Photoelectrochemical Properties of Chemically Exfoliated MoS₂

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1 **Abstract**

2 Group 6 transition metal dichalcogenides (TMD) such as MoS₂ are promising candidates for
3 photocatalysis and photoelectrochemical applications. Despite their promise, scalability
4 remains a challenge for TMD-based photoanodes. Here we investigate the
5 photoelectrochemical properties of ultra-thin films of chemically exfoliated MoS₂ and its
6 composites with TiO₂ nanoparticles. We show that MoS₂ monolayer films exhibit
7 photoelectrochemical properties similar to bulk materials, generating photocurrent at
8 excitation wavelengths above the direct band gap edge at ~ 660 nm (~ 1.9 eV). We also
9 demonstrate that MoS₂ monolayers sensitized to TiO₂ behave as effective photosensitizers. We
10 find that in TiO₂-MoS₂ composite photoanodes, photoexcited electrons in MoS₂ are able inject
11 into TiO₂ whilst holes are removed by the electrolyte so as to generate electrical current from
12 incident light. Our results demonstrate the potential of solution-processed MoS₂ monolayers
13 for photoelectrochemical applications.

14

15 **Keywords**

16 Photoelectrochemical cells, monolayer molybdenum disulfide, titanium dioxide sensitization.

1 **Introduction**

2 Molybdenun disulphide (MoS_2) is a semiconductor belonging to a class of compounds
3 known as layered transition metal dichalcogenides (TMDs).[1] Structurally, TMDs are
4 composed of covalently bound X–M–X planes (where M and X represent transition metal and
5 chalcogen atoms, respectively) held together by weak Van der Waals (VDW) interactions,
6 analogous to a graphite-type layered structure. The strong anisotropy of the structure readily
7 enables the isolation of individual monolayers via cleavage along the weakly bound VDW
8 planes.[2] Atomically thin, mono- and few-layered sheets of MoS_2 exhibit a range of intriguing
9 properties that are absent in the bulk form and have sparked a recent resurgence of interest in
10 TMDs. In particular, the recently reported emergence of photoluminescence in monolayer
11 MoS_2 has attracted significant interest. The emergence of photoluminescence is attributed to
12 the evolution of the bulk material from an indirect semiconductor (with a band gap of 1.29 eV)
13 to a direct semiconductor (with a band gap of 1.90 eV) when reduced to a monolayer sheet.[3]
14 Mono- and few-layer MoS_2 has also been highlighted as an attractive candidates for
15 nanoelectronics offering high carrier mobility, large on/off ratio, and minimal sub-threshold
16 swing when implemented as the channel material in field effect transistors.[4-6] Remarkable
17 mechanical stability of atomically thin MoS_2 sheets against bending,[6] and stretching also
18 emphasise distinct physical attributes of this material.[7] These recent findings highlight the
19 potential of MoS_2 in various opto-electronic applications.[8]

20 Due to both its suitable band gap for solar spectrum absorption and its photocatalytic
21 stability against photocorrosion,[9, 10] MoS_2 and other group 6 TMDs have long been
22 considered as ideal photoanode materials for photocatalysis and photoelectrochemical cells
23 (PECs).[10-12] Early work on PEC solar cells with TMD bulk single crystal photoanodes
24 demonstrated energy conversion efficiency of up to 6%.[13, 14]. In photocatalysis, MoS_2
25 nanocrystals grown on wider gap semiconductor such as TiO_2 serves as a sensitizer and

enabling enhanced production of hydrogen[15] and degradation of organic molecules.[16-18]. Similarly, WS₂ [19] and WSe₂[20] particles have also shown to be effective photosensitizers to TiO₂ surfaces in analogy to quantum dot sensitization.[21]

Despite the promising photocatalytic and PEC properties, scalability remains a common challenge for TMD-based photoanodes. Growth of bulk single crystals is slow, energetically costly and the crystal sizes are typically limited to a few centimeters. Whilst thin film deposition via sputtering and evaporation offer potential routes to scaling up, crystal quality is often compromised [13, 22-24]. Chemical synthesis of TMD nanoparticles is to date, however, limited by poor control of particle structure and scalability. In contrast, atomically thin sheets of TMDs offer solution based routes toward scalable synthesis.[25-27] Chemical exfoliation of bulk TMDs is an efficient route for producing monolayer TMDs in aqueous colloidal suspensions[28]. The exfoliated sheets can be readily deposited uniformly over large areas [26] or hybridized with other materials,[29] enabling simple and scalable schemes for PEC device implementation.

