Electronic Supplementary Material (ESI) for Energy & Environmental Science
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*Electronic Supplementary Information*

# A $H_2$-evolving photocathode based on direct sensitization of $MoS_3$ with an organic photovoltaic cell

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## S-1. Details of experimental procedures

Concentrations of suspensions were determined by thermogravimetric analysis (TGA) with a Q50 V20.10 Build 36 device, with a platinum pan and nitrogen as balance and sample gas.

XPS data were collected by an Axis Ultra DLD (Kratos Analytical) under ultra-high vacuum conditions ($<10^{-8}$ Torr), using a monochromatic Al Kα X-ray source (1486.6 eV). The spectra were analyzed with Avantage software (Thermofisher). For insulating substrates, an unfocused electron cloud was used to overcompensate the charges. Before and after each measurement, the Au $4f_{7/2}$ peak was measured on a pure gold sample determining the binding energy shift and allowing the recalibration of energies.
For quantification, relative sensitivity factors from the supplier were used.

Structural properties were determined by Transmission Electronic Microscopy. Images were taken on a TECNAI 120 Spirit G2 from FEI and a CCD camera on column bottom Orius from Gatan in 4K steps. Energy-dispersive analysis (EDX) was similarly carried out. The suspension was drop-cast on a copper Delta Microscopy TEM grid coated with carbon.

The thickness of the films was determined by measuring the profile of the surfaces previously scratched with a razor blade, using an Ambios Technology Inc. profilometer, model XP-200 Sylus.

The morphology of the oxide films electrodes was investigated by SEM Hitachi S-4500.

Electrochemical measurements were recorded by BioLogic Model VSP 0254. A three-electrode configuration was used. For polarisation and electrolysis measurements, a glassy carbon plate was used as the auxiliary electrode and an Ag/AgCl (KCl sat.) electrode was used as the reference electrode. Potentials are quoted against the Reversible Hydrogen Electrode (i.e. the apparent standard potential of the $H^+/H_2$ couple at the given pH). The potential of the Reversible Hydrogen Electrode (RHE) is defined as $E_{RHE} = -0.059$ pH. Thus potentials measured versus the Ag/AgCl electrode can be converted versus the RHE by using the following formula: $E_{vs\ RHE} = E_{vs\ Ag/AgCl} + E°_{Ag/AgCl} + 0.059$ pH. With a pH close to 0, the formula becomes: $E_{vs\ RHE} = E_{vs\ Ag/AgCl} + 0.21$ (V). The $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple ($E^0$ = 0.56 V vs. SHE in HCl 0.1 M)[1] has then been used for the standardisation of the measurements.
Impedance spectra were carried out in $H_2SO_4$ 0.5 M at -0.4 V vs. Ag/AgCl (close to the onset potential), from 100 000 Hz to 0.1 Hz (or 0.01 Hz).

During controlled-potential coulometry (electrolysis) experiments, we analysed $H_2$ evolution with a Perkin-Elmer Clarus 500 gas chromatograph equipped with a porapack Q 80/100 column (6’ 1/8”) thermostated at 40°C and a TCD detector thermostated at 100°C. Nitrogen under 1 bar was used as the carrier gas. An aliquot (50 µL) of the head-space volume of the cell was injected and analysed. The amount of $H_2$ in this sample was quantified thanks to a calibration curve and the total amount of evolved $H_2$ was determined knowing the volume of the head-space of the cell and neglecting the amount of $H_2$ solubilized in the aqueous electrolyte.

Deposition of layers by spray-casting was carried out by an Aztek A470 airbrush with a 9344C nozzle and nitrogen at an operating pressure of 2.5 bar. The substrate was fixed on a vertical heated stand.

Deposition of layers by spin-coating was carried out by a Laurell Technologies Corporation device, model WS-400B-6NPP/LITE/OND, under $N_2$ purge. Typical parameters were 2000/4/60 (from 0 to 2000 rpm in 4s, and dwelling time 60s).

The samples were illuminated with a 300 W xenon lamp (Oriel, ozone free) operated at 280 W coupled with a water-filled Spectra-Physics 6123NS liquid filter for elimination of IR radiations, a Spectra-Physics 59472 UV cut-off filter ($\lambda$ >400 nm) and a 0.5 $cm^2$ circular mask. Irradiance at the substrate surface was measured to 600 $mW.cm^{-2}$ (~6 sun) thanks to a Coherent PowerMax-USB PM150-50C Power Sensor.

