto the ITO from briefly sonicated MoS$_2$ powder (i.e. no Li-intercalation-based exfoliation process). Thus, the bulk MoS$_2$ sample should have retained its semiconducting properties with an indirect bandgap. Positive short-circuit currents were observed for all MoS$_2$ films under visible-light illumination ($\lambda = 400$–710 nm), in which the electrons were collected at the working electrode (i.e. MoS$_2$-deposited ITO anode). The holes, created by electron injection from MoS$_2$ to the ITO, were reduced by oxidation of the electrolyte:

$$\text{ascorbate} \rightarrow \text{dehydroascorbate} + 2e^- + 2H^+ \quad (1)$$

The oxidized electrolyte (dehydroascorbate) diffuses to the counter electrode (Pt cathode) and becomes reduced to its initial form. As shown in Figure 2c, the annealed MoS$_2$ film demonstrates a clear response to light irradiation and a maximum photocurrent of approximately 0.12 $\mu$A was observed. Under identical conditions, bulk MoS$_2$ exhibited photocurrent responses that were an order of magnitude weaker at approximately 0.01 $\mu$A, whereas as-deposited thin MoS$_2$ film in metallic 1T phase did not generate stable photocurrents, as anticipated.$^{[1b,4c,18]}$

### 2.2. Porphyrin-Functionalized MoS$_2$ Films

MoS$_2$ thin films were functionalized with porphyrin molecules and their properties were compared with those of pristine MoS$_2$ films. Figure 3a shows the absorption spectra of the MoS$_2$ film before and after ZnT4 adsorption. The porphyrin-functionalized MoS$_2$ mostly follows the absorption features of the pristine film, but a minor change is observed at approximately $\lambda = 450$ nm, which corresponds to the Soret band (singlet-state transition from $S_0$ to $S_1$ of ZnT4).$^{[19]}$ Porphyrin molecules have strong optical absorption in the Soret ($\lambda = 400$–450 nm) and Q ($S_0 \rightarrow S_1; \lambda = 550$–650 nm) bands due to their electron-rich systems, and the transition energies depend strongly on the presence and type of core metal ions (Figure S1 in the Supporting Information).$^{[20]}$ The weak Soret and Q-band signatures, compared with MoS$_2$ absorption, suggest that the amount of adsorbed porphyrins is minimal.

To examine the porphyrin adsorption further, we raster-scanned PL spectra from an area of the MoS$_2$ film (20 $\times$ 20 $\mu$m$^2$) before and after ZnT4 functionalization by using $\lambda = 633$ nm excitation. The PL emission at $\lambda = 660$ nm was used to reconstruct a 2D image of the pristine MoS$_2$ film (Figure 3b, left), which exhibited near-uniform emission properties. Compared with the pristine film, there was a drastic PL enhancement across the entire area after ZnT4 functionalization (Figure 3b, right). Here, the PL measurements were performed on exactly the same spot before and after porphyrin adsorption, and both the 2D PL maps were reconstructed on the same intensity scale. To verify the porphyrin functionalization further, only
part of the film was immersed in a porphyrin solution, and a PL map was recorded that spanned both pristine and functionalized domains (Figure S8). A stark difference in PL intensity was observed between the pristine and functionalized regions, which confirmed the porphyrin adsorption. Porphyrin molecules, including ZnT4, exhibit strong emission properties after photoexcitation; they emit fluorescence through singlet-state transitions ($S_1 \rightarrow S_0$) or phosphorescence after intersystem crossing ($T \rightarrow S_0$) or both.\cite{20a} Porphyrins such as FePP do not display strong emission due to efficient nonradiative decay through the d orbital of the core metal ion.\cite{21} ZnT4 shows strong fluorescence emission from $\lambda = 600$ to 700 nm after excitation (Figure S1).\cite{22} Therefore, the PL intensity increase shown in Figure 3b is attributed to the ZnT4 porphyrins, and indicates their adsorption on the MoS$_2$ film. From the absorption and PL emission results in Figure 3, we concluded that MoS$_2$ films are functionalized with porphyrins.

To elucidate the nature of the MoS$_2$–porphyrin interaction, we examined the Raman spectra of MoS$_2$ nanolayers before and after porphyrin functionalization (in this case, FePP). We found that there were no significant changes in the MoS$_2$ signatures ($A_{1g}$ and $E_{2g}$) before and after functionalization with the porphyrins. This observation suggests that porphyrin molecules do not form chemical bonds with 2D MoS$_2$; rather, they interact with MoS$_2$ through physisorption. Additionally, a recent study revealed that organometallic compounds adsorbed on TMDC nanolayers demonstrate consistent X-ray photoelectron spectroscopy (XPS) features regardless of the adsorption.\cite{11b} Our results strongly suggest that metalloporphyrins physically adsorb on the MoS$_2$ nanolayers instead of forming chemical bonds.

