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ARTICLE

Efficient Harvesting and Storage of Solar Energy of an All-Vanadium Solar Redox Flow Battery with a MoS_2@TiO_2 Photoelectrode

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Solar redox flow batteries constitute an emerging technology that provide a smart alternative for the capture and storage of discontinuous solar energy through the photo-generation of the discharged redox species employed in traditional redox flow batteries. Here, we show that a MoS_2-decorated TiO_2 (MoS_2@TiO_2) photoelectrode can successfully harvest light to be stored in a solar redox flow battery using vanadium ions as redox active species in both catholyte and anolyte, and without the use of any bias. MoS_2@TiO_2 photoelectrode achieved an average photocurrent density of ~0.4 mA cm^{-2} versus 0.08 mA cm^{-2} for bare TiO_2, when tested for the oxidation of V^{4+} to V^{5+}, attributed to a more efficient light harvesting and charge separation for the MoS_2@TiO_2 relative to TiO_2. The designed solar redox flow cell exhibited an optimal overall solar-to-output energy conversion efficiency (SOEE) of ~4.78%, which outperforms previously reported solar redox flow batteries. This work demonstrates the potential of MoS_2@TiO_2 photoelectrode to efficiently convert solar energy in to chemical energy in a solar redox flow battery, and it also validates the great potential of this technology to increase reliability in renewable energies.

Introduction

The direct storage of sunlight in the form of hydrogen *via* overall water splitting using photoelectrochemical cells (PECs) has been the subject of extensive research in the last few decades.[1-4] The main benefit of this technology is the clean production of hydrogen through the use of solar energy.[5,6] However, the sluggish kinetics of water splitting, particularly the oxygen evolution reaction, the low overall energy conversion efficiency, and the high cost of transportation and storage of hydrogen have somewhat slowed down the take-off of the hydrogen economy.[7,8] Because of this, researchers are increasingly shifting their efforts towards the development of alternative technologies that can offer faster chemical reaction kinetics to store solar energy. Among them, solar redox flow batteries (SRFBs) have attracted recent attention. SRFBs are hybrids between PECs and redox flow batteries (RFBs). They use renewable light energy to charge redox substances and solar energy in the form of chemical energy.[9-16] One example of recent developments in this area is the SRFB designed by Yangen *et al*. that used I^{3-}/I^- and Br^-/Br^{3-} as redox active pairs.[17] The SRFB was driven by a WO_3-decorated $BiVO_4$ photoanode and provided 1.25% solar-output energy conversion efficiency. Yan *et al.* reported a SRFB consisting of a Li_2WO_4/LiI redox couple and a dye-sensitised TiO_2 photoelectrode, enabling a battery capacity of 0.0195 mA h mL^{-1} at a discharge density of 0.075mA·cm^{-2} [1]. Recently, Amirreza *et al*. built a tandem with a bare hematite photoanode and two dye-sensitised solar cells connected in series[2]; the conversion efficiency from solar to chemical energy of the AQDS (anthraquinone-2,7-disulfonate) / iodide SRFB using only hematite as the photoanode was about 0.1%.

Due to its high reversibility and fast react kinetics, all-vanadium redox flow batteries have been widely researched and developed around the world[3-6], including vanadium-based SRFBs, too. Hao *et al*. applied a nitrogen-doped TiO_2 photoanode to a microfluidic all-vanadium photoelectrochemical cell with average photocurrent density of 0.1 mA cm^{-2} [7]. Zi *et al.* demonstrated an AQDS/V^{4+} SRFB able to generate a relatively stable photocurrent of 0.14 mA cm^{-2} using TiO_2 nanoparticles supported on fluorine-doped tin oxide (FTO) as photoanode.[8] Titanium dioxide (TiO_2) has been extensively investigated as a photocatalyst since the discovery of its unique properties in 1972, including remarkable stability against photocorrosion and wide band gap, large enough to provide sufficient energy to drive a variety of useful reactions.[9-12] Although the stability of TiO_2 is excellent, the lack of visible light absorption along with the rapid recombination of photogenerated electron-hole pairs produced usually results in low quantum efficiency and poor photocatalytic activity[13]. Multiple strategies to improve the photocatalytic performance of TiO_2 have been explored, including doping with different elements[7, 14, 15], decorating with noble metals[16, 17], and

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engineering heterojunctions with other semiconductors[18, 19]. Coupling TiO_2 with other semiconductors to form heterojunctions is an effective way to boost the performance of TiO_2 [20, 21] via bending of the photoelectrode band structure, which in turn provides an easier transfer path for the photogenerated electrons and holes and enables a more efficient process[22, 23]. In addition, the design of a heterojunction with a semiconductor of smaller band gap provides a pathway to utilise the visible region of the solar spectrum, increasing the overall efficiency[24, 25]. Some reported examples of such systems include $Cu_2O@TiO_2$[26], $g\text{-}C_3N_4@TiO_2$[27] and $MoS_2@TiO_2$[28, 29].

Here we present for the first time a SRFB with exceptional solar-to-output energy conversion efficiency (SOEE), consisting of a $MoS_2@TiO_2$ photoelectrode (photoanode) and carbon felt as counter electrode (cathode). Specifically, we have studied the redox pairs V^{5+}/V^{4+} and V^{4+}/V^{3+}, which redox potentials match the band gap of the photoelectrode heterojunction. We synthesised the $MoS_2@TiO_2$ thin films supported on FTO glass substrate via a hydrothermal route. The deposition of MoS_2 decorated TiO_2 ensured an increased specific surface area and effective light response, which translated into an enhanced photon capturing and charge transfer. When sunlight reaches the photoelectrode, the photogenerated holes oxidize V^{4+} to V^{5+} at the interface between photoelectrode and anolyte, while the photogenerated electrons reduce V^{4+} to V^{3+} at the interface between carbon felt and catholyte. Thus, the oxidized and reduced forms of V^{4+}, V^{5+} and V^{3+}, respectively, retain the chemical energy that can be converted to electricity via the reverse reaction (**Figure 1**). This SRFB can be written as $TiO_2/MoS_2(s)|V^{4+}, V^{5+}||V^{4+}, V^{3+}|$carbon. The developed system provides ~0.4 mA cm^{-2} photocurrent which is higher than the similar TiO_2-based all-vanadium systems with acidic electrolytes[7, 8]. This is the first time that the $MoS_2@TiO_2$ photoelectrode has shown good catalytic activity for vanadium redox couples, with an overall SOEE of 4.78%, remarkably higher than previously reported SRFB systems (**Table S1, Supporting Information).**[30, 31]

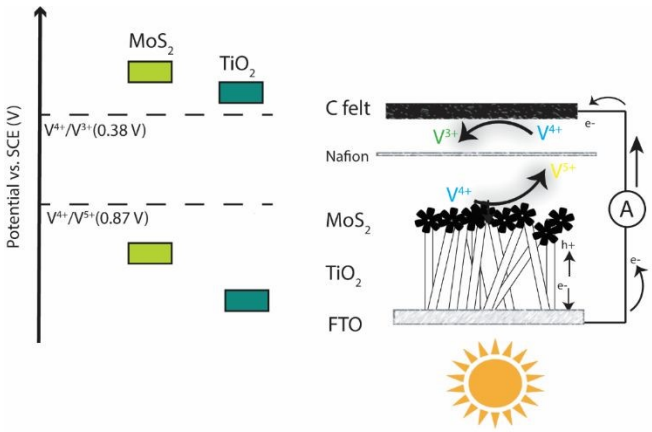

Figure 1. Schematic representation of the SRFB system studied in this work.