While chemical exfoliation of MoS₂ has been demonstrated since the 1960s,[28] deposition of exfoliated sheets in uniform monolayered thin films form was only achieved recently.[26] Here, we investigate the PEC properties of chemically exfoliated MoS₂ mono- and few-layer thin films and their composites with TiO₂ nanoparticles where the MoS₂ nanosheets act as effective sensitizers.[30] We demonstrate that chemically exfoliated monolayers of MoS₂ largely preserve the photocatalytic properties of the bulk material and that they allow facile photosensitization of TiO₂ nanoparticles via ligand-free direct adsorption. The photocurrent response of MoS₂-sensitized TiO₂ demonstrates the suitability of the orbital energy levels of exfoliated monolayer MoS₂ for charge transfer to TiO₂. Our analysis suggests that improvement in c-axis conductivity of restacked MoS₂ sheets enhance the transport of

photoexcited carriers. These results highlight monolayer MoS₂ as a potentially exciting new class of semiconducting nanoparticles that can be readily implemented into PEC applications.

Experimental Methods

Preparation of MoS₂ thin films

MoS₂ nanosheets and films were prepared by forced hydration exfoliation of Li_xMoS₂ following the method described in reference [26]. The films with thicknesses spanning 1.7 – 18.9 nm were prepared on fluorine doped tin oxide (FTO) conductive glass. The films were annealed in nitrogen atmosphere at 300 °C for 1 hour in order to stabilize the desired 2H phase (See Ref [26] for details). Film thickness was estimated from the UV-Visible absorbance spectra in reference to the empirical data of reference[26].

Preparation of MoS₂-TiO₂ films

MoS₂-TiO₂ composite films were prepared by dispersing Degussa P25 TiO₂ into the aqueous solutions of 0.1 mg/ml MoS₂ nanosheets. The solutions were sonicated for 40 min, stirred and then separated by centrifugation. The transparent supernatant was removed and the remaining off-white pellet was re-dispersed in ethanol as a paste. UV-Visible analysis of the transparent supernatant confirmed the transfer of MoS₂ to the solid paste. The resultant paste was left to stir for >12 hours. Films were prepared by a doctor blade technique.

Three batches of films were prepared. Each batch contained a different ratio of MoS₂-TiO₂. Batch A and B contained 0.4 mg MoS₂, however, A contained double the quantity of TiO₂ (0.5 g) relative to B (0.25 g). A TiO₂ only reference film was also prepared by the same method. Each paste was prepared with a quantity of ethanol proportionate to the quantity of TiO₂. Each film was prepared using the same volume of paste (20 µL) on FTO conductive glass using the doctor blade technique. The films were annealed for 30 min under a flow of argon at 300°C. The thickness of prepared films (determined by SEM) was approximately 10 µm.

Photocurrent measurements

Photoelectrochemical measurements were recorded at room temperature in an in-house designed three-electrode cell fitted with fused silica windows. A 75 W Xeon lamp and PTi LPS-220B power supply in conjunction with a PTi SID-101 monochromator and a PTi optical chopper were used to illuminate the samples. A computer controlled μ AutolabI potentiostat coupled with a lock-in amplifier were used to measure photocurrent. All measurements were recorded against a Ag/AgCl/1M KCl reference electrode with a platinum mesh counter electrode. 1 M Na₂SO₃ was used as a hole scavenger. All photoanodes were illuminated from the MoS₂-TiO₂ side. The lamp intensity was monitored with a PM100A, Thorlabs power meter.

Results and Discussion

The absorption spectra of the MoS₂ thin films (Figure 1 (a)) exhibit the characteristic optical peaks of bulk MoS₂. These peaks in the visible region (400-800 nm) correspond to the optical transitions between d-orbitals (Figure 1 (b)) that non-bonding states of MoS₂.^[31] The energy band structure of MoS₂ and the optical transitions associated with the absorption peaks are illustrated in Figure 1b.^[32, 33] The A/B peaks correspond to the band edge excitons at the K and K' points of the Brillouin zone^[34] while the C/D transitions are interband transitions from the occupied dz² orbital to unoccupied dxy, x²-y² and dxz, yz orbitals. The measured A/B excitonic peaks (Figure 1a) show a slight blue shift by approximately 14 nm as film thickness decreases from 18.9 nm to 1.7 nm (prominent in normalized spectra, supporting information Figure S2) due to confinement effects.^[26] The A exciton peak for the 1.7 nm thickness film is located at 655 nm, consistent with the previously reported peak position for mechanically exfoliated MoS₂ monolayers.^[3]