Absorption spectra and 2D PL maps were also recorded with ZnPP, FePP, and ZnTPP (Figures S2–4), which together clearly show the adsorption of the porphyrins on MoS$_2$ films. For the MoS$_2$ films with and without ZnPP (Figure S2a) and FePP (Figure S3a), no apparent changes were observed in the absorption spectra, whereas ZnPP PL emission was evident on the MoS$_2$. Although FePP on MoS$_2$ does not display any PL signature due to its nonradiative decay mechanism, the film shows a strong photocurrent enhancement (see below). Given the similar molecular structures, ZnPP and FePP should have comparable surface coverage on MoS$_2$. Compared with ZnPP and FePP, the signatures of the adsorbed ZnTPP molecules appear to be more prominent in both the absorption spectrum and the PL map (Figure S4). Additionally, we measured the 2D PL map of the as-deposited MoS$_2$ functionalized with ZnPP. Given that the unannealed MoS$_2$ sample is non-emissive due to its metallic 1T phase (Figure 2b), the PL emission clearly shows the attachment of ZnPP (Figure S5).

The effects of porphyrin functionalization on the photocurrents are presented in Figure 4. Figure 4a shows that the photocurrent of the MoS$_2$ film functionalized with ZnPP increases by nearly an order of magnitude from 0.14 to 1.1 $\mu$A, compared with the pristine film, under visible-light illumination. The photocurrent of the MoS$_2$–ZnPP was also measured as a function of irradiation intensity, and demonstrated a monotonic increase with increasing intensity, as expected (Figure S9). To elucidate the origin of the photocurrent enhancement, the corresponding action spectra were collected, and are shown in Figure 4b. Here, the photocurrents of pristine MoS$_2$ and MoS$_2$–ZnPP films were measured from $\lambda = 350$ to 800 nm with increments of 25 nm, which were then compared with the absorption spectrum of a pristine MoS$_2$ film. It should be noted that the MoS$_2$ film in the photocurrent action spectra measurement was thicker than other MoS$_2$ samples; because the light power after the monochromator was significantly lower at each wave-
length, a greater amount of MoS$_2$ flakes was used to obtain sufficient photocurrent. The photocurrents of both MoS$_2$ and MoS$_2$-ZnPP films generally follow the absorption spectrum. Notably, the photocurrent of MoS$_2$-ZnPP at each measured wavelength is two times greater than that of the pristine film. This observation indicates that the adsorbed porphyrin molecules facilitate charge separation after photoexcitation and suppress recombination in MoS$_2$, which thus enhances photocurrent generation throughout the visible range. From the photocurrent of the MoS$_2$-ZnPP film, we estimate that the incident photon-to-current efficiency (IPCE) at $\lambda = 425$ nm is approximately 1%.

A closer examination revealed several important details in the action spectra. Although the photocurrent from $\lambda = 550$ to 700 nm generally follows the A and B excitonic features, the photocurrent is not as prominent as the absorption. In comparison, the photocurrent from $\lambda = 350$ to 500 nm matches the C exciton feature closely, which suggests that the charge separation and recombination suppression in the MoS$_2$ film by interfacial porphyrins are more efficient in high-energy excitons. Another interesting feature is the small, yet distinct, absorption peak at approximately $\lambda = 425$ nm that corresponds to the Soret band of ZnPP. The sharp increase in photocurrent at the Soret band may result from the charge-transfer process from the photoexcited ZnPP to the conduction band of MoS$_2$. These results indicate that the adsorbed porphyrins could contribute as photosensitizers although their contributions to the entire photocurrent are very modest. The majority of the photocurrent originating from MoS$_2$ and porphyrins helps separate the photogenerated charge and collect photocurrent. Otherwise, the photocurrent would mostly follow the absorption features of the porphyrins rather than MoS$_2$, which was observed previously with porphyrin–carbon nanotube hybrids.$^{[20a]}$ Finally, the relative amount of MoS$_2$ flakes (i.e. thickness of the film) and adsorbed porphyrins is critical in determining photocurrent outputs, as seen in Figure 4. Given that porphyrins adsorb on the MoS$_2$ surface, the degree of photocurrent increase would not be strongly dependent upon the thickness of MoS$_2$ films. The thin MoS$_2$-ZnPP film ($\approx 1.8$ $\mu$m of MoS$_2$ flakes) generated a nearly tenfold increase compared with pristine MoS$_2$ (Figure 4a), whereas the thick film ($\approx 18$ $\mu$m of MoS$_2$ flakes) produced a twofold enhancement (Figure 4b). In a thicker film, the separated charges have a greater probability of recombination before reaching the ITO electrode.