Experimental

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Material preparation

Preparation of TiO_2 nanorod arrays. TiO_2 nanorod arrays (NRs) on FTO were prepared using a hydrothermal method reported elsewhere[32]. Briefly, 60 mL deionised water was mixed with 30 mL of concentrated hydrochloric acid (36.5% by weight), and the solution was sonicated for 15 min. Then, 0.1, 0.3, or 0.5 mL of titanium (IV) butoxide (purum, ≥ 97%, gravimetric, Sigma) were added to the solution and sonicated for further 15 min. The FTO substrates were placed into the Teflon liner (200 mL). The hydrothermal synthesis was conducted at 180 °C for 12 h. The resultant sample was rinsed extensively with deionised water, then dried at 80 °C for 1 h and thermally treated at 500 °C in air for 1 h.

Fabrication of MoS_2 nanoflowers onto TiO_2 NRs ($MoS_2@TiO_2$). MoS_2 nanoflowers were grown onto the TiO_2 NRs (0.1/0.3/0.5 mL) by a facile hydrothermal reaction[28]. Firstly, 242 mg (0.001 mol) $Na_2MoO_4{\cdot}2H_2O$ powder (99%, Sigma) and 242 mg (0.002 mol) L-Cysteine (99.99%, Sigma) were mixed in 90 mL deionised water under magnetic stirring for 10 min, then transferred to a Teflon-lined autoclave and stirred for additional 5 min. Subsequently, the TiO_2 NRs previously prepared were placed into the autoclave containing the MoS_2 precursors. The hydrothermal synthesis and deposition of MoS_2 onto the TiO_2 NRs were conducted at 200 °C for 12 h, followed by rinsing with deionized water and drying at 80 °C for 1 h. The resultant samples were labelled as $MoS_2@TiO_2$-0.1, $MoS_2@TiO_2$-0.3 and $MoS_2@TiO_2$-0.5.

Characterisation

The morphology and microstructure of the prepared photoelectrodes were characterised using a field-emission scanning electron microscope (FESEM, Philips FEI Quanta 200 FEG) equipped with an energy dispersive X-ray spectrometer (EDS, operating at an accelerating voltage of 30 kV). The crystal phases of samples were determined by X-ray diffraction (XRD) with Panalytical Xpert Pro diffractometer using Cu Kα radiation source (1.5418 Å). The optical absorption properties were determined by using a UV–vis spectrophotometer (Lambda 950, PerkinElmer) equipped with an integrating sphere (PerkinElmer) within a wavelength range of 350 to 800 nm and a step of 1 nm. The surface chemical states of photocatalysts were analysed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Nexsa X-ray spectrometer, Al Kα monochromatic X-ray source). ICP-MS analysis was performed using a Microwave Plasma Atomic Emission Spectroscopy (4210 MP-AES).

Electrochemical and photoelectrochemical characterisation

A three-electrode electrochemical cell was employed to study the electrochemical behaviour of the carbon felt electrode against vanadium ion species. The carbon felts (3.18 mm thick, 99.0% Alfa Aesar) were pre-treated in a MTI 1200x tubular furnace at 800 °C for 2 h, using a heating rate of 3 °C min^{-1} and a nitrogen flow rate of 0.5 l min^{-1}. [33] The size of the carbon felt electrodes was 1.0 cm^2 (0.32 cm^3). KCl saturated calomel Hg_2Cl_2

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electrode (SCE) and Pt foil were employed as reference and counter electrodes, respectively. Cyclic voltammetry (CV) experiments were conducted between -1.0 and 1.6 V *versus* SCE, at a scan rate of 10 mV s^{-1}, and electrolyte with a concentration in 0.1 M or 1.0 M V^{4+} (vanadium IV oxide sulfate hydrate, Sigma-Aldrich, 97%) and 1.0, 2.0 or 3.0 M H_2SO_4 (Sigma, 98%). Electrochemical impedance spectroscopy (EIS) experiments were conducted using a frequency range of 0.1 MHz to 0.1 Hz and a perturbation of 10 mV. All the electrochemical experiments were carried out using a potentiostat Gamry IFC5000-05520.

Photoelectrochemical studies were conducted in a three-electrode electrochemical cell using TiO_2 or MoS_2@TiO_2 as working electrode, and SCE and Pt foil as reference and counter electrodes, respectively. 0.1 M and 1.0 M V^{4+} in 3.0 M H_2SO_4 were used as the electrolyte. Linear sweep voltammetry (LSV) measurements were conducted at a scan rate of 10 mV s^{-1} in the voltage range of -0.5 V to 0.5 V *vs.* SCE. EIS photoelectrochemical experiments were also conducted at frequency range of 0.1 MHz to 0.1 Hz and 10 mV perturbation. The illuminated area (back illumination) of the working electrode was 1.0 cm^2. The photoelectrode was irradiated by simulated solar light (400 W Xe lamp) using an AM 1.5 G filter. The power density of the incident light was calibrated to 100 mW cm^{-2} by using an optical power meter with silicon photodetector (Newport 818-SL) as a certified reference. The illuminated area of the working electrode was 1.0 cm^2.

Redox flow battery testing

Charge-discharge experiments were conducted in the voltage range 0 to 1.1 V using a current density of 1.0 mA cm^{-2} with 1.0 M V^{4+}. The electrolyte was pre-discharged to 0 V at current density of 0.1 mA cm^{-2}. Carbon felts separated by a Nafion® membrane were used as positive and negative electrodes. The discharge current density after photocharge is 0.4 mA cm^{-2}. The carbon felts underwent the same thermal treatment described in the electrochemical characterisation section. The Nafion membrane (115, 0.005 in. Thick, DuPont de Nemours & Co) was subjected to the following treatment prior to their use: firstly, immersed in 50 mL 5 wt.% H_2O_2 80 °C 1 h, followed by an hour treatment at 80 °C in distilled water, and another hour at 80 °C in 1.0 M H_2SO_4. The membrane was finally treated at 80 °C for 1h in distilled water. A volume of 20 mL was employed as initial catholyte and anolyte, respectively. The experiment was carried out using a peristaltic pump with double head to control the flow of electrolyte on both sides of the redox flow cell to 2.5 mL min^{-1}. The size of carbon felt as working electrode for redox flow battery testing is 5.0 cm^2 (1.59cm^3).

Solar flow battery testing

The SRFB consisted of a modified redox flow battery (**Figure S1a, Supporting Information**), with a window in the anolyte side to enable the irradiation of the photoanode with the Xe lamp light source, and a redox flow battery (**Figure S1b, Supporting Information**), coupled to two electrolyte tanks and a peristaltic pump. All electrochemical data were collected using a Gamry IFC5000-05520 potentiostat. The solar flow cell assembly included the MoS_2@TiO_2 photoelectrode and carbon felt, separated by a Nafion® membrane. Both carbon felts and Nafion® membrane were pretreated as explained in the previous section. Photocharging of the SRFB was conducted without any external bias through irradiation of the photoanode using simulated solar light (400 W Xe lamp) using an AM 1.5 G filter. As the SRFB photocharges, the V^{4+} present oxidises to V^{5+} in the anolyte and reduces to V^{3+} in the catholyte. EIS studies of MoS_2@TiO_2-0.5 were conducted in SRFB configuration, using 1.0 M V^{4+} in 3.0 M H_2SO_4, frequency range 0.1 MHz - 0.1 Hz and perturbation of 10 mV. The illuminated area of the working electrode in the solar flow cell was 5.0 cm^2.