Figure 1. (a) UV-vis absorbance of the MoS₂ thin films deposited on FTO conductive glass and annealed in a nitrogen environment at 300°C. The average film thicknesses were calculated from the empirical data of reference.[26] Inset shows a photo of a MoS₂ thin film deposited on a glass substrate. (b) Simplified orbital energy structure of MoS₂ adapted from ref[31]. The transitions labelled A, B, C and D correspond to the transitions labelled in (a).

Photocurrent measurements were conducted on thin MoS₂ films with thicknesses ranging from 1.7 to 18.9 nm. The photocurrent density (I_s) and incident lamp power (P) were measured as a function of wavelength (λ). Photocurrent is typically characterized by incident-photon-to-current-efficiency (IPCE),

$$IPCE = \frac{hc}{\lambda e} \left[\frac{I_s}{P} \right] \quad (1)$$

where h is Planck's constant, c is the speed of light and e is the elemental charge.

We employed absorbed photon-to-current efficiencies (APCE) to characterize the quantum yield photocurrent efficiencies of our samples and to compare samples of different thicknesses.

APCE (Equation 2) is calculated by dividing IPCE by light harvesting efficiency of the sample;

$$APCE = IPCE / (1 - T(\%)) \quad (2)$$

where $T(\%)$ is the transmittance and thus the denominator is the fraction of incident photons absorbed by the sample. Here it is assumed that reflectance is negligible compared to absorbance. APCE spectra for the films prepared with different film thickness are presented in Figure 2a.

Figure 2. (a) Averaged (3 data for each film thickness) APCE spectra of the n-type MoS₂ films of different film thickness (solid lines with symbols) conducted at 0 V potential against Ag/AgCl/1 M KCl reference electrode. The spectra are overlaid with the normalized UV-vis absorbance of a thin (1.7 nm) MoS₂ thin film (solid black line). It is of note that relatively large APCE signals recorded for $\lambda > 680$ nm is due to accentuated noise (the monolayer has extremely low absorbance across this region, see supporting information Figure S1 for IPCE data). (b) Wavelength specific APCE values plotted with respect to film thickness. (c) The average IPCE photocurrent response plotted against potential (vs SHE reference electrode) of a 4 nm MoS₂ film on FTO substrate. Between every second and third potential photocurrent measurement, the IPCE was re-measured at 0 V to confirm that the sample had not degraded from the photocatalytic efficiency. (d) The possible mechanistic routes for the decay of excited electrons. k_1 and k_2 are the possible routes of injection of the electron into the FTO. k_3 corresponds to thermalization of excited electrons in the upper orbital energy to conduction band minimum and k_4 represents recombination loss mechanisms.

1 For all samples positive photocurrent signal was recorded, and hence the material is an n-
2 type semiconductor. For samples thinner than 5 nm, photocurrent signal were observed for
3 wavelengths less than 700 nm. The monolayer film revealed the highest APCE values. For most
4 samples, the photocurrent spectra consisted of features near 590-670 nm, corresponding to
5 the A/B optical transitions. However, clear features corresponding to C/D absorption peaks at
6 400 – 480 nm were absent. Similar behaviour has been previously reported for bulk single
7 crystals of MoSe₂ and WSe₂. [22] Nevertheless, the APCE values show little fluctuations across
8 the spectrum above the direct band edge (~650 nm) indicating that the efficiency of
9 photoexcited electrons injection into FTO is not strongly dependent on the excited states of
10 MoS₂. With regards to stability, it is of note that samples stored in the dark between
11 measurements were stable with respect to photocurrent efficiency over the 12 month period
12 that data were collected.