2.3. Interfacial Charge-Transfer Mechanism

In addition to ZnPP, seven other porphyrin species (H$_2$T$_4$, ZnT$_4$, ZnTPP, H$_2$T$_4$PP, GaPP, H$_2$PP, and FePP; see Figure 1 for molecular structures) were explored for their ability to enhance the photocurrent of MoS$_2$ under identical experimental conditions. Here we define the photocurrent enhancement, or $(I-I_o)/I_o$, as the change in photocurrent after porphyrin functionalization over the initial photocurrent of pristine MoS$_2$ film ($I_o$). This photocurrent enhancement is presented as a function of the HOMO level of each porphyrin species in Figure 5a.$^{[23]}$ All the detailed photocurrent measurements can be found in Figure S6. The porphyrin species show a wide range of enhancement activities. Although ZnPP demonstrates an increase of nearly an order of magnitude, there were no significant changes in the measured photocurrent after adsorption of H$_2$T$_4$ and ZnTPP. Both ZnT$_4$ and H$_2$T$_4$PP exhibited an approximately 100% enhancement in the photocurrent (i.e. a twofold increase in photocurrent). The MoS$_2$ films functionalized with GaPP and H$_2$PP showed almost the same photocurrent enhancement, whereas FePP and ZnPP improved the photocurrent generation in MoS$_2$ films by approximately 500 and 800%, respectively. The lack of enhancement with H$_2$T$_4$ and ZnTPP is not due to the inefficiency of porphyrin functionalization, as discussed earlier. A porphyrin emission was observed for all.

Figure 5. a) Photocurrent enhancement of MoS$_2$ films functionalized with various porphyrin species. The photocurrent enhancement or $(I-I_o)/I_o$ is defined as the change in photocurrent before and after porphyrin adsorption over the initial photocurrent of pristine MoS$_2$. The photocurrent enhancement is strongly correlated with the HOMO level of the porphyrin. The blue shading is a guide for the eye. b) Proposed mechanism of photocurrent enhancement in MoS$_2$ films after engineering an interface with porphyrin species. Red and blue arrows indicate electron injection and hole transfer, respectively. Grey lines show light illumination, and green arrows represent possible charge-recombination pathways.
samples except for MoS$_2$-FePP because FePP is nonemissive. Additionally, porphyrins from the same family, such as GaPP, H$_2$PP, FePP, and ZnPP, should have similar adsorption properties, yet they show drastic differences in photocurrent enhancement.

The three porphyrin families (T4, TPP, and PP) may be considered in understanding photocurrent enhancement behavior. Both H$_2$T4 and ZnT4 have a pyridium substituent group, which provides positive charge in aqueous electrolyte solutions. For H$_2$TPP and ZnTPP, a net neutral charge is expected given their phenyl ligand.

The carboxylic moieties of ZnPP, FePP, GaPP, and H$_2$PP render them negatively charged in the aqueous phase. Although both T4 and TPP families show relatively small enhancement behavior compared with the PP family, the ligand groups of the three families do not consistently match the photocurrent enhancements. Additionally, the metal cations at the porphyrin cores are not correlated with the photocurrent activities; for example, there is no enhancement with ZnTPP, whereas ZnPP shows a drastic increase.

We found that the photocurrent enhancement is strongly associated with the HOMO levels of the porphyrin species, as shown in Figure 5a. The enhancement factor increases exponentially as a function of the HOMO level of the porphyrin (Figure S7):

$$I - I_0 = 0.22 + 0.14 e^{(HOMO-LUMO)/0.5}$$

in which $I$ and $I_0$ represent the photocurrents of the porphyrin-functionalized and pristine MoS$_2$, respectively, and VBM is the valence band maximum of MoS$_2$. From the strong correlation of the photocurrent enhancement with the HOMO level (Figure 5a), we propose a mechanism for the interfacial charge-transfer process in the MoS$_2$–porphyrin hybrid system, as illustrated in Figure 5b. Upon photoabsorption, electrons in the pristine MoS$_2$ film are excited into the conduction band (CB) and may then be injected into the ITO working electrode. As the transferred electrons are collected at the ITO, the work function of which is placed approximately 0.45 eV lower than the conduction band minimum (CBM) of MoS$_2$, the holes left in MoS$_2$ can be reduced by an electrolyte reaction with a redox potential that is positioned significantly higher than the VBM of MoS$_2$. The oxidized dehydroascorbate molecules diffuse to the counter electrode and become reduced to ascorbate, which completes the electrical circuit. In addition to the photogenerated electrons in the CB of MoS$_2$, there is also a minor source of photocurrent depending on the molecules used. A class of porphyrins (e.g., ZnPP in Figure 4b) can contribute to the current as a photosensitizer, by injecting electrons into MoS$_2$ that can then be shuffled and collected at the electrode.