Results and discussion

Three TiO_2 thin films were synthesised using different amounts of titanium (IV) butoxide (0.1, 0.3 and 0.5 mL) and deposited onto FTO using a hydrothermal route. The TiO_2 films (**Figure 2**) displayed a rod-like morphology typically observed in the literature[36] with a crystal structure corresponding to rutile, as determined by x-ray diffraction (**Figure S2, Supporting Information**).

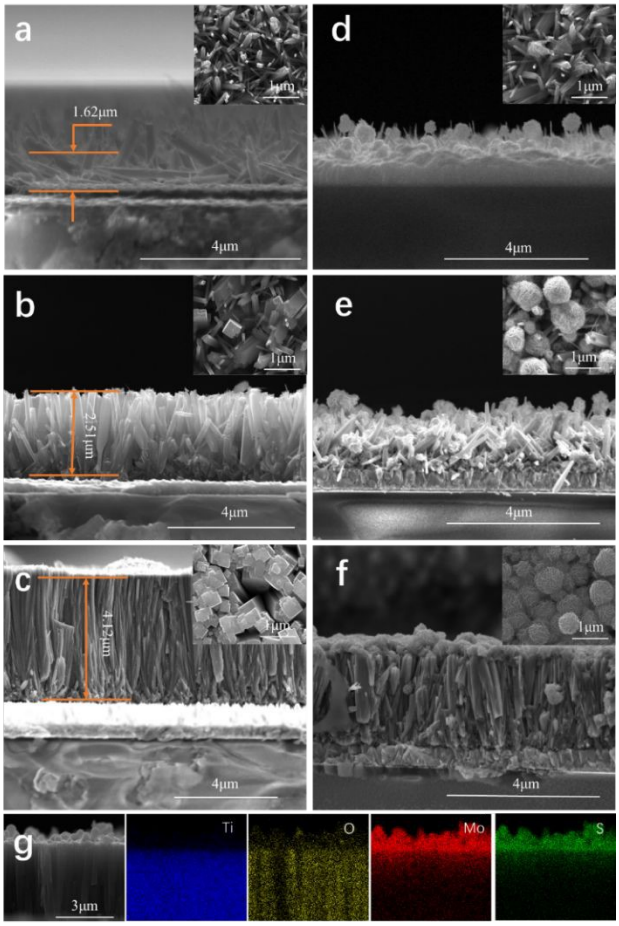

Figure 2. SEM images of TiO_2 thin films obtained using (a) TiO_2-0.1, (b) TiO_2-0.3 and (c) TiO_2-0.5. (d) MoS_2@TiO_2-0.1, (e) MoS_2@TiO_2-0.3 and (f) MoS_2@TiO_2-0.5; (g) EDS of MoS_2@TiO_2-0.5.

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The TiO_2 rods became larger with increasing the amount of titanium (IV) butoxide. The TiO_2 rods produced using 0.1 mL of precursor were relatively short (~1.6 µm) and randomly oriented (**Figure 2a**). As the amount of precursor is increased to 0.3 mL, generally the TiO_2 rods thicken and their length increased by almost 1 µm, to ~2.5 µm (**Figure 2b**). However, in this case, size, length, and orientation of the rods was still inhomogeneous. As the amount of titanium (IV) butoxide was further increased to 0.5 mL, the TiO_2 rods became much thicker (4.12 µm). Moreover, the orientation and size of the rods tended to be more uniform (**Figure 2c**). The film itself also grew into a denser more compacted layer with additional titanium (IV) butoxide.

MoS_2 nanoflowers were grown onto the three TiO_2 films prepared. In the case of the MoS_2@TiO_2-0.1 film, only a small amount of MoS_2 deposited onto the TiO_2 rods, and also in the space between rods (**Figure 2d**). The synthesis and growth of MoS_2 onto TiO_2 with a tighter surface structure (MoS_2@TiO_2-0.3 and MoS_2@TiO_2-0.5) prevented the MoS_2 nanoflowers from depositing into the space between TiO_2 rods, leading to the formation of more uniform MoS_2 layers (**Figure 2e, f**). A higher magnification of the MoS_2 nanoflowers on the upper right corner of **Figure 2f**, showed that each MoS_2 nanoflower had a diameter of ~500 nm and exhibited > 100 sheets. According to literature, the higher the number of layers of MoS_2 nanosheets, the higher the photocatalytic performance, as more nanosheets will provide more active sites and area for the reaction[32, 34, 35]. EDS data (**Figure 2g** and **Figure S3, Supporting Information**) for MoS_2@TiO_2-0.5 material supported the SEM data.

The UV-vis absorption spectra of TiO_2 and MoS_2@TiO_2 photoelectrodes in front illumination mode (**Figure 3a**) showed the increase in light absorption within the visible range for the samples containing MoS_2, as expected. The back illumination spectra (**Figure S4, Supporting Information**) displayed similar behaviour with additional features due to interference in the case of MoS_2@TiO_2 photoelectrodes, although some reports have suggested that the additional bands observed may be due to MoS_2[25-30]. XPS was used to analyse the oxidation state and electronic environment of Ti, Mo, S and O. The Ti 2p line XPS spectrum for TiO_2-0.5 (**Figure 3b**) confirmed that the surface of TiO_2 mainly consists of Ti^{4+} $2p_{1/2}$, Ti^{4+} $2p_{3/2}$, Ti-O bond and O-H bond as expected for TiO_2, with binding energies of 465.1 eV, 459.4 eV, and 530.6 eV and 532.3 eV, respectively[32]. In **Figure 3c, d**, the Mo 3d and S 2p line XPS spectra for MoS_2@TiO_2-0.5 are shown, respectively. The Mo 3d line XPS spectrum indicated the existence of two different states of MoS_2: 1T-MoS_2 and 2H-MoS_2, both with Mo^{4+} as the dominant oxidation state. Previous research has indicated that Mo 3d and S 2p XPS signals of the 1T-MoS_2 phase exhibit a higher binding energy (about 1 eV) than the corresponding signals for 2H-MoS_2[36]. The 2H and 1T phases exhibited binding energies of 229.4 ad 232.2 eV for $3d_{1/2}$ and $3d_{3/2}$, respectively for 2H-MoS_2 and of 228.1 and 231.3 eV for $3d_{5/2}$ and $3d_{3/2}$, respectively for 1T-MoS_2 [37]. Two small features at 235.2 eV (Mo $3d_{3/2}$) and 233.6 eV (Mo $3d_{5/2}$) attributed to Mo^{6+} from some MoO_3 formed at the surface were also observed[38, 39]. A clear peak corresponding to S 2s at 225.5 eV could also be detected. The S 2p line (**Figure 3d**) exhibited two doublets corresponding to $2p_{1/2}$ and $2p_{3/2}$ at binding energies of 163.2 eV and 161.4 eV, respectively[40]. Additionally, peak contributions corresponding to bridging disulfides found in 1T-MoS_2 were observed at 162.3 eV for $2p_{1/2}$ and at 160.9 eV for $2p_{3/2}$ [41]. The XPS survey spectra corresponding to TiO_2-0.5 and MoS_2@TiO_2-0.5 and the XPS O 1s line for MoS_2@TiO_2-0.5 are shown in **Figure S5, Supporting Information**.

