

*Electronic Supplementary Information*

**Photoelectrochemical Water Oxidation using a  $\text{Bi}_2\text{MoO}_6$  /  $\text{MoO}_3$  Heterojunction Photoanode Synthesised by Hydrothermal Treatment of an Anodised  $\text{MoO}_3$  Thin Film**

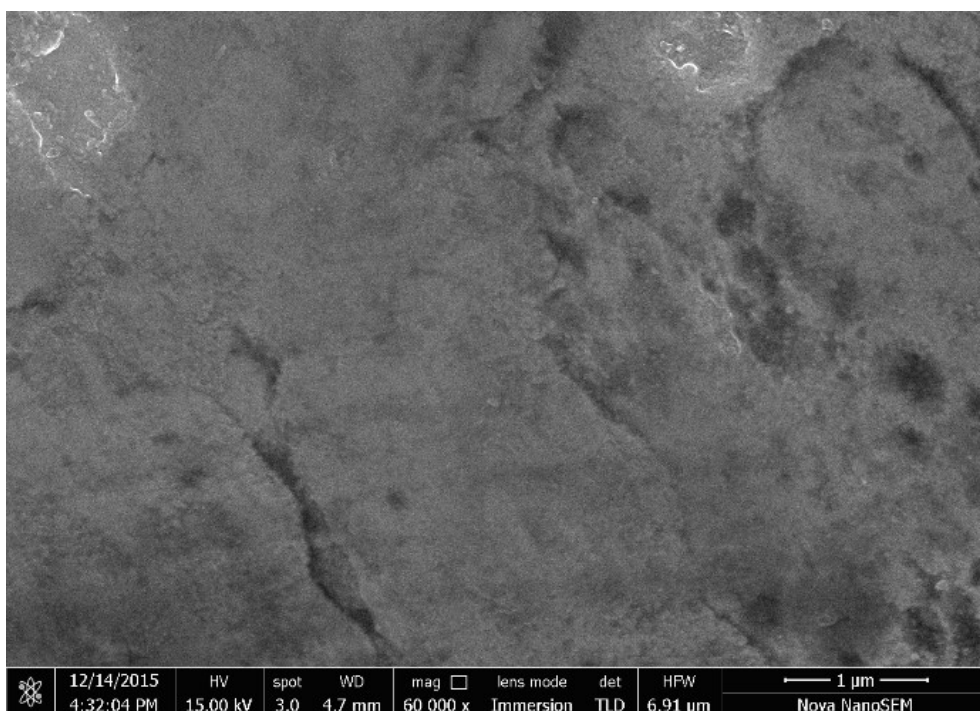
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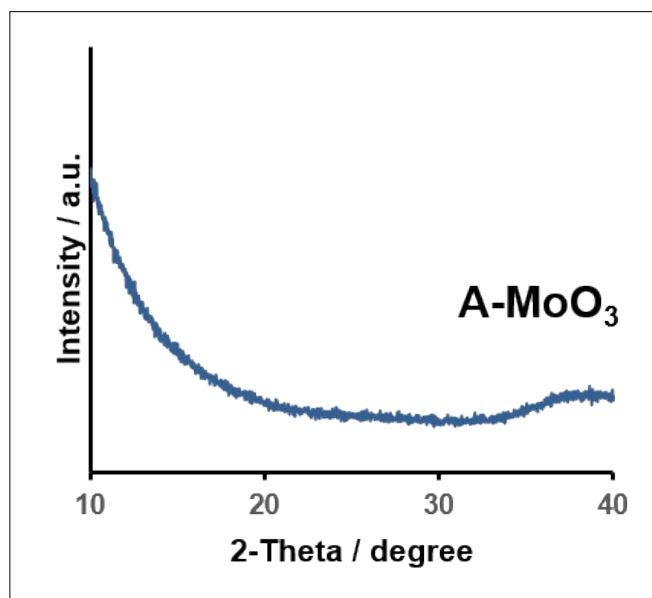
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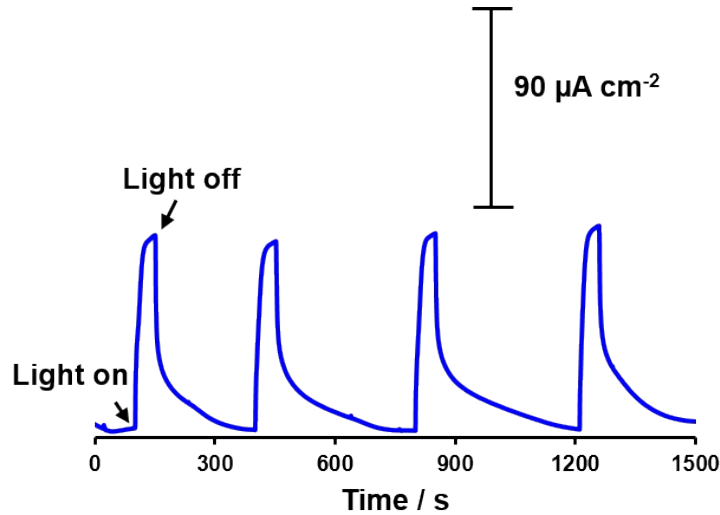
**Fig. S1:** SEM image of a Mo foil purchased from Sigma Aldrich before anodisation