13 An increase in film thickness from 1.7 nm to 10 nm leads to an increase in the light
14 harvesting efficiency ($1 - T(\%)$) of MoS₂ films by 600 % (Figure 1 (a)). The corresponding
15 APCE values decreased by 50 – 70 times. The decrease in APCE is dramatic with photocurrent
16 response, plummeting with film thickness of around ~2 nm, or when the film becomes multi-
17 layered (Figure 2 (b)). At 10nm, the photocurrent signal is reduced to experimental noise
18 level. We propose that the decrease in efficiency is due to a combination of factors. Firstly, the
19 out-of-plane charge mobility is considerably lower than the in-plane mobility as a consequence
20 of the layered structure of MoS₂. For monolayer MoS₂ where the transport distance and
21 therefore time for electrons to reach the FTO interface is minimized, the photocurrent
22 efficiency is highest. On the other hand, for samples of thickness greater than a monolayer, the
23 transit time for electrons/holes to reach FTO/electrolyte interface is significantly increased
24 and the exciton recombination can take place before electrons and holes are separated. Since
25 the MoS₂ sheets are randomly stacked, the inter-plane charge transport is limited compared to

1 commensurately stacked single crystals. Hence, as the thickness of absorbing material
2 increases, kinetics tends to favour exciton recombination rather than separation leading to a
3 decrease in the APCE.

4 Another possible explanation is the evolution of MoS₂ band structure with thickness. Bulk
5 MoS₂ is an indirect semiconductor and thus a defining indirect transition exists at energies
6 lower than the direct band gap transition corresponding to A/B excitons. This may therefore be
7 a competing relaxation mechanism for an exciton relative to injection into FTO. As the film
8 becomes thicker, A/B excitons have additional pathway for relaxation to lower energy and
9 recombination, thus reducing the probability of electron injection to FTO electrode.

10 In order to investigate the energetics of the materials interface, the influence of potential
11 difference on the photocurrent response was monitored. When a potential difference of an
12 appropriate range is applied across the cell the flatband position of MoS₂ films can be
13 approximated as the potential at which the photocurrent response of the material is
14 suppressed, coincident with the irreversible reduction of MoS₂ and hence injection of electrons
15 into the conduction band of MoS₂. As shown in Figure 2 c, we observed that photocurrent
16 associated with A/B and C/D excitations is dependent on the potential applied across the cell
17 (Figure 2c). These results suggest that electrons excited to the conduction band can thermalize
18 to form band edge A/B excitons from where they are also able to contribute to photocurrent
19 (transfer into the FTO). The photocurrent signal corresponding to A/B transitions was not
20 observed at potentials lower than -0.13 ± 0.05 V (vs SHE electrode). It is also of note that if the
21 potentials applied was lower than this value, upon re-increasing the potential applied the
22 photocurrent response was not reproducible. Thus we propose the irreversible reduction of
23 the film (injection of electron into the conduction band of the MoS₂ from the FTO) at potentials
24 of this value and lower. Hence we approximate this potential as the flat band potential of the
25 A/B exciton conduction band. We detail the possible mechanistic routes for electron-hole pairs

1 associated with C/D peaks in Figure 2d. k_1 and k_2 transitions correspond to injection of
2 electrons into FTO and hence these routes contribute to photocurrent whereas k_3 and k_4
3 transitions correspond to thermalization and recombination processes. The fact that IPCE
4 from C/D transitions changes with the applied potential indicates that electron thermalization
5 to direct band edge (k_3) is favourable compared to direct transfer into FTO (k_2).

6 Our photocurrent spectra highlight that chemically exfoliated MoS₂ monolayers retain bulk
7 PEC properties and demonstrate that these materials are potentially useful as photoactive
8 components in PEC solar cells. However, to achieve higher photon-to-current conversion
9 efficiencies, alternative photoanode architectures should be explored whereby the surface area
10 of the MoS₂ monolayers is increased per unit area of illumination to overcome the small
11 absorption cross section of the atomically thin sheets and also encourage exciton separation.
12 In the remainder of this paper, we discuss the PEC properties of MoS₂-TiO₂ hybrid
13 photoelectrodes. The structure of the electrodes is analogous to the photoanodes used in dye-
14 sensitized solar cells (DSSC)[30] where the exfoliated MoS₂ can be seen as a sensitizer to the
15 mesoporous TiO₂. In such devices, photoexcited electrons in MoS₂ are expected to first inject
16 into and subsequently diffuse through the TiO₂ to the FTO substrate while the holes in MoS₂
17 are removed by the electrolyte solution that penetrates into the mesoporous structure. The
18 holes are transferred via electrolyte diffusion towards the counter electrode where electrons
19 re-enter the cell, thus completing the circuit. For electron injection into TiO₂ to occur, it is
20 required that the conduction band minimum of MoS₂ lie above that of TiO₂. In previous
21 studies,[35, 36] such band alignment was achieved with MoS₂ nanoparticles where, as a
22 consequence of quantum confinement, the band gap is significantly increased and the
23 conduction minimum is pushed up (relative to that of the bulk material). Earlier studies on
24 both nano-crystalline and few-layered MoS₂ and WS₂ have suggested that electron injection is
25 indeed possible for the MoS₂-TiO₂ systems.[19, 37] Below we reveal a different scenario with

1 monolayers of MoS₂ where we demonstrate that lowest energy excitons are less likely to
 2 contribute to photocurrent.

