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MoS$_2$/WS$_2$ Heterojunction for Photoelectrochemical Water Oxidation

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ABSTRACT

The solar-assisted oxidation of water is an essential half reaction for achieving a complete cycle of water splitting. The search of efficient photoanodes which can absorb light in the visible range is of paramount importance to enable cost-effective solar energy-conversion systems. Here we demonstrate that atomically thin layers of MoS$_2$ and WS$_2$ can oxidize water to O$_2$ under incident light. Thin films of solution-processed MoS$_2$ and WS$_2$ nanosheets display n-type positive photocurrent densities of 0.45 mA cm$^{-2}$ and O$_2$ evolution under simulated solar irradiation. WS$_2$ is significantly more efficient than MoS$_2$, however, bulk heterojunctions of MoS$_2$ and WS$_2$ nanosheets results in a 10-fold increase in incident-photon-to-current-efficiency compared to the individual constituents. This proves that charge carrier lifetime is tailorable in atomically thin crystals by creating heterojunctions of different compositions and architectures. Our results suggest that the MoS$_2$ and WS$_2$ nanosheets and their bulk heterojunction blend are interesting photocatalytic systems for water oxidation, which can be coupled with different reduction processes for solar-fuel production.

KEYWORDS: photoanode, water splitting, heterojunction, MoS$_2$, WS$_2$
INTRODUCTION

Photoelectrochemical (PEC) water splitting to obtain hydrogen and oxygen gases is extensively investigated as solar energy-conversion system to address the environmental impact arising from the consumption of fossil fuels. Cost effective energy conversion is sought to be able to make this process technologically viable. Any reductive half-reaction for the production of H₂ or further, to reduce CO₂ to hydrocarbon species, requires an oxidative half-reaction, which is the oxidation of water to O₂ (oxygen evolution reaction, OER).¹ The water oxidation half reaction is energetically more demanding (4 electron-hole pairs per O₂ molecule versus 2 electron-hole pairs per H₂ molecule) compared with the proton reduction reaction, and thus it is the rate-limiting factor for a complete cycle of water splitting. To enable water oxidation, the valence band maximum of a semiconductor has to be more positive than the water oxidation potential. Until now, metal oxide materials have demonstrated to oxidize water to O₂ under simulated solar irradiation with high efficiency (WO₃ IPCE 40% at 300 nm of incident radiation in HClO₄ electrolyte)²,³. While these metal oxides are earth abundant and stable in acidic and alkaline conditions, they have poor absorption in the visible region of the solar spectrum due to their large band gaps and in some cases suffer from short hole diffusion length.⁴ This poor absorption in the visible region and short hole diffusion length are key limitations in the employment for PEC water splitting. Furthermore, their valence band edge potential is normally significantly more positive than the oxidation potential of water, resulting in ~1.5 eV absorbed energy to be lost through thermal relaxation.⁵ Alternative materials, including sulfides/selenides (chalcopyrite-type semiconductors and CdS), oxynitrides and ternary metal oxides, which have higher lying p-band levels than oxygen, have been investigated. Therefore, these materials have a
valence band maximum closer to the oxidation potential for water whilst also having smaller band gaps compared with the oxides. A representative example is BiVO$_4$ which can display photocurrent up to 6.72 mA (at 1.23 V versus the reversible hydrogen electrode (RHE) under 1-sun illumination) in a heterojunction system, however, BiVO$_4$ still has a large band gap of 2.4 eV. While the oxynitrides suffer from low stability and necessitate the addition of co-catalysts and chalcopyrite-type semiconductors and CdS are highly unstable in electrolyte solutions and they normally do not exhibit suitable valance band level for water oxidation.

Bulk sulfides of Group VI-transition metal dichalcogenide (TMDC) materials (MoS$_2$ and WS$_2$) are layered materials formed by tri-atom thick sheets of covalently bonded sulfur-metal species that are held together by van der Waals forces. Like graphene, a single tri-atom thick sheet is stable in air and wet conditions including acidic media. This family of materials has recently attracted renewed interest owing to its unique light-matter interactions. These interactions arise from a combination of their intrinsic two-dimensionality, without dangling-bonds, their d-electron orbital character, and their anisotropic structure. They absorb 5-10% of incident light in the visible range, and mechanically exfoliated flakes have shown photovoltaic characteristics. A range of optoelectronic devices, predominantly based on isolated flakes have been demonstrated, including photodiodes, light emitting devices, and photodetectors.