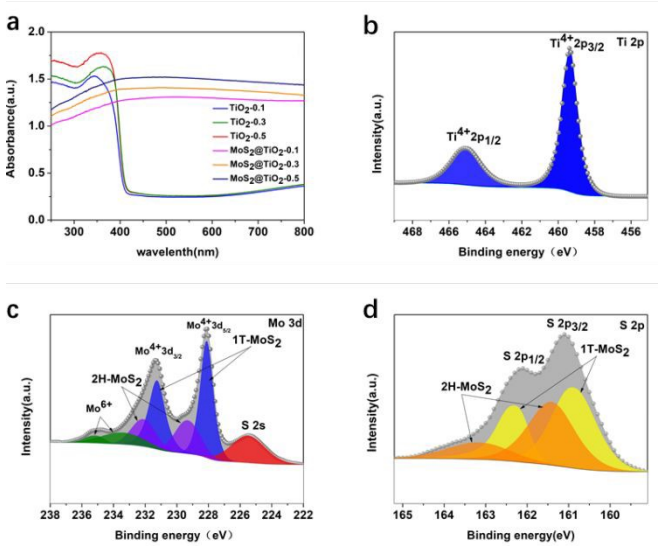

Figure 3. UV-vis spectra of TiO_2-0.5 and MoS_2@TiO_2-0.5 using (a) front-illumination mode, XPS spectra of (b) Ti 2p from TiO_2-0.5, and XPS spectra of (c) Mo 3d, (d) S 2p from MoS_2@TiO_2-0.5

To study the influence of the electrolyte on the performance of the system, a CV experiment using carbon felt as working electrode with 1.0M/2.0M/3.0M sulfuric acid (without any V species) was conducted (**Figure S6, Supporting Information**). The results showed that the ionic conductivity increased with increasing the concentration of sulfuric acid. CV and EIS of 0.1 M V^{4+} in different sulfuric acid concentrations were also conducted in a three-electrode electrochemical cell configuration (**Figure S7, Supporting Information**). The results suggested that a higher concentration of H_2SO_4 facilitates the electrochemical reaction, resulting in more reversible redox processes at the highest concentration, 3.0 M H_2SO_4. The EIS result in **Figures S7c and d** confirmed that higher concentration of sulfuric acid as electrolyte can decrease the resistance through increasing the ionic conductivity of the electrolyte. The CV result indicated a redox potential difference between 0.1 M V^{3+}/V^{4+} and V^{4+}/V^{5+} of ~0.49 V in 3.0 M H_2SO_4 using thermally treated carbon felt as the working electrode (**Figure 4a**). There exists a reduction peak corresponding to V^{3+}/V^{2+}; however, no oxidation peak V^{2+} to V^{3+} was observed. This has been previously reported in the literature, due to the extremely easy oxidation of V^{2+} in air.[42,43]. In order to match the photocurrent density, 1.0 mA cm^{-2} was selected as the charge and discharge current density to test the reversibility and stability of the V^{3+}/V^{4+} and V^{4+}/V^{5+} redox pairs. The redox flow cell assembled with the

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same carbon felts and redox pairs exhibited a good reversibility upon charge and discharge cycling (**Figure 4b**) with an average capacity of 1077 mAh L^{-1} and coulombic efficiency of 99.2% at a current density of 1.0 mA cm^{-2} within 25 cycles (**Figure 4c**).

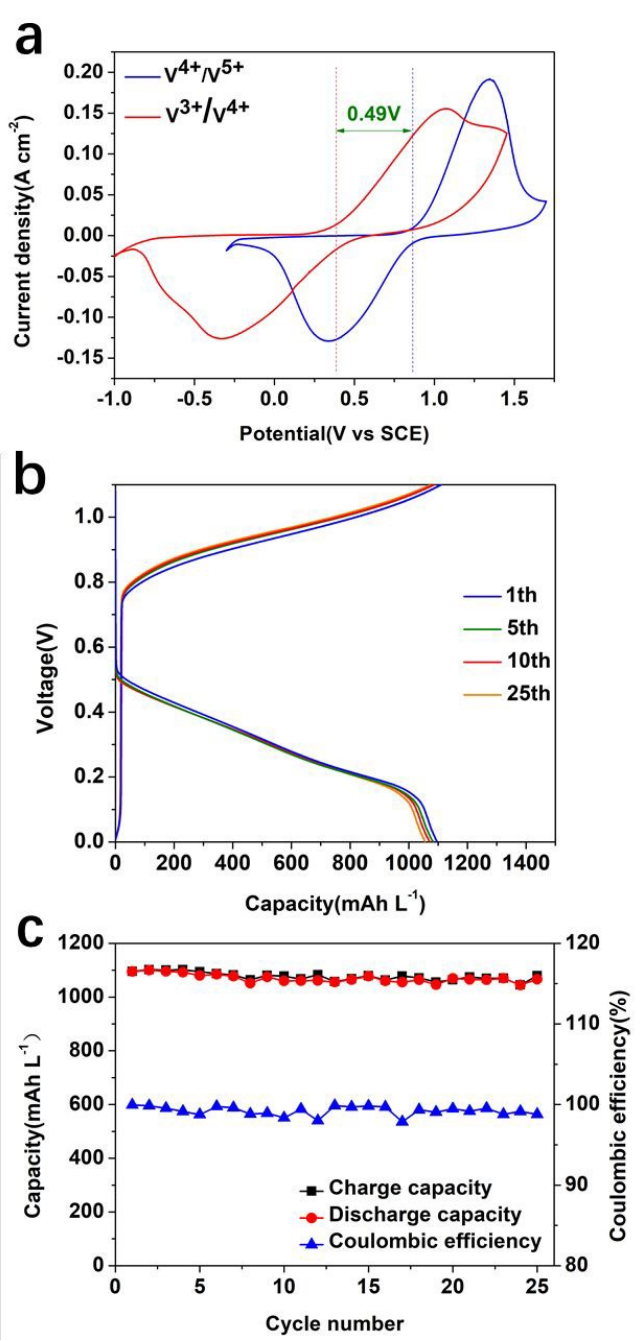

Figure 4. (a) CV in 0.1 M V^{3+}/V^{4+} and V^{4+}/V^{5+}, with a three-electrode electrochemical cell using in 3.0 M H_2SO_4, carbon felt, SCE and a Pt coil as working, reference, and counter electrode, respectively. (b) Charge/discharge experiments for a redox flow cell using 1.0 M V^{4+}, 3.0 M H_2SO_4 electrolyte, current density of 1.0 mA cm^{-2} from 0 V to 1.1 V. (c) charge-discharge capacity and coulombic efficiency of the RFB.

The redox processes of $V^{4+}/V^{5+}$and V^{4+}/V^{3+} redox pairs in SRFB can be summarised in Equation 1, 2, 3 as follows:

$$\text{Anolyte: } V^{4+} \rightleftharpoons V^{5+} + e^- \quad E_0 = 0.87 \text{ V } \textit{vs} \text{ SCE} \tag{1}$$

$$\text{Catholyte: } V^{3+} \rightleftharpoons V^{4+} + e^- \quad E_0 = 0.38 \text{ V } \textit{vs} \text{ SCE} \tag{2}$$

$$\text{Overall: } 2V^{4+} \rightleftharpoons V^{5+} + V^{3+} \quad E_0 = 0.49 \text{ V } \textit{vs} \text{ SCE} \tag{3}$$

After testing the performance of the RFB using V^{3+}/V^{4+} and V^{4+}/V^{5+}, the electrochemical behaviour of the TiO_2 and MoS_2@TiO_2 photoanodes against V^{4+}. **Figure 5a** and **5b** shows the LSV measurements in 0.1 M and 1.0 M V^{4+}, respectively, in 3.0 M H_2SO_4 for TiO_2-0.5 and MoS_2@TiO_2-0.5. The MoS_2@TiO_2 photoelectrode exhibited much higher performance than TiO_2-0.5, being able to achieve a photovoltage of ~450 mV *vs* SCE, about ~100 mV higher than the TiO_2-0.5 photoelectrode for both V^{4+} concentrations. Upon applying potential bias, there is an expected increase in photocurrent for both photoelectrodes, which is also more noticeable in the case of MoS_2@TiO_2-0.5. In the case of the MoS_2@TiO_2-0.5, the increase rate is faster for the more concentrated V^{4+} electrolyte (1.0 M), reaching 0.6 mA cm^{-2} compared to ~0.4 mA cm^{-2} for 0.1 M V^{4+} at 0.4 V *vs* SCE. Interestingly, there was no significant effect on the photocurrent response when increasing the V^{4+} concentration for the TiO_2-0.5 photoelectrode when applying bias. We attribute this to the fact that the TiO_2 photoelectrode is already performing as its maximum capacity, in terms of the holes that can produce at a given time, so a higher concentration of V^{4+} would not change the number of holes that can reach to the interface of electrolyte/TiO_2.