3 The composite films were prepared by the mixing of TiO₂ nanoparticles and a prepared
 4 colloidal suspension of chemically exfoliated MoS₂ monolayers (Figure 3a). The mesoporous
 5 structure of the composites is shown in Figure 3b. A typical transmission electron microscope
 6 (TEM) image of the composite is shown in Figure 3c where MoS₂ sheets can be readily
 7 observed. The composite films were also characterized by Raman spectroscopy to confirm the
 8 presence of MoS₂. The Raman spectra of MoS₂-TiO₂ composite films overlaid with spectra of
 9 TiO₂-only films are shown in Figure 3. Differences between the two spectra reveal two distinct
 10 vibrational modes of MoS₂ (E_{2g}^1 and A_{1g}) indicating that the exfoliated MoS₂ remain intact
 11 during the preparation of the composite.

12
 13 **Figure 3.** (a) Schematic illustration of the fabrication of a TiO₂-MoS₂ composite film. (b) SEM
 14 and (c) TEM images of the composite. The arrows in (c) indicate the distinct fringes suggesting
 15 the presence of MoS₂ sheets. (d) Raman spectra of MoS₂-TiO₂ with TiO₂ overlaid and the

1 difference between the two spectra. Two vibrational modes of MoS₂ (E_{2g}^1 and A_{1g}) are evident
2 in the difference spectrum.
3
4

5 The photocurrent responses of TiO₂-MoS₂ composite photoanodes are shown in Figure 4.
6 Three sets of films were prepared, two containing MoS₂ monolayer sheets, and a control
7 sample containing TiO₂ only. The successful sensitization of TiO₂ with MoS₂ is indicated by the
8 extension of the photocurrent response into the visible region of the spectrum relative to the
9 TiO₂ only film. An increase of 500% for film IPCE was achieved for the sensitized film relative
10 to the 1.7 nm MoS₂ only (Figure S1) film on FTO, indicating successful utilization of high
11 surface area in mesoporous TiO₂ structure. It is also noteworthy that the estimated APCE
12 values (Figure S3) are of the same order of magnitude to monolayer MoS₂ values. Conversely
13 to thin MoS₂ films where excitations above the direct band edge lead to generation of
14 photocurrent (Figure 2), photocurrent is suppressed at wavelengths above 600 nm for the
15 composite films. Estimated APCE is also found to vanish above 600 nm (not shown).
16

Figure 4. (a) Averaged IPCE (3 data sets) photocurrent spectra (solid lines) of TiO_2 - MoS_2 composite (red and blue) and TiO_2 only films (green). The spectra are overlaid with the normalized absorbance of 1.7 nm MoS_2 . (b) Schematics of the band structure of MoS_2 and TiO_2 at the interface. Measured flat band potential of MoS_2 (-0.13 eV vs SHE) and estimated flat band potential of TiO_2 (-0.8 eV vs SHE) are shown along with the band gap of the two materials. Electron injection into TiO_2 conduction band from band edge excitons (A/B transitions) is energetically unfavourable. On the other hand, electrons excited into the upper d-orbitals of MoS_2 via C/D transitions can inject into TiO_2 conduction band.

Despite the successful sensitization of TiO_2 , we observe relatively low IPCE values. The enhancement in IPCE is minor when MoS_2 loading is doubled. We speculate that a sizeable fraction of the TiO_2 /electrolyte interface remains unsensitized because the MoS_2 nanosheets do not uniformly coat the entire TiO_2 surface and that some of the MoS_2 sheets may also be positioned at the interface of TiO_2 particles, inhibiting electron transport. In addition to the MoS_2 crystal distribution, the crystal size and resultant constraints on charge carriers must also be considered. A carrier lifetime of $100 \text{ ps} \pm 10 \text{ ps}$ and a corresponding diffusion length of

450 nm have recently been measured for ultrathin MoS₂ layers.[38] Given that an exciton that reaches a crystal edge will recombine due to crystal defects, the crystal sizes utilized in this work (less than 300 – 800 nm diameter) may limit the photocurrent efficiencies of our devices. The likelihood of an exciton reaching the TiO₂ interface (rather than the crystal edge) is increased for larger sized monolayer crystals. We therefore highlight sensitization with larger crystals as a possible route to higher photocurrent efficiencies.