The pristine two-dimensionality of monolayers results in direct band gap transitions in the visible range, specifically at $\sim$2.0 eV for WS$_2$, and at $\sim$1.8 eV for MoS$_2$. While in bulk form they retain an indirect band gap comprised between 1.1 and 1.4 eV. Interestingly, these two materials are isostructural and present very similar electronic band structure. Recently, computational studies have suggested that the valence band edges of monolayer MoS$_2$ and
WS$_2$ are more positive than the oxidation potential of water (1.23 V vs SHE), whereas their bulk counterparts do not meet the thermodynamic requirements for photoelectrochemical water splitting.\textsuperscript{23} Further, as expected for the higher lying S 2p-orbitals, the valence band edges are closer to the water oxidation potential compared to metal oxide semiconductors. This indicates a potential use as photoanodes for water oxidation.\textsuperscript{21,22} Furthermore, previous reports, have shown the ability of single crystal WS$_2$\textsuperscript{24} and MoS$_2$ in bulk and monolayered form\textsuperscript{25–28} to oxidize electrolytes normally with a significantly smaller oxidation potential than water. In addition, the conduction band edge of WS$_2$ is above the reduction potential of protons [$E^0_\text{water} = 0$ V vs standard hydrogen electrode (SHE)], which presents the possibility to use the same material for a complete cycle of water splitting. The use of atomically thin layers as photocatalysts would have significant advantages over traditional bulk materials, such as increased specific surface area, lack of crystallographic defects that normally plague the surface of crystalline materials, and potential solution processability to fabricate photoelectrodes compatible with inexpensive roll-to-roll deposition systems. Further, the versatility offered by the deposition from liquid phase can facilitate the fabrication of novel heterojunction systems and integration with organic materials.\

Here we demonstrate that chemically exfoliated MoS$_2$ and WS$_2$ nanosheets can oxidize water in a complete photoelectrochemical cell. Both materials show n-type positive photocurrents under incident light at low applied overpotentials producing measurable O$_2$ gas evolution. Interestingly, the efficiency can be significantly increased if the two materials are interfaced forming a heterojunction. Analogously to bulk heterojunction organic solar cells, we fabricate films formed by co-exfoliated MoS$_2$ and WS$_2$ nanosheets blended together to form a \textit{van der Waals} bulk heterojunction (B-HJ) consisting of percolating networks of the two materials. The heterojunction exhibits photocurrent and incident-photon-to-current-efficiencies (IPCE) 10 times
higher than the films comprised of the individual constituents. We attribute this to the more efficient exciton dissociation enabled by the creation of atomically thin p-n junctions analogous to MoS$_2$/WS$_2$ bilayer heterostructures grown via CVD,$^{29,30}$ which can occur at faster timescales than the charge carriers recombination in individual WS$_2$ and MoS$_2$ layers.$^{31}$ The charges separated states in the bulk heterojunction have also been predicted to be long-lived despite the close contiguity of electrons and holes, increasing the chance of the water oxidation reaction to occur.$^{32}$ Remarkably, bulk heterojunctions built from solution processable nanosheets present charge carriers dynamics analogous to a bilayer heterostructured system.

RESULTS AND DISCUSSION

WS$_2$ and MoS$_2$ monolayers were obtained via the redox reaction of Li-intercalated powders in water.$^{33,34}$ This process leads to the formation of colloidal suspensions of mono- and few-layered nanosheets (Figure 1a). The photoanodes were prepared by restacking the exfoliated nanosheets from solution onto F:SnO$_2$ doped glass (FTO). To do so, we exploit the liquid-liquid interfacial tension between two immiscible solvents in order to achieve a self-assembly of the TMDC nanosheets at water-organic interfaces. This can be performed by mixing the aqueous suspension of exfoliated nanosheets and a few millilitres of hexane to form globules of organic phase, covered by the nanosheets, in water. When agitation ceases, the globules migrate to the liquid-air interface where they blend to form a self-assembled thin layer of TMDC between hexane and water. The thin layer can then be deposited on a substrate via dip-coating.