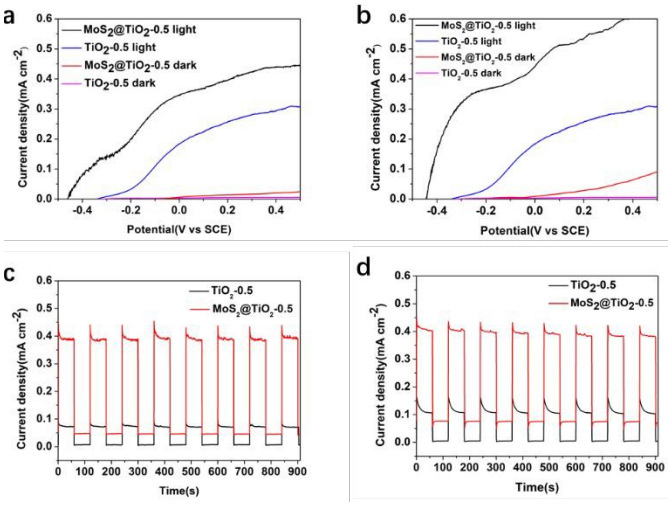

Figure 5. LSV in (a) 0.1 M V^{4+} and (b) 1.0 M V^{4+} with a three-electrode electrochemical cell using in 3.0 M H_2SO_4, SCE and a Pt coil as reference and counter electrode, respectively. Chopped-

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chronoamperometry experiment for a SRFB using TiO_2-0.5 or MoS_2@TiO_2-0.5 as photoanodes and thermal treated carbon felt as cathode in (c) 0.1 M V^{4+} and (d) 1.0 M V^{4+} with 3.0 M H_2SO_4 2.5 mL min^{-1} flow rate and light source 100 mW cm^{-2} (AG1.5).

Chronoamperometric measurements of all the photoelectrodes (TiO_2-0.1, TiO_2-0.3, TiO_2-0.5 and their MoS_2@TiO_2 counterparts, **Figure S8, Supporting Information)** conducted in a SRFB configuration showed that the performance of the samples was much more affected by the densification level and thickness of the TiO_2 layer than by the presence of MoS_2 for the samples TiO_2-0.1, TiO_2-0.3, MoS_2@TiO_2-0.1 and MoS_2@TiO_2-0.3, all of which exhibited a similar photocurrent response. This is likely due to a better alignment of the TiO_2 rods for the more compact samples[32], TiO_2-0.5 and MoS_2@TiO_2-0.5. Therefore, a significant enhancement in the photoresponse when adding MoS_2 was only observed for these more compact TiO_2 layers, with the sample MoS_2@TiO_2-0.5, exhibiting 0.4 mA cm^{-2} *versus* 0.08 mA cm^{-2} for TiO_2-0.5 in 0.1 M V^{4+}. Chopped-chronoamperometry experiments in 0.1 M (**Figure 5c**) and 1.0 M V^{4+} (**Figure 5d**), in 3.0 M H_2SO_4 also revealed that the MoS_2@TiO_2-0.5 photoanode presented a stable photocurrent density and quick photoresponse in V^{4+} flowing electrolyte.

A stability test was carried out for the best performing photoelectrode, MoS_2@TiO_2-0.5 in 1.0 M V^{4+}, 3.0 M H_2SO_4 electrolyte using a SRFB configuration. **Figure 6a** shows the photocharging process conducted for five cycles. As it can be observed, full photocharge was achieved in ~60 min. As the number of charge/discharge cycles increased, the photocurrent density of MoS_2@TiO_2-0.5 decreased. After each full photocharge and discharge, the photocurrent density decreased from ~0.4 mA cm^{-2} to 0.26 mA cm^{-2} for the 5th cycle. This is attributed to the low stability of MoS_2 under the harsh acidic working conditions and more studies to protect the MoS_2 are currently being explored to mitigate this effect. The fluctuations observed in the charge profiles are due to the slow photocorrosion process affecting the MoS_2 under the acidic working environment. When the photons inject into the MoS_2@TiO_2 photoanode, the photoanode would like to create a stable equipotential interface and dynamic equilibrium between MoS_2@TiO_2 photoanode surface and electrolyte. Due to the existing of MoS_2 photocorrosion, the interface must re-establish itself after the photocorrosion of MoS_2, leading to photocharge fluctuations. This phenomenon was also observed for the 0.1 M V^{4+} concentration electrolyte (**Figure S9a, Supporting Information**). **Figure 6b** shows the discharge experiment after each full photocharge. Compared to the poor discharge performance (25.52 mAh L^{-1} to 18.11 mAh L^{-1}) when using 0.1 M V^{4+} electrolyte (**Figure S9b, Supporting Information**), the much higher capacity (98.93 mAh L^{-1} to 74.26 mAh L^{-1}) of 1.0 M V^{4+} (**Figure 6c**) can provide higher discharge potential to overcome the multiple resistances present in the system. The coulombic efficiency for 1.0 M and 0.1 M V^{4+} after five cycles is ~90% (Figure 7c) and ~80% (**Figure S9c, Supporting Information**), respectively. A SOC of 9.03% after 80 min of the first photocharging cycle was observed, decreasing to 6.78% after 80 min into the fifth photocharging cycle.

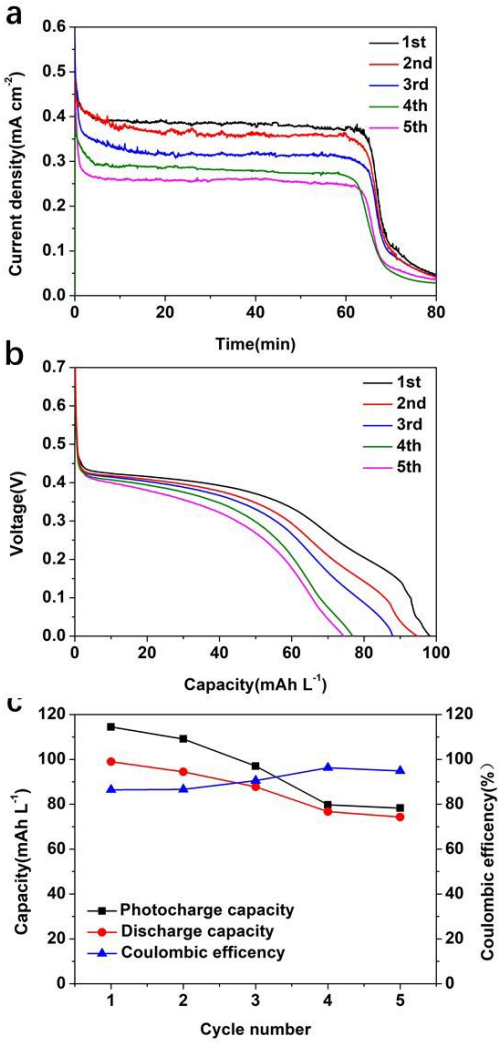

Figure 6. (a) Cyclic photocharge, (b) discharge of MoS_2@TiO_2-0.5 and (c) the capacity and coulombic efficiency in the vanadium ion concentration of 1.0 M V^{4+}. The discharge current density is 0.4 mA cm^{-2}. (100 mW cm^{-2}(AG1.5) with 3.0 M H_2SO_4 and 2.5 mL min^{-1} flow rate).