The photocurrent spectra for TiO₂-MoS₂ composite can be explained by the energy band alignment of MoS₂ and TiO₂. The flat band potential of TiO₂ corresponds to the minimum energy required for a photoexcited electron in MoS₂ to inject into TiO₂ conduction band. The flat band position of mesoporous TiO₂ has been shown to be strongly dependent on the pH of the penetrating electrolyte solution.[39] We can estimate the flat band potential of our TiO₂ to be at approximately -0.80 V (vs. SHE). The relevant band positions/gaps of MoS₂ and TiO₂ are shown on a comparable scale in Figure 4(b), which reveals that A/B excitons in the lower conduction band of MoS₂ are of insufficient energy to inject into the TiO₂ conduction band. The position of the C/D flat band potential is estimated above the conduction band of TiO₂ and thus excited electrons have sufficient energy to inject into TiO₂.[40] It may be noted that the observation of photocurrent from C/D absorption bands suggest more favourable kinetics of electron transfer from MoS₂ to TiO₂, in contrast to MoS₂ thin film injection into FTO.

Conclusions

We studied the PEC properties of chemically exfoliated MoS₂. MoS₂ thin films on FTO and TiO₂-MoS₂ composites on FTO show that photoexcited electrons in MoS₂ can be transferred to the electrode while the holes are removed by the electrolyte, leading to generation of photocurrent. Photocurrent dependence on MoS₂ film thickness reveals an acute drop in efficiency with increasing film thickness such that monolayer MoS₂ films produce the highest

photocurrent. We speculate that low charge carrier mobility in layered structures and in particular in the re-stacked structure (in contrast to single crystals) of the exfoliated films prevent efficient transport of charges to transfer interfaces.

We have successfully translated the aqueous solution-processability of exfoliated MoS₂ and its PEC stability to sensitization of the mesoporous TiO₂. We have demonstrated that simple direct adsorption of MoS₂ sheets onto TiO₂ surfaces leads to effective sensitization and enhanced photocurrent efficiencies of the photoanode due to enhanced absorption per unit volume. Contrary to the photocurrent spectra of MoS₂ films on FTO, only the C/D absorption contributes to the photocurrent in the composite films. We have also shown that the conduction band minimum of MoS₂ lies below that of TiO₂ such that electron injection from A/B excitons is suppressed.

Appropriate band gap energies and photostability in combination with solution-processability of MoS₂ monolayers highlight the material as a promising candidate for PEC applications. In particular we demonstrate that a new type of semiconductor-sensitized PEC solar cells can be fabricated with MoS₂ monolayers. We believe that optimization of the photoanode architecture, utilization of larger monolayer crystals and use of other types of transition metal dichalcogenides such as WSe₂ could significantly enhance photocurrent efficiencies.

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1 Supporting Information

2
3 **Figure S1.** IPCE spectra for the different thicknesses for the MoS₂ only films. The normalized
4 absorbance for the thinnest film is also plotted.

7 **Figure S2.** Normalized absorbance spectra (a) entire spectra, (b) 400 – 500 nm only, highlighting the
8 red shift in absorbance peak for the thinnest films.

Figure S3. Estimated APCE for the composite films A and B (estimated by calculation of the known concentrations of MoS₂ dispersed into each film).

Photocurrent measurements of the MoS₂-TiO₂ hybrid photoanodes was also measured utilizing iodine/triiodide electrolyte. The results are presented in Figure S4. Analogous to Figure 4 a photocurrent corresponding to excitons A/B is suppressed relative to the absorbance spectrum for the thin films. We therefore verify the assertion that conduction band is approximately -0.13 V $\pm$ 0.05V (against SHE reference).

Figure S4. Average photocurrent for two ratios of MoS₂/TiO₂ samples. Averages are calculated for 2 samples for each ratio and 3 measurements for each sample. Photocurrent was measured with Iodide/triiodide electrolyte.

1 Table of Contents

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4 Atomically thin molybdenum disulfide films are shown to be photoelectrochemically active and
5 stable. Sensitization of the wide band gap semiconductor titanium dioxide is also realised
6 highlighting the unexplored potential of 2D crystals in photoelectrochemistry.