2.4. Effect of Bias Voltage

Last, we examined the effects of bias voltage on photocurrent measurements of MoS$_2$ and MoS$_2$-ZnPP films (Figure 6). Here, a voltage range from $-200$ to $200$ mV against the Ag reference electrode was applied. As seen in Figure 6a and c, the photocurrent responses of pristine MoS$_2$ at zero bias voltage (short-circuit current) are nearly identical to those shown in Figure 2c and Figure 4a. Once a positive voltage is applied, the photocurrent and dark currents (i.e. baseline) both experience increases. For example, the photocurrent and dark current increase from approximately 110 to 200 nA and from approximately 0 to 450 nA at 50 mV, respectively. Both currents gradually increase with increasing bias voltage. At 200 mV, the photocurrent from the pristine MoS$_2$ film reached approximately 300 nA, which is about three times greater than with no bias voltage. Negative bias voltages, however, reversed this trend. At $-50$ mV, photocurrents were barely observed, whereas the dark current became negative at approximately $-300$ nA. An increase in negative bias voltage leads to negative photocurrent, which implies that photogenerated electrons are collected at the counter electrode instead of the working electrode. After a further increase in negative bias voltage, the negative photocurrent escalated, to about $-250$ nA at $-200$ mV.

The MoS$_2$ film functionalized with ZnPP shows behavior that is generally similar to pristine MoS$_2$ under various bias voltages.
es, as shown in Figure 6b and c. At 50 mV, the ZnPP-MoS 2 film experienced a photocurrent enhancement from approximately 1 to 1.2 μA, whereas the dark current also increased from approximately 0 to 0.55 μA. Both the photocurrent and the dark current continued to increase, reaching approximately 1.4 and 4.5 μA, respectively, at 200 mV. Similar to pristine MoS 2, the photocurrent gradually decreased with increasing negative bias voltage from 1 μA at 0 mV to zero at −200 mV. Negative photocurrent would be observed at more-negative bias voltages.

The effects of bias voltage can be understood within our proposed mechanism. With a positive bias voltage, the work function of the ITO may be shifted downward against the vacuum, away from the CBM of MoS 2. As a result, the electron flow from MoS 2 or MoS 2–porphyrin films to the ITO becomes more favorable due to a larger driving potential and reduced recombination within the system, which results in increased photocurrent. In contrast, negative voltages raise the ITO work function and thus the difference between the ITO and the CBM of MoS 2 is decreased, which reduces the driving potential for electron flow into the ITO. A further increase in negative bias voltage can place the ITO work function above the CBM of MoS 2, which changes the direction of electron flow (i.e. negative photocurrent). The negative photocurrents grow with higher ITO work function at greater negative bias voltages. The adsorbed porphyrin molecules make a significant impact not only on the photocurrent magnitude but also on the reversal of the photocurrent direction. The inflection point changes from approximately −50 mV with pristine MoS 2 to roughly −200 mV with the MoS 2–ZnPP sample, as shown in Figure 6c. Thus, ZnPP is responsible for the difference in the inflection points (≈150 mV), which is less than the gap (≈500 mV) between the ITO work function and the CBM of MoS 2. This discrepancy may be understood by considering that our MoS 2 thin films are few-layers thick, unlike the CBM and VBM of monolayers shown in Figure 5b, and thus the actual gap should be smaller. Overall, these results confirm the effective modulation of MoS 2 properties by interfacial porphyrins.

3. Conclusion

We have successfully fabricated large-area 2D MoS 2 films from chemically exfoliated flakes and studied their optical and photoelectrochemical properties. Eight porphyrin species from three distinct families were examined for their ability to modulate the photoelectrochemical properties of MoS 2 films. We observed a maximum tenfold increase in photocurrent from the porphyrin-functionalized MoS 2 compared with pristine MoS 2. The photocurrent enhancements correlate to the HOMO energies of the porphyrins. The higher the energy of the HOMO, the greater the photocurrent enhancement produced by the functionalized MoS 2 films. The interfacial porphyrins significantly suppress charge recombination pathways and enhance the photocurrent. We also demonstrate that adsorbed porphyrins significantly modulate both the magnitude of the photocurrent and the direction of electron flow. Our results are critical to understanding the fundamental properties of MoS 2 interfaced with porphyrins or other organic compounds in the context of using TMDCs as light-harvesting materials.

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Keywords: light harvesting · molybdenum disulfide · nanolayers · photocurrent · porphyrins

Engineering Chemically Exfoliated Large-Area Two-Dimensional MoS₂ Nanolayers with Porphyrins for Improved Light Harvesting

Layer by layer: Modulation of the photoelectrochemical properties of MoS₂ nanolayers is achieved by interfacial engineering with an array of porphyrin molecules. A maximum tenfold increase in photocurrent is observed for MoS₂ with Zn-centered protoporphyrins. A unique modulation of photoelectrochemical properties of 2D semiconductors and a fundamental understanding of photoinduced charge transfer for MoS₂-based light harvesting is presented.