During photocharge process, the carriers from the semiconductor are excited to the conduction band and oxidise V^{4+} to V^{5+}. The photoexcitation and electron transfer can be represented as follows:

$TiO_2 + h\,\nu = e^-(TiO_2) + h^+(TiO_2)$ (formation) (step1)

$e^-(TiO_2) + h^+(TiO_2) = TiO_2 + h\,\nu$ (recombination) (step 2)

$e^-(TiO_2) + h^+(TiO_2) = e^-(MoS_2) + h^+(MoS_2)$ (interface) (step 3)

$e^-(MoS_2) + h^+(MoS_2) = MoS_2 + h\,\nu$ (recombination) (step 4)

$V^{4+} + h^+(MoS_2) = V^{5+}$ (production) (step 5)

The average SOEE during photocharge in the SRFB was calculated according to the Equation 4 [44]:

$$SOEE\ (\%) = (\int I_{dis} \times dt \times \Delta E_0) / (P_{in} \times S \times t) \times 100 \quad (4)$$

Where I_{dis} is the discharge current density, ΔE_0 is the potential difference of the two redox couples at reversible state, t is the illumination time (0.5 h or 1.33 h), P_{in} is the incident solar power (100 mW cm^{-2}), and S is the area of the solar flow cell window (5.0 cm^2).

As recorded in **Table 1**, the calculations showed the SOEE of the SRFB in 1.0 M V^{4+} reaches a value of 4.78% in the first cycle and remains at 3.26% in the fifth cycle.

Sample / Cycle	0.1 M			1.0 M		
	Photocharge capacity (mAh L^{-1})	Discharge capacity (mAh L^{-1})	SOEE (%)	Photocharge capacity (mAh L^{-1})	Discharge capacity (mAh L^{-1})	SOEE (%)
1	32.68	25.52	0.17	114.44	98.93	4.78
2	26.23	22.50	0.14	109.09	94.47	4.31
3	23.92	21.00	0.12	96.99	87.79	3.99
4	21.38	18.69	0.11	79.72	76.74	3.49
5	21.28	18.11	0.09	78.29	74.26	3.26

Table 1. Dependence of SOEE from cycling chronoamperometry plot under illumination for the MoS_2@TiO_2

EIS studies showed an increase in the impedance of MoS_2@TiO_2-0.5 with photocharging (**Figure S10, Supporting Information)** reaching almost three times the initial value after 2 hours, revealing an increase in resistance as the photocharging process progresses, which was attributed to the low stability of the photoelectrode under strong acid electrolyte. This was confirmed via SEM images acquired after each cycle (**Figure S11, Supporting Information**). The SEM images clearly show degradation of the MoS_2 layer upon cycling and suggest that the increase in resistance observed in the EIS may be linked to this degradation of MoS_2. The photoexcitation and electron transfer may be represented as shown in the Equation S1, Supporting Information.[60] The amounts of Mo and Ti leached from the photoanode were determined by ICP-MS and the results are shown in **Figure S12, Supporting Information**. The concentration of Mo in the electrolyte increases with the number of cycles, as expected, supporting the results obtained by SEM and EIS. The TiO_2 layer was less affected by the cycling, but slight leaching was also detected for the 1.0M V^{4+} electrolyte.

To understand the influence of the photoanode structure and to use its light absorption ability to effectively photocharge our solar flow cell, EIS was measured under both dark and light conditions for 0.1 and 1.0 M V^{4+} (**Figures 7a-d**). EIS data for TiO_2 and MoS_2@TiO_2 photoanodes both for low (0.1 M V^{4+}) and high electrolyte concentration (1.0 M V^{4+}) showed that the increase in thickness of the TiO_2 leads to a decrease in impedance, effect that remains after adding the MoS_2 layer. In the low frequency range in dark conditions, the mass transfer dominates the reaction for TiO_2-0.5.

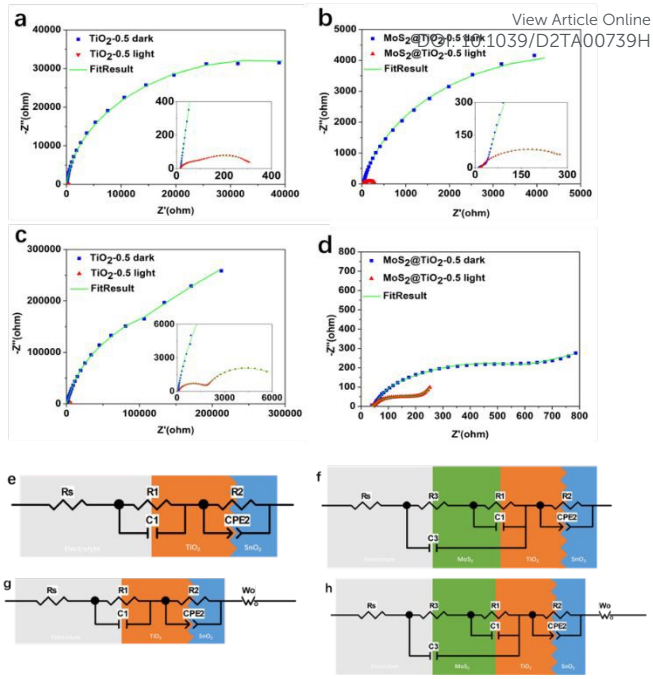

Figure 7. EIS of TiO_2-0.5 or MoS_2@TiO_2-0.5 as the working electrode under dark and light illumination (100 mW cm^{-2}, AG1.5) in a three-electrode electrochemical cell using (a,b) 0.1 M V^{4+} or (c,d) 1.0 M V^{4+} in 3.0 M H_2SO_4 as electrolyte and KCl saturated calomel Hg_2Cl_2 electrode (SCE) and a Pt coil as reference and counter electrodes, respectively. Equivalent circuit model used to simulate the experimental data of (e) TiO_2-0.5 and (f) MoS_2@TiO_2-0.5 in 0.1M V^{4+} and (g) TiO_2-0.5 and (h) MoS_2@TiO_2-0.5 in 1.0 M V^{4+}.

However, under illumination, the upward trend disappears, which means charge transfer dominates in that case (**Figure 7a, c**). For MoS_2@TiO_2-0.5, EIS results demonstrate that the addition of MoS_2 to the TiO_2 layer enhances the charge transfer properties of the photoelectrode (**Figure 7b, d**). Under illumination, the process remains dominated by mass transport effect for MoS_2@TiO_2-0.5 photoanode at low frequencies, confirming its better performance compared to TiO_2-0.5. The equivalent circuits for TiO_2-0.5 and MoS_2@TiO_2-0.5 in 0.1 M V^{4+}(**Figure 7e, f)** exhibit slightly different interface components due to the differences in morphology and roughness of both photoelectrodes[45]. The EIS data taken in a three-electrode electrochemical cell and equivalent circuit for TiO_2/FTO and MoS_2@TiO_2/FTO systems show that at lower V^{4+} concentration, the diffusion resistance is also lower, because when the charge transfer dynamics are not very fast, the charge transfer process and the mass transfer process (caused by diffusion) control the overall reaction: electrochemical polarisation and concentration polarisation coexist. When the concentration is low, the charge transfer process is the rate-determining process. At higher concentration of V^{4+}, mass transport is introduced in the equivalent circuit as the Warburg impedance (W_o in the equivalent circuit, (**Figure 7g, h**), in addition to the charge transfer resistance, as there is an increase in diffusion resistance, when increasing concentration of V^{4+}.