The designed assembly method leads to the formation of optically homogeneous films over $>10$ cm$^2$ (Figure 1b) comprised of chemically exfoliated WS$_2$ and MoS$_2$ nanosheets arranged in a randomly oriented mosaic-like structure.$^{35,36}$ Films were fabricated using exfoliated MoS$_2$,
exfoliated WS$_2$, or by co-exfoliated MoS$_2$ and WS$_2$ nanosheets. The co-exfoliated nanosheets produced a \textit{van der Waals} bulk heterojunction consisting of percolating networks of the two materials (represented by the schematic in Figure 1c). Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to investigate the distribution of the individual MoS$_2$ and WS$_2$ nanosheets in the bulk heterojunction films on FTO glass. The ToF-SIMS showed that both were dispersed across the substrates in a mixed manner, that is, there was no observed localization of only MoS$_2$ or only WS$_2$ regions (Figure S1, Supporting Information). The thickness of the films produced via the dip-coating method can be finely controlled between 4nm and 2µm (Figure 1d and 1e). In this work, we produced and photoelectrochemically characterized films of WS$_2$ nanosheets, MoS$_2$ nanosheets, and their bulk heterojunctions with thickness between 4 and 60 nm and an active area of 0.5cm$^2$. The produced uniform films comprise of semi-planar restacked nanosheets as XRD (Figure S2, Supporting Information), SEM (Figure 1f) and STEM (Figure S3, Supporting Information) characterization show. XRD patterns (Figure S2, Supporting Information) further elucidate that the stacking nature of the nanosheets is analogous to TMDC films obtained by other liquid-phase deposition techniques.$^{33,37,38}$
Figure 1. Chemically exfoliated MoS$_2$ and WS$_2$ nanosheets and bulk heterojunction films: a) aqueous suspension of co-exfoliated MoS$_2$ and WS$_2$ nanosheets; b) large-area continuous film of MoS$_2$/WS$_2$ bulk heterojunction; c) pictorial representation of a MoS$_2$/WS$_2$ bulk heterojunction electrode formed by a percolating network of MoS$_2$ and WS$_2$ nanosheets; d) atomic force microscope (AFM) image of a MoS$_2$/WS$_2$ bulk heterojunction showing e) a thickness profile of $\sim$4 nm (scale bar 3 µm); f) planar (scale bar 200 µm) and cross sectional SEM micrographs of a MoS$_2$/WS$_2$ bulk heterojunction film deposited on FTO glass (scale bar 1 µm).

As a consequence of the lithium intercalation, MoS$_2$ and WS$_2$ nanosheets acquire a metallic behaviour adopting a distorted octahedral coordination (1T phase, Fig. S4).$^{33,34,39,40}$ The semiconducting trigonal prismatic configuration (2H phase), required for the OER, is recovered by annealing at 350 °C in nitrogen atmosphere.$^{37,40}$ Raman spectroscopy maps of MoS$_2$ over 60 nm films, reveal the in-plane mode $E_{2g}^{1}$ shifts at lower energy while the out-of-plane mode $A_{1g}$
shifts at higher energy with respect to monolayer (Figure 2a, Figure S5c and e, Supporting Information). Thus, the energy difference between the two modes ranges from 20±0.6 cm⁻¹ to 24±0.6 cm⁻¹ (Figure S5g, Supporting Information). This suggests that overall the restacked nanosheets have a level of electronic coupling comparable with mono- to a few- layers.\textsuperscript{41,42}

Similarly, Raman characterization of 60 nm WS\textsubscript{2} films shows an energy difference between the in-plane E\textsubscript{1} and the out-of-plane A\textsubscript{1} modes comprised between 66±0.2 cm⁻¹ and 68 ±0.2 cm⁻¹ (Figure 2a and S5d, f and h), suggesting the formation of a nanosheets network with electronic coupling comparable to mono- and a few- layers.\textsuperscript{43,44} Analogous to bilayer heterostructured TMDCs, the Raman spectra of the bulk heterojunctions appear as superposition of both the MoS\textsubscript{2} and WS\textsubscript{2} spectra across the entire sample area (Figure 2a).\textsuperscript{31,45,46} Intensity maps of the A\textsubscript{1} mode of MoS\textsubscript{2} and WS\textsubscript{2} show uniform distribution of the two materials across the film (Figure S6, Supporting Information). The energy differences between the MoS\textsubscript{2} and WS\textsubscript{2} Raman modes suggest comparable interaction between the layers as in the individual constituents films. The predominant mono- to few- layered nature of the restacked nanosheets, demonstrably proves that interlayer coupling remains weak probably due to quasi- planar restacking of the nanosheets. The absorption of incident light by MoS\textsubscript{2} and WS\textsubscript{2} films in the spectral range from the near-IR to the UV region shows the presence of features known as A, B and C transitions (Figure 2b).\textsuperscript{36,47,48} The A and B exciton peaks shift slightly with the number of layers as these transitions are dictated by the d- orbitals of the metal atoms. The C transitions are mostly affected by \textit{van der Waals} interactions involving the p-orbitals of the S atoms and thus this peak occurs at distinctly different energies for mono- versus multi- layered materials.\textsuperscript{48,49} In our case, the C peaks of MoS\textsubscript{2} and WS\textsubscript{2} are centred at ~ 470 nm and ~ 455 nm respectively, while the A and B transitions are positioned at ~ 676 nm and ~ 623 nm in MoS\textsubscript{2} and ~ 628 nm
and ~ 526 nm in WS₂, overall suggesting a predominant contribution from few-layered nanosheets. The absorption peak positions were extracted by fitting the UV-Vis spectra, which were corrected to the scattering due to the thickness of the films (~ 60 nm) and fitted using a combination of Lorentzian functions (Figure S7). Visible light absorption of MoS₂/WS₂ bulk heterojunctions appears as a superposition of the excitonic transition of the single constituents, as expected if they contribute independently to the overall spectrum (Figure 2b).

Photoluminescence (PL) spectroscopy was employed to confirm the position of the optical band gap of both MoS₂ and WS₂ and to provide an indication of interlayer coupling. PL spectra of MoS₂/WS₂ bulk heterojunctions extracted from spatial maps (Figure 2c, Figure S8, Supporting Information) over 60 nm thick films show superimposed light emission peaks from the A transitions of both MoS₂ and WS₂ constituents with overall lower intensities (25-30%) compared to the individual constituents that might be an indication of formation of a type II junction between the two materials. Although the intensity of the light emitted is lower than monolayers, the peak position appears at 1.88 eV for MoS₂ and 1.98 eV for WS₂, indicating a contribution from the monolayers, and suggesting that restacking does not entirely quench the PL (Figure 2c).
Figure 2. Physical characterization of MoS$_2$ (black line), WS$_2$ (blue line) and MoS$_2$/WS$_2$ heterojunctions (red line): a) Raman spectra of 60 nm films deposited onto SiO$_2$ (285 nm)/Si wafer; b) UV-Vis absorbance spectra of 60 nm films deposited onto quartz glass; c) photoluminescence spectra of 60nm films deposited onto SiO$_2$ (285 nm)/Si wafer.
The electrical behaviour (Figure S9, Supporting Information) and PEC activity for water oxidation of MoS$_2$ and WS$_2$ nanosheets, and their bulk heterojunctions were studied. The PEC properties were characterized in a complete photoelectrochemical cell using an aqueous electrolyte in acidic conditions. NaClO$_4$ was utilized as the electrolyte as chlorine is in its highest oxidation state (VII) and it cannot be further oxidized, ruling out any contribution to the photocurrent due to the oxidation of the electrolyte.$^{26,27}$ Linear sweep voltammetry (LSV) of chemically exfoliated WS$_2$ and MoS$_2$ nanosheet films were recorded both in the dark and under light irradiation with the difference between light and dark current corresponding to the photocurrent (Figure 3a, blue and black lines). Both WS$_2$ and MoS$_2$ photoanodes exhibit positive photocurrents at low applied overpotentials, with an onset at $\sim +0.6$ V vs RHE for WS$_2$ and $\sim +0.7$ V vs RHE for MoS$_2$. WS$_2$ films exhibit higher photocurrents compared with MoS$_2$ at the same applied potentials ($+1$ V vs RHE).

Chronoamperometry (CA) scans (Figure 3b), recorded under chopped irradiation further confirm the larger photocurrent generated by WS$_2$ electrodes. Shallow slopes in the CA profiles of both materials indicate slow photocurrent decays attributed to slow charge carrier recombination. This slow recombination can be ascribed to the presence of intrinsic defects in the form of S vacancies which generate mid-gap trap states,$^{42,50,51}$ preventing fast charge recombination. Our observation that this effect is more pronounced in MoS$_2$ than WS$_2$ can be explained by MoS$_2$ retaining larger amount of intrinsic defects compared with WS$_2$.$^{42,52,53}$ These intrinsic defects can lead to trapping of excitons over a time scale between 0.6 to 5 ps in monolayer MoS$_2$,$^{42,52,54}$ which is faster than the direct charge carrier recombination observed in monolayer MoS$_2$ (50 ps)$^{55}$ and monolayer WS$_2$ (100 ps),$^{10}$ thus explaining the higher photocurrent measured for WS$_2$ compared with MoS$_2$ nanosheets.
Figure 3. Photoelectrochemical characterization of MoS$_2$, WS$_2$ and MoS$_2$/WS$_2$ bulk heterojunction photoanodes: a) linear sweep voltammetry curves and b) chronoamperometry (+1 V vs RHE, under intermitted illumination) scans recorded for WS$_2$ (blue line), MoS$_2$ (black line) and MoS$_2$/WS$_2$ bulk heterojunction (red line) photoanodes of ~60 nm thickness; c) O$_2$ sensor reading showing oxygen evolution when a WS$_2$/MoS$_2$ photoanode is irradiated (1 sun, 100 mW/cm$^2$) in a complete PEC cell at constant temperature (298 K) (red dashed line is a linear fitting of the experimental data); d) incident-photon-to-current efficiency (IPCE) % spectrum and related optical absorbance for the MoS$_2$/WS$_2$ bulk heterojunction electrode (~80 nm thickness).
A significant improvement in the photoelectrochemical performances arises when chemically exfoliated WS$_2$ and MoS$_2$ nanosheets are blended together to form a bulk heterojunction electrode (Figure 4). The photocurrent generated by the heterojunction is one order of magnitude larger with respect to photocurrents measured in MoS$_2$ electrodes and two times higher compared with WS$_2$ electrodes (Figure 3a and 3b).

The increase of the photocurrent can be explained as due to spatial charge carrier separation occurring when WS$_2$ and MoS$_2$ nanosheets are interfaced forming a type II junction (Figure 3b). Recently, it has been shown that assembled MoS$_2$ and WS$_2$ monolayers, either mechanically exfoliated or CVD grown, display a type II band alignment where excitons are likely to be dissociated and thus holes transfer to the valence band of WS$_2$ monolayers while electrons transfer to the conduction band of MoS$_2$ monolayers.$^{31,45,46}$ This occurs in a very short time scales of 30-50 fs which is much shorter than the intralayer relaxation processes (10 ps) of possible trapping by intrinsic defects (0.6-5 ps), thus leading to efficient charge separation.$^{42,56,57}$
Indeed, it has been observed and predicted that interlayer excitons in bilayer heterostructures present much longer lifetimes, on the orders of nanoseconds\textsuperscript{10}. Specifically, in a MoSe\textsubscript{2}/WSe\textsubscript{2} bilayer heterostructure,\textsuperscript{58} electrons localized on the MoSe\textsubscript{2} and holes on the WSe\textsubscript{2} monolayer can have life times over \(~\sim 1.8\) ns at 20 K in non-bias conditions, which is 10 times longer than lifetimes in defect-free monolayer material.\textsuperscript{10} Although these exciton lifetimes are estimated without any bias applied, they provide an indication of charge carrier dynamics. CA scans of bulk heterojunctions (Figure 3b) show similar features as those of the individual constituents. The initial decay of the photocurrent in Figure 3b could be attributed to the initial adsorption of molecular oxygen which could limit the active area of the electrode as observed in other photoanode materials such as \(\alpha\)-Fe\textsubscript{2}O\textsubscript{3} \textsuperscript{59}. This is supported by the fact that the photocurrent stabilizes after \(~\sim 40\) sec of light illumination with no significant consecutive decay. In addition, XPS characterization before and after photoelectrochemical testing of the B-HJ electrodes has confirmed that there is no appreciable degradation of both WS\textsubscript{2} and MoS\textsubscript{2} under the operational conditions of the photoelectrochemical cell (Figure S10). Although XPS characterisation show a minimal oxidation of the single constituents after electrochemical characteriasation, we ruled out a contribution of WO\textsubscript{3} in the photocurrent trend during photoassisted water oxidation by testing a fully oxidised WS\textsubscript{2} photoanode. If the photocurrent observed was to be attributable to a contribution of WO\textsubscript{3}, this would result in a gradual increase of the current with increasing oxidation of the material over time, which has not been observed. In figure S12 we compare a pristine WS\textsubscript{2} photoanode with a fully oxidised photoanode, showing that the IPCE of the fully oxidised electrode (Figure S12c, Supporting Information) is greater in the UV region of the solar spectrum whereas is close to zero in the visible range. The slow rise and decay of the photocurrent in Figure 3b may also suggest that in addition to trap states, a spatial separation of
the photon-generated charge carriers occurs which suppresses electron/hole recombination.\textsuperscript{31,45,46}

This separation therefore leads to more efficient water oxidation as holes are left solely on the WS\textsubscript{2} valence band and are more accessible to water molecules in the electrolyte. Long lived excitons are desirable to ensure e\textsuperscript{-}/h\textsuperscript{+} dissociation before exciton recombination as observed for several metal oxide photoanodes where hole lifetimes ranging from hundreds of milliseconds to seconds are required in order to allow water oxidation.\textsuperscript{60}

The comparison of the UV-Vis spectra recorded for a bulk heterojunction electrode before and after 1 hour of constant polarization under chopped simulated solar radiation (1 sun, 100 mW cm\textsuperscript{-2}) in acidic conditions at applied voltages lower than 1 V, does not show any appreciable difference, confirming the chemical and photochemical stability of both MoS\textsubscript{2} and WS\textsubscript{2} under conditions in which water oxidation can occur (Figure S13, Supporting Information). The stability of the films, under the operational conditions of the photoelectrochemical cell, has been also corroborated by XPS characterization (Figure S10, Supporting Information) and long chronoamperometry scans (Figure S11, Supporting Information). By measuring LSV and CA from both, the front (EE, Electrode/Electrolyte) and the back (SE, Substrate/Electrolyte) side of the transparent photoanode, no appreciable differences in the current values were observed, indicating that electron transport through the films does not affect the photocurrent (Figure S14, Supporting Information). This also confirms that the dip-coating deposition method employed to prepare TMDCs electrodes allow a good adhesion of the film to the substrate.

To qualitatively determine the amount of oxygen evolved during a PEC reaction the bulk heterojunction electrode was placed in a fully degassed cell under the application of a positive external bias, irradiated at 1sun (100 mW cm\textsuperscript{-2}) at a constant temperature of 298 K and the amount of dissolved oxygen gas was measured using a polarographic electrode. The
concentration of oxygen within the cell was recorded as a function of time (Figure 3c), indicating a sharp and linear increase in amount of dissolved oxygen when the WS$_2$/MoS$_2$ electrode is irradiated with simulated solar radiation. When the light is switched off, the O$_2$ concentration firstly decreases drastically which is attributed to the fast consumption of oxygen localized close to the sensor tip. Eventually the oxygen reading drops once the sensor tip consumes all the O$_2$ gas. The faradic efficiency of the bulk heterojunction electrodes was calculated for four different samples giving an average value of 62%, and a value of 67% for the best performing electrode confirming that the majority of the photogenerated holes which survive initial recombination are responsible for water oxidation.

Incident-photon-to-current efficiency (IPCE) recorded for a WS$_2$/MoS$_2$ bulk heterojunction electrode between 450 and 800 nm is reported in Figure 3d along with the corresponding absorption. IPCE characterization confirms the lower efficiency of MoS$_2$ compared with WS$_2$ as already observed in the photocurrent measurements. The IPCE of MoS$_2$/WS$_2$ bulk heterojunction (~0.1% at 600nm) is one order of magnitude higher compared to the IPCE of MoS$_2$ (~0.01% at 600nm, Figure S15, Supporting Information) films and two times higher compared to the IPCE of WS$_2$ (~0.04% at 600nm) films. The efficiency profile is in good agreement with the absorption spectra of the films, showing distinct peaks corresponding to the A, B and C transitions of MoS$_2$ and WS$_2$, indicating that the observed anodic photocurrents are a result of the light absorbed by both MoS$_2$ and WS$_2$.

Thinner films show lower IPCE across the whole visible range, indicating that the amount of light absorbed is a determining factor for efficiency (Figure S15, Supporting Information). The IPCEs (%) at 600 nm of incident light for different films thicknesses (between 40 nm and 80 nm) of the different materials have been compared in Figure 5a. The B-HJ phase presents the highest
efficiencies for the different film thicknesses, followed by WS$_2$. Films of exfoliated MoS$_2$ exhibit the lowest IPCEs. To obtain further insights into the influence of the film thickness on the IPCE, we calculated the absorbed photon-to-current efficiency (APCE), which describes the photocurrent collected per incident photon absorbed (Figure 5b). APCE was calculated using equation Equation 1:

$$APCE = \frac{IPCE}{1 - 10^{-A}}$$  Equation 1

where $A$ is the absorbance of the thin film at a given wavelength. We observe that the APCE decreases with increasing thickness for single constituents as well as B-HJ electrodes suggesting that thinner films are inherently more efficient in the photocatalytic process than thick films. This can be explained with an increased probability of electron-hole recombination with increased film thickness. Further, we also photoelectrochemically characterised thin films prepared with different atomic ratios of MoS$_2$ and WS$_2$. The MoS$_2$:WS$_2$ ratio of 75:25 at. % shows IPCE slightly higher than MoS$_2$, whereas the MoS$_2$:WS$_2$ ratio of 25:75 at. % exhibits IPCE higher than WS$_2$ but lower compared to the 50:50 at. % ratio of the B-HJ (Figure 5c, d).

We can therefore confirm that the IPCE is the highest when the interfacial area of WS$_2$ and MoS$_2$ is maximized. To further confirm that the type II junction strongly affects the charge carrier dynamics, we have investigated different structuring of the heterojunctions. The planar heterojunction of FTO/MoS$_2$/WS$_2$ shows lower efficiency (IPCE of 0.014% at 600nm, Figure S16, Supporting Information) than bulk heterojunctions, however higher than the individual constituents. This is likely to be due to the limited interfacial area between MoS$_2$ and WS$_2$. While an inverted planar heterojunction, namely FTO/WS$_2$/MoS$_2$ shows on average a lower IPCE in the visible range (Figure S16, Supporting Information), which is comparable to the
IPCE recorded for MoS$_2$ electrodes (Figure S15, Supporting Information). This is explained by the lower level of the MoS$_2$ valence band edge with respect to WS$_2$, which therefore tends to confine holes in the WS$_2$ film and similarly electrons in the MoS$_2$ film.

**Figure 5.** IPCE% and APCE% recorded at 600 nm of incident light for MoS$_2$ (black squares), WS$_2$ (blue squares) and B-HJ (red squares) films of different thicknesses: a) IPCE % and b) APCE%. c) IPCE % as a function of the incident wavelengths, recorded for 60 nm films prepared with different MoS$_2$:WS$_2$ ratios; 75:25 at. % (green dots), MoS$_2$:WS$_2$ ratio of 25:75 at. % (purple dots) and 50:50 at. % (red dots); d) IPCEs (%) at 600 nm of incident light versus MoS$_2$ and WS$_2$ atomic at 600 nm of incident light for 60 nm thick electrodes.
The high light absorption in combination with modest photocurrent suggests that optimization of the electronic coupling between the thin films and the substrates to favour the electrons injection in the transparent electrode, along with further development of thin films fabrication would improve the efficiency beyond ~0.1% IPCE at 600 nm. This is lower than IPCEs of metal oxides, such as WO$_3$ (~40% at 300 nm of incident light), in the UV range however, it is in the same order of magnitude as reported for thin films of exfoliated WSe$_2$ nanosheets (IPCE 0.2%) used as photocathode for water reduction. The addition of a Pt/Ru or Pt co-catalysts on the WSe$_2$ materials, either single crystal or exfoliated, have shown a significant increase in the photocurrent. Thus, the use of a co-catalyst, could provide an increase of the IPCE in the sulfides system.

CONCLUSIONS

In conclusion, we have demonstrated that chemically exfoliated MoS$_2$ and WS$_2$ nanosheets can oxidize water evolving O$_2$ gas in an acidic environment under incident illumination by simulated sun light. This oxygen evolution occurs without the need of any co-catalysts and protection layers. The efficiency is nearly one order of magnitude higher in MoS$_2$/WS$_2$ heterojunction electrodes. This enhancement arises from the promotion of electron-hole dissociation by the band alignment formed at the interfaces of the two materials, and the extension of the charge carriers lifetime against recombination. Our results provide crucial insights on the energy conversion mechanisms in a solution-processable atomically thin non-oxide materials systems with the band gap in the visible range, chemically stable in acidic conditions and with inherently high surface area, paving the way towards designing new photocatalysts for water oxidation.
EXPERIMENTAL SECTION

Exfoliation of TMDCs: WS$_2$ and MoS$_2$ mono-layers were obtained via the redox reaction of Li-intercalated powders in water. Commercially available powders of WS$_2$ and MoS$_2$ (WS$_2$: Aldrich powder, 2µm, 99%, MoS$_2$: Aldrich powder, 6µm,) were first intercalated with lithium ions, from LiBH$_4$ (Sigma Aldrich ≥95%) in N$_2$ atmosphere and held at 350°C for 72 hours. After intercalation, milli-Q (18Ω cm$^{-2}$) water was added to the powders and lithium ions undergo a redox reaction evolving H$_2$ (g) and forming LiOH upon contact with water. This release of hydrogen gas separates the layers of TMDCs leading to an effective delamination allowing for the formation of colloidal suspensions of mono- and few-layered nanosheets (Figure 1a).$^{33,34}$ The suspension was sonicated using a VWR USC300T sonic bath (80W) for 30 minutes at 0°C to facilitate exfoliation. LiOH formed during the redox reaction and the unexfoliated platelets were removed by gravimetric centrifugation (Centrifuge: Thermo Scientific, Sorvall Lynx 6000) by applying several centrifugational cycles of 30 min at centrifugal forces comprise between 87,207-119xg. Colloidal aqueous suspension of predominantly single layered nanosheets were obtained and stored in the dark at 5°C.

Thin film preparation: To obtain continuous films over large areas we developed a liquid-liquid self-assembled method, which allow formation of a space confined arrangement of exfoliated nanosheets at the interface of two immiscible solvents. Precise control of the film thickness was enabled by the varying the exfoliated nanosheets concentration and the withdrawing speed of the substrate. Exfoliated nanosheets suspensions were diluted in 10mL of milli-Q water and 1mL of hexane (VWR 98%) and the pH was adjusted to ~ 2.5 by adding HCl 37% (VWR). Upon stirring, the exfoliated nanosheets migrate at the water/hexane interface forming a space-confined layer of material. Thin films were prepared using a KSV Nima dip-coater by
immersing and withdrawing FTO glass substrates at a speed of 30mm/min. The latter were previously cleaned via sonication in acetone, isopropanol and DI water and treated for 3 minutes with oxygen plasma etching in order to increase the hydrophilicity of the substrates (Solarus, Gatan 950, Advanced plasma system).

**Physical characterization:** Spatial maps of Raman modes and photoluminescence were collected using an inVia confocal microscope Raman spectrometer (Renishaw) equipped with a 532nm excitation wavelength. The spectra were collected under a 100x objective using a grating of 1800 line/mm, which provides a resolution of ~ 1.5 cm\(^{-1}\). The laser power onto the sample was less than 200 µW. The absorption spectra of the films deposited on fused silica substrates were recorded by using a UV-Vis spectrometer (Perkin Elmer, Lambda 25) between 200 and 1000 nm. The cross sectional morphology of the films was characterized using a LEO 1525 field-emission scanning electron microscope.