A scanning electron microscopy (SEM) image of the Mo foil is shown in Fig. S1. The Mo foil exhibits a flat and rough surface with no distinct morphological features.



**Fig. S2:** XRD pattern of an as-anodised MoO<sub>3</sub> thin film in 0.5 wt% NaF aqueous electrolyte at an anodisation voltage of 2.5 V for 20 min

The as-anodised, A-MoO<sub>3</sub> thin film is amorphous, as shown by the XRD pattern in Figure S2



**Fig. S3:** Chrono-amperometry of  $\text{Bi}_2\text{MoO}_6/\text{MoO}_3$  thin film under visible light illumination under an applied bias of 0.1 V vs Ag/AgCl in 0.1 M  $\text{Na}_2\text{SO}_4$  aq. electrolyte, Pt as counter electrode, illumination source: 300 W Xe lamp with a cut off filter,  $\lambda \geq 420$ . Light-on cycle: 50 s.

The chrono-amperometry profile of the  $\text{Bi}_2\text{MoO}_6/\text{MoO}_3$  thin film under a potential of 0.1 V vs Ag/AgCl and visible light illumination ( $\lambda \geq 420$  nm) is shown in Fig. S3. The  $\text{Bi}_2\text{MoO}_6/\text{MoO}_3$  thin film exhibited four reproducible photocurrent cycles, showing a magnitude of  $94 \mu\text{Acm}^{-2}$ , which illustrates its stability and visible light activity.

#### **Details of calculation of expected $\text{O}_2$ from matching photocurrent magnitude under assumption of 100% Faradaic efficiency**

The expected amount of  $\text{O}_2$  gas is calculated from the measured photocurrent under the assumption of 100% Faradaic conversion efficiency, as shown in Eq 1 – 4. The amount of electric charge,  $Q$ , generated by the photocurrent,  $I$ , can be calculated using the integral of  $I$  with respect to time, as shown in Eq. (1). The water oxidation reaction, involves the transfer of 4 moles of electrons per mole of  $\text{O}_2$  produced, as shown in Eq. (2). By applying Faraday's constant, as shown in Eq (3), the expected amount of  $\text{O}_2$  gas produced at the measured photocurrent level can be calculated using Eq (4).

$$Q = \int_0^t I dt \quad \text{Eq. (1)}$$

Where,  $Q$  is the electric charge (C),  $I$  is the photocurrent (A) and  $t$  is the time (s);



$$1 \text{ Faraday} = 9.6485 \times 10^4, \text{ coulombs/faraday } (C \text{ mol}^{-1}) \quad \text{Eq. (3)}$$

$$n_{O_2} = \frac{Q}{n_{e^-} \times F} \quad \text{Eq. (4)}$$

Where,  $n_{O_2}$  is the expected amount of oxygen evolved ( $\mu\text{mol}$ ),  $Q$  is the electric charge (C),  $n_{e^-}$  is the number of moles of electrons consumed for every mole of  $O_2$  evolved, (hence,  $n_{e^-} = 4$ ) and  $F$  is the Faraday's constant as shown in Eq. (3).