## S-2. Supplementary Figures

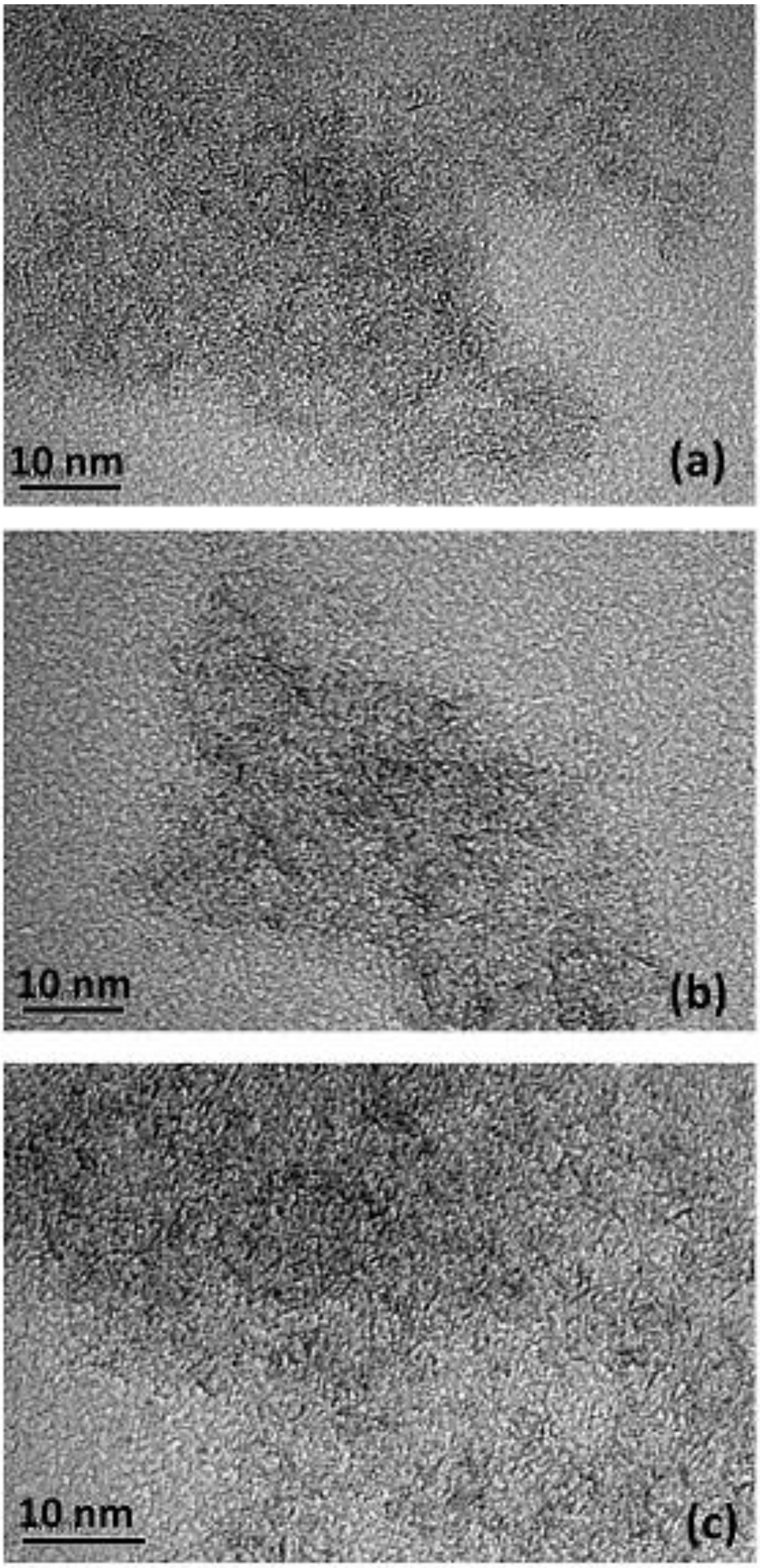

**Fig. S1** TEM images of $MoS_3$ nanoparticles. The pH at the end of the precipitation was (a) pH = 2.0, (b) pH = 2.7, (c) pH = 3.5

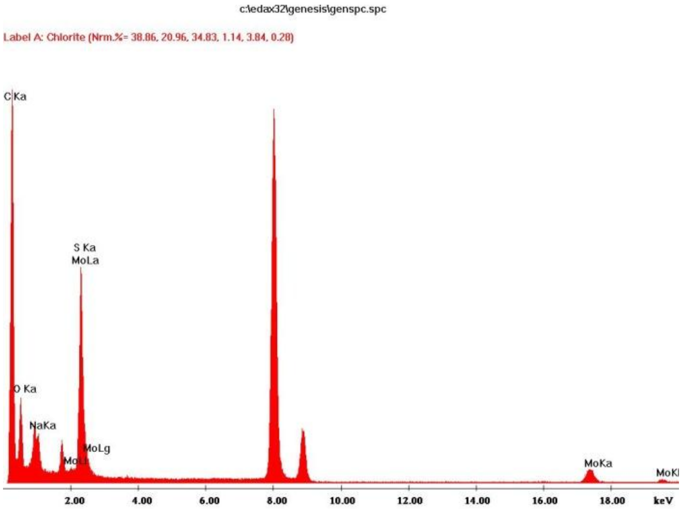

**Fig. S2** EDX spectrum of $MoS_3$ particles (final pH = 2.7) deposited on a copper grid, measured on an aggregated area.

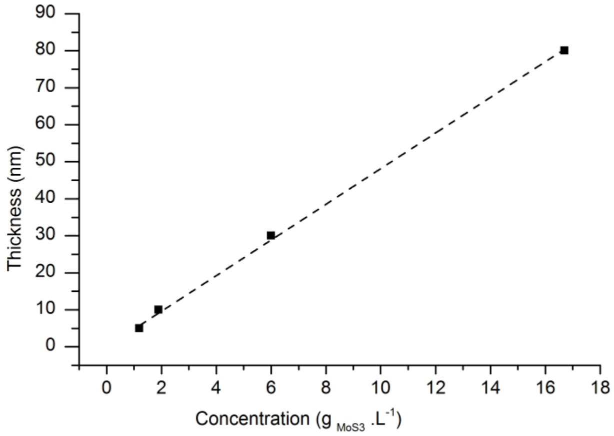

**Fig. S3** Thickness (determined by profilometry) of the films obtained by spin coating of $MoS_3$ suspensions in acetone with various concentrations.