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The fitted data for the TiO_2-0.5 and MoS_2@TiO_2-0.5 photoelectrodes in 0.1 M V^{4+} and 1.0 M V^{4+} are consistent with the results obtained from both dark and light experiments. Rs represents the series resistance (resistance of electrolyte solution and cable of potentiostat), R1 and C1 represent the charge transfer resistance and capacitance of the electrolyte/TiO_2 interface in TiO_2-0.5 while in MoS_2@TiO_2-0.5 they present MoS_2/TiO_2 interface, R2 and CPE2 represent the charge transfer equivalent structure of the interface between SnO_2 (FTO) and TiO_2. In MoS_2@TiO_2-0.5, the R1 and C1 represent the impedance of MoS_2/TiO_2. Because the MoS_2 nanoflowers cannot form a dense layer to separate the TiO_2 and the electrolyte, R3 and C3 is the collective effect representing the charge transfer resistance and capacitance of the electrolyte/MoS_2 and electrolyte/TiO_2 interfaces. The C3 element in parallel with R1, C1 and R3 is also associated with the same phenomenon. The main values of the circuit elements in dark and in light are listed in **Table 2**. The fitting models results of TiO_2-0.1/0.3 and MoS_2@TiO_2-0.1/0.3 in 0.1 M V^{4+} and 1.0 M V^{4+} fit well with the original data in **Figure S13, S14, Supporting Information**. The equivalent circuit is applicable for all the TiO_2 and MoS_2@TiO_2 combinations.

Table 2. **Equivalent circuit main parameters of EIS.**

Sample \ Element		R3(Ω)	C3(F)	R1(Ω)	C1(F)	R2(Ω)	CPE2-T(F)	CPE 2-P
0.1 M V^{4+}	TiO_2-0.5 dark	N/A	N/A	1.7	5.0×10^{-6}	70441	1.9×10^{-5}	0.9
	TiO_2-0.5 light	N/A	N/A	32.9	4.3×10^{-5}	297.3	7.5×10^{-4}	0.5
	MoS_2@TiO_2-0.5 dark	6.6	3.7×10^{-6}	13.4	2.0×10^{-5}	10160	1.9×10^{-4}	0.8
	MoS_2@TiO_2-0.5 light	3.1	1.3×10^{-5}	23..9	1.1×10^{-3}	291.3	1.4×10^{-3}	0.9
1.0 M V^{4+}	TiO_2-0.5 dark	N/A	N/A	1921	3.1×10^{-6}	2.6×10^{5}	1.4×10^{-6}	0.9
	TiO_2-0.5 light	N/A	N/A	2943	1.4×10^{-4}	1776	4.3×10^{-6}	0.8
	MoS_2@TiO_2-0.5 dark	100.2	9.3×10^{-5}	53.8	3.4×10^{-4}	377.3	5.4×10^{-4}	0.8
	MoS_2@TiO_2-0.5 light	40.5	1.1×10^{-4}	19.3	6.2×10^{-4}	30.9	2.7×10^{-3}	1.0

In dark conditions, due to the poor conductivity of the TiO_2, a large charge transfer resistance (R_{ct}) is generated at the interface between TiO_2 and SnO_2 (TiO_2/SnO_2), hindering electron transport. In 0.1M V^{4+} and 1.0 M V^{4+}, under illumination, by comparing the sum of the charge transfer resistance of R1+R2+R3, it is demonstrated that the introduction of MoS_2 interface makes it easier for electrons to transfer in the photoanode, which makes the transmission of the photogenerated electrons in the photoelectrode more efficient. In addition, the injection of photon significantly reduces the R_{ct} of the interface, especially in the TiO_2/SnO_2 interface. Due to the photon injection, many carriers are generated and moved to the interface (MoS_2/TiO_2, TiO_2/SnO_2, electrolyte /TIO_2 and electrolyte/MoS_2). The enrichment of positive and negative charges on both sides of the interface increases the capacitance under illumination. By comparing the capacitance of TiO_2 and MoS_2@TiO_2, it can be concluded that MoS_2@TiO_2 exhibits more carriers accumulated at the interface, which also confirms that the heterojunction of MoS_2@TiO_2 can effectively increase the carrier density in the photoanode.

Conclusions

TiO_2 and MoS_2@TiO_2 thin films supported on FTO were synthesised and tested as photoelectrodes in a solar redox flow battery using vanadium redox actives species. Different thicknesses of TiO_2 layer were produced. The results showed that a larger amount of Ti precursor resulted in more uniform, thicker, denser TiO_2 thin film with more aligned TiO_2 rods. This, in turn, led to a more efficient attachment of the MoS_2 nanoflower overlayer that also translated into a higher photocurrent response. The designed MoS_2@TiO_2 photoelectrode exhibited around 5 times higher activity than bare TiO_2 for charging the all-V SRFB tested in this work. This was attributed to a better separation of charge carriers. The SRFB with 1.0 M V^{4+} electrolyte exhibited a remarkable performance, with an average capacity of 1077 mAh L^{-1} and coulombic efficiency of 99.2% at a current density of 1.0 mA cm^{-2} within 25 cycles, charged only by solar energy without the need of any bias. The SOEE attained 4.78% efficiency. The photoelectrode interfaces were analysed in detail through EIS, and successfully confirmed the enhancement of photocurrent response with the addition of the MoS_2 layer to the TiO_2 photoelectrode. This indicates that the highly active MoS_2@TiO_2 photoanode is promising for the enhancement of photocurrent density in the system studied. The MoS_2 facilitated charge carrier separation and provided active sites for oxidation of redox species. However, the low stability of the photoanode under strong acidic conditions led to a significant degradation of the photoelectrode after only five cycles, resulting in the leaching of metal to the electrolyte. More research is currently under way into approaches to protect the photoelectrode against degradation.