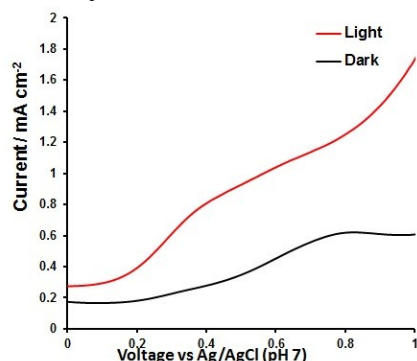
### Origin of dark current in $\text{MoO}_3$ and $\text{Bi}_2\text{MoO}_6/\text{MoO}_3$ films

The observed dark current was not attributed to parasitic oxidation of the Mo foil. If the dark current was due to the metallic Mo foil under +ve applied bias, the phenomenon would be analogous to anodisation of the metal foil, i.e. electrochemical oxidation of metal to generate current in the dark. During anodic oxidation of a metal foil, the current profile will steadily decay over time (in the range from 10 mins to hours), as shown in the figure below. The steady decay of current is due to the formation of an oxide barrier layer on the metal foil, thus leading to the higher resistance of the electrochemical system <sup>[1]</sup>. We are one of the active research groups in the anodisation field and such current profiles are typically observed in various kinds of metal foil (e.g. Mo, W, Ti)<sup>[1]</sup>. However, the current profile of our activity measurement (Fig. 6) is stable over eight hours under 1 V vs Ag/AgCl. A decay of current due to the formation of an oxide barrier layer was not observed. Therefore, oxidative corrosion of the metal foil is unlikely. Furthermore, in an unstable photoanode experiencing parasitic oxidation of the underlying metal, Faradaic efficiency for oxygen evolution will not reach 100% as observed in our work (because the holes generated are consumed to oxidise the metal instead of the water).

We attribute the dark current to the intrinsic characteristics of  $\text{MoO}_3$ .  $\text{MoO}_3$  has been used as the cathode material in Li-battery systems <sup>[2]</sup> as  $\text{MoO}_3$  has a layered structure which facilitates the intercalation/deintercalation of  $\text{Li}^+$ . In this work, the  $\text{MoO}_3$  and  $\text{Bi}_2\text{MoO}_6/\text{MoO}_3$  films exhibited a +ve dark current from  $-0.7$  to  $+0.5$  V vs Ag/AgCl. When the same current profile is presented using  $\text{Li}^+/\text{Li}$  as the reference electrode, the resulting voltage range (2.1-3.3 V vs  $\text{Li}^+/\text{Li}$ ) typically yields a dark current which derives from the process of cation deintercalation <sup>[2]</sup> (Note that cation intercalation into  $\text{MoO}_3$  can be induced by the photoexcited electrons within  $\text{MoO}_3$  or by electrochemical intercalation during the cathodic CV scan. These phenomena have been reported when using  $\text{WO}_3$  and  $\text{MoO}_3$ <sup>[1d, 3]</sup>. Please see the references below for further details).

Hence, the dark current observed in this work is attributed to the intrinsic property of the underlying  $\text{MoO}_3$  but not from the Mo foil. As experimental evidence, we also coated a layer of  $\text{MoO}_3$  particles on a conducting carbon fibre electrode (Toray paper) to avoid the presence of Mo foil. As can be seen in Figure S4, the  $\text{MoO}_3$ -coated carbon fibre film provides a dark

current across the window of the applied voltage. On the other hand, the current generated under illumination (Figure S4 and Figure 6 in the manuscript) is significantly distinct from the dark current and thus the photoactivity can be evaluated.



**Figure S4.** Dark and light current profiles of MoO<sub>3</sub> particles coated on conducting carbon fibre paper.

## **References**

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