**Photoelectrochemical characterization:** Thin films electrodes of TMDCs were tested in a home-built PEEK three electrode photoelectrochemical cell with a Pt counter electrode and a commercial Ag/AgCl(sat) reference electrode (Basi, MF-2052). The electrolyte was a 0.5M NaClO\(_4\) solution (Fisher Scientific, Lab reagent grade) in milli-Q water (pH 1, HClO\(_4\) (VWR, 70%)) and the active area of the electrodes was 0.5cm\(^2\). The electrolyte was degassed with Ar for 20 minutes prior electrochemical measurements in order to remove any dissolved oxygen. Electrochemical measurements were carried out using a Gamry Interface 1000 potentiostat; LSV measurements were recorded by applying a voltage to the working electrode which was swept anodically between 0.55 and +1.15V versus a RHE at a scanning speed of 10mV s\(^{-1}\) in the dark and under irradiation (Hg Lamp, Omnicure serie 1500 coupled with a wave-guide and unfiltered, power on the sample area 1.4W cm\(^{-2}\)). Chronoamperometry measurements were recorded by
applying a constant voltage (+1V vs RHE) to the working electrode and recording the evolution of the photocurrent over time under chopped irradiation. IPCE measurements were recorded by applying a constant voltage (+1V vs RHE) to the working electrode and measuring dark currents and photocurrents as a result of monochromatic light illumination using a filtered Horiba Xe arc lamp. The power of the monochromatic incident light was recorded using a Gentec XLP-12-3S-VP power meter equipped with UNO power monitor. All the voltages were applied versus the Ag/AgCl R.E. following the conversion $V_{(\text{vs RHE})} = V_{(\text{vs Ag/AgCl})} + [0.059 \times \text{pH}] + 0.224$.

*Dissolved O$_2$ measurements:* Dissolved oxygen was recorded using a Unisense microsensor monometer polarographic electrode. A MoS$_2$/WS$_2$ bulk heterojunction electrode was inserted in a tightly closed cell equipped with a quartz window and immersed in the electrolyte. A constant voltage of +1V vs RHE was applied during the measurement. The solution was fully degassed by flowing N$_2$ gas for 30 minutes in order to remove any dissolved oxygen and kept in constant stirring during the measurements. The polarographic electrode reading was stabilized in the dark for 10 minutes and subsequently the sample was irradiated under 1 sun (100mW cm$^{-2}$ at simulated AM 1.5G conditions) constant illumination using a filtered Xe arc lamp. The temperature of the solution was monitored during the measurement in order to correct the polarographic electrode reading. The Faradic efficiency was calculated by dividing the amount of oxygen measured under irradiation by the maximum theoretical amount of oxygen which can be produced at the photoanode under constant irradiation. The theoretical amount of oxygen was calculated from the known incident photon density at the sample area and the photocurrent generated as a result of irradiation.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ASSOCIATED CONTENT

Supporting Information. ToF-SIMS maps of MoS$_2$/WS$_2$ bulk heterojunctions; X-ray diffraction (XRD) Characterization of MoS$_2$, WS$_2$ films and bulk powders; Scanning Transmission Electron Microscopy of a B-HJ film; Raman Spectroscopy maps of MoS$_2$, WS$_2$ and B-HJ films, UV-Vis spectroscopy of MoS$_2$ and WS$_2$ films; photoluminescence maps of MoS$_2$ and WS$_2$ films; electrical measurements of MoS$_2$, WS$_2$ and B-HJ electrodes; X-Ray photoelectron spectroscopy of B-HJ electrodes before and after photoelectrochemical characterization; characterization of an oxidized WS$_2$ electrode; chemical and photochemical stability of MoS$_2$/WS$_2$ bulk heterojunction electrodes; chronoamperometry scans of front vs back illumination for MoS$_2$/WS$_2$ bulk heterojunction photoanodes; incident-photon-to-current efficiencies (IPCE) recorded for different MoS$_2$/WS$_2$ bulk heterojunction film thicknesses, incident-photon-to-current efficiencies (IPCE) for planar heterojunctions of WS$_2$ and MoS$_2$;

Bibliography. This material is available free of charge via the Internet at

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ABBREVIATIONS

APCE (Absorbed photon-to-current efficiency), B-HJ (Bulk heterojunction), CA (Chronoamperometry), EE (Electrode/electrolyte), FTO (Fluorine doped tin oxide), IPCE (Incident photon-to-current efficiency), LSV (Linear sweep voltammetry), OER (Oxygen evolution reaction), PEC (Photoelectrochemical), PL (Photoluminescence), RHE (Reversible hydrogen electrode), SE (Substrate/electrolyte), SEM (Scanning electron microscopy), SHE (Standard hydrogen electrode), STEM (Scanning Transmission Electron Microscopy), TMDC (Transition metal dichalcogenide), ToF-SIMS (Time of flight secondary ion mass spectrometry), XPS (X-ray photoelectron spectroscopy), XRD (X-ray diffraction).

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