Author Contributions

GT: investigation, formal analysis, methodology, visualisation, writing-original draft and editing. RJ: formal analysis, writing and editing. JB: writing and editing. MT: writing and editing. AJS: conceptualisation, formal analysis, resources, funding acquisition, writing and editing.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1. Yan, N.,Li, G.and Gao, X. *Journal of Materials Chemistry A,* 2013, **1**, 7012-7015.
2. Khataee, A.,Azevedo, J.,Dias, P.,Ivanou, D.,Dražević, E.,Bentien, A.and Mendes, A. *Nano Energy,* 2019, **62**, 832-843.
3. Skyllas-Kazacos, M.,Rychcik, M.,Robins, R. G.,Fane, A.and Green, M. *Journal of the electrochemical society,* 1986, **133**, 1057.
4. Skyllas-Kazacos, M.,Chakrabarti, M.,Hajimolana, S.,Mjalli, F.and Saleem, M. *Journal of the electrochemical society,* 2011, **158**, R55.
5. Vázquez-Galván, J.,Flox, C.,Jervis, J.,Jorge, A.,Shearing, P.and Morante, J. *Carbon,* 2019, **148**, 91-104.
6. Delgado, N. M.,Monteiro, R.and Mendes, A. *Nano Energy,* 2021, 106372.
7. Feng, H.,Jiao, X.,Chen, R.,Zhu, X.,Liao, Q.,Ye, D.,Zhang, B.and Zhang, W. *Journal of Power Sources,* 2019, **419**, 162-170.
8. Wei, Z.,Almakrami, H.,Lin, G.,Agar, E.and Liu, F. *Electrochimica Acta,* 2018, **263**, 570-575.
9. Fujishima, A.,Rao, T. N.and Tryk, D. A. *Journal of photochemistry and photobiology C: Photochemistry reviews,* 2000, **1**, 1-21.
10. Cui, H.,Zhao, W.,Yang, C.,Yin, H.,Lin, T.,Shan, Y.,Xie, Y.,Gu, H.and Huang, F. *Journal of Materials Chemistry A,* 2014, **2**, 8612-8616.
11. Butburee, T.,Bai, Y.,Wang, H.,Chen, H.,Wang, Z.,Liu, G.,Zou, J.,Khemthong, P.,Lu, G. Q. M.and Wang, L. *Adv Mater,* 2018, **30**, e1705666.
12. Fujishima, A.and Honda, K. *nature,* 1972, **238**, 37-38.
13. Nakata, K.and Fujishima, A. *Journal of photochemistry and photobiology C: Photochemistry Reviews,* 2012, **13**, 169-189.
14. Akpan, U.and Hameed, B. *Applied Catalysis A: General,* 2010, **375**, 1-11.
15. Ohno, T.,Mitsui, T.and Matsumura, M. *Chemistry letters,* 2003, **32**, 364-365.
16. Subramanian, V.,Wolf, E. E.and Kamat, P. V. *J Am Chem Soc,* 2004, **126**, 4943-50.
17. Zheng, Z.,Huang, B.,Qin, X.,Zhang, X.,Dai, Y.and Whangbo, M.-H. *Journal of Materials Chemistry,* 2011, **21**, 9079-9087.
18. Gao, C.,Wei, T.,Zhang, Y.,Song, X.,Huan, Y.,Liu, H.,Zhao, M.,Yu, J.and Chen, X. *Adv Mater,* 2019, **31**, e1806596.
19. Humayun, M.,Raziq, F.,Khan, A.and Luo, W. *Green Chemistry Letters and Reviews,* 2018, **11**, 86-102.
20. Bessekhouad, Y.,Robert, D.and Weber, J.-V. *Catalysis today,* 2005, **101**, 315-321.
21. Low, J.,Yu, J.,Jaroniec, M.,Wageh, S.and Al-Ghamdi, A. A. *Adv Mater,* 2017, **29**, 1601694.
22. Sotelo-Vazquez, C.,Quesada-Cabrera, R.,Ling, M.,Scanlon, D. O.,Kafizas, A.,Thakur, P. K.,Lee, T. L.,Taylor, A.,Watson, G. W.and Palgrave, R. G. *Advanced Functional Materials,* 2017, **27**, 1605413.
23. Wang, H.,Zhang, L.,Chen, Z.,Hu, J.,Li, S.,Wang, Z.,Liu, J.and Wang, X. *Chem Soc Rev,* 2014, **43**, 5234-44.
24. Li, J.,Zhang, M.,Li, X.,Li, Q.and Yang, J. *Applied Catalysis B: Environmental,* 2017, **212**, 106-114.
25. Yuan, N.,Zhang, J.,Zhang, S.,Chen, G.,Meng, S.,Fan, Y.,Zheng, X.and Chen, S. *The Journal of Physical Chemistry C,* 2020, **124**, 8561-8575.
26. Cheng, B. Y.,Yang, J. S.,Cho, H. W.and Wu, J. J. *ACS Appl Mater Interfaces,* 2016, **8**, 20032-9.
27. Alcudia-Ramos, M.,Fuentez-Torres, M.,Ortiz-Chi, F.,Espinosa-González, C.,Hernández-Como, N.,García-Zaleta, D.,Kesarla, M.,Torres-Torres, J.,Collins-Martínez, V.and Godavarthi, S. *Ceramics International,* 2020, **46**, 38-45.
28. He, H.,Lin, J.,Fu, W.,Wang, X.,Wang, H.,Zeng, Q.,Gu, Q.,Li, Y.,Yan, C.and Tay, B. K. *Advanced Energy Materials,* 2016, **6**, 1600464.
29. Yang, L.,Majumdar, K.,Liu, H.,Du, Y.,Wu, H.,Hatzistergos, M.,Hung, P. Y.,Tieckelmann, R.,Tsai, W.,Hobbs, C.and Ye, P. D. *Nano Lett,* 2014, **14**, 6275-80.
30. Li, W.,Fu, H. C.,Li, L.,Caban-Acevedo, M.,He, J. H.and Jin, S. *Angew Chem Int Ed Engl,* 2016, **55**, 13104-13108.
31. Cheng, Q.,Fan, W.,He, Y.,Ma, P.,Vanka, S.,Fan, S.,Mi, Z.and Wang, D. *Advanced Materials,* 2017, **29**, 1700312.
32. Liu, Y.,Li, Y.,Peng, F.,Lin, Y.,Yang, S.,Zhang, S.,Wang, H.,Cao, Y.and Yu, H. *Applied Catalysis B: Environmental,* 2019, **241**, 236-245.
33. Ribadeneyra, M. C.,Grogan, L.,Au, H.,Schlee, P.,Herou, S.,Neville, T.,Cullen, P. L.,Kok, M. D.,Hosseinaei, O.and Danielsson, S. *Carbon,* 2020, **157**, 847-856.
34. Wang, D.,Xu, Y.,Sun, F.,Zhang, Q.,Wang, P.and Wang, X. *Applied Surface Science,* 2016, **377**, 221-227.
35. Liu, C.,Wang, L.,Tang, Y.,Luo, S.,Liu, Y.,Zhang, S.,Zeng, Y.and Xu, Y. *Applied Catalysis B: Environmental,* 2015, **164**, 1-9.
36. Geng, X.,Sun, W.,Wu, W.,Chen, B.,Al-Hilo, A.,Benamara, M.,Zhu, H.,Watanabe, F.,Cui, J.and Chen, T. P. *Nat Commun,* 2016, **7**, 10672.
37. Chang, K.,Hai, X.,Pang, H.,Zhang, H.,Shi, L.,Liu, G.,Liu, H.,Zhao, G.,Li, M.and Ye, J. *Adv Mater,* 2016, **28**, 10033-10041.
38. Zhou, X.,Lickleder, M.and Schmuki, P. *Electrochemistry Communications,* 2016, **73**, 33-37.
39. Liu, H.,Lv, T.,Zhu, C.,Su, X.and Zhu, Z. *Journal of Molecular Catalysis A: Chemical,* 2015, **396**, 136-142.
40. Vrubel, H.,Merki, D.and Hu, X. *Energy & Environmental Science,* 2012, **5**, 6136-6144.
41. Sun, M.,Wang, Y.,Fang, Y.,Sun, S.and Yu, Z. *Journal of Alloys and Compounds,* 2016, **684**, 335-341.
42. Wang, W.and Wang, X. *Electrochimica Acta,* 2007, **52**, 6755-6762.
43. Ulaganathan, M.,Jain, A.,Aravindan, V.,Jayaraman, S.,Ling, W. C.,Lim, T. M.,Srinivasan, M. P.,Yan, Q.and Madhavi, S. *Journal of Power Sources,* 2015, **274**, 846-850.
44. Liao, S.,Zong, X.,Seger, B.,Pedersen, T.,Yao, T.,Ding, C.,Shi, J.,Chen, J.and Li, C. *Nat Commun,* 2016, **7**, 11474.
45. Fakhr Nabavi, H.and Aliofkhazraei, M. *Surface and Coatings Technology,* 2019, **375**, 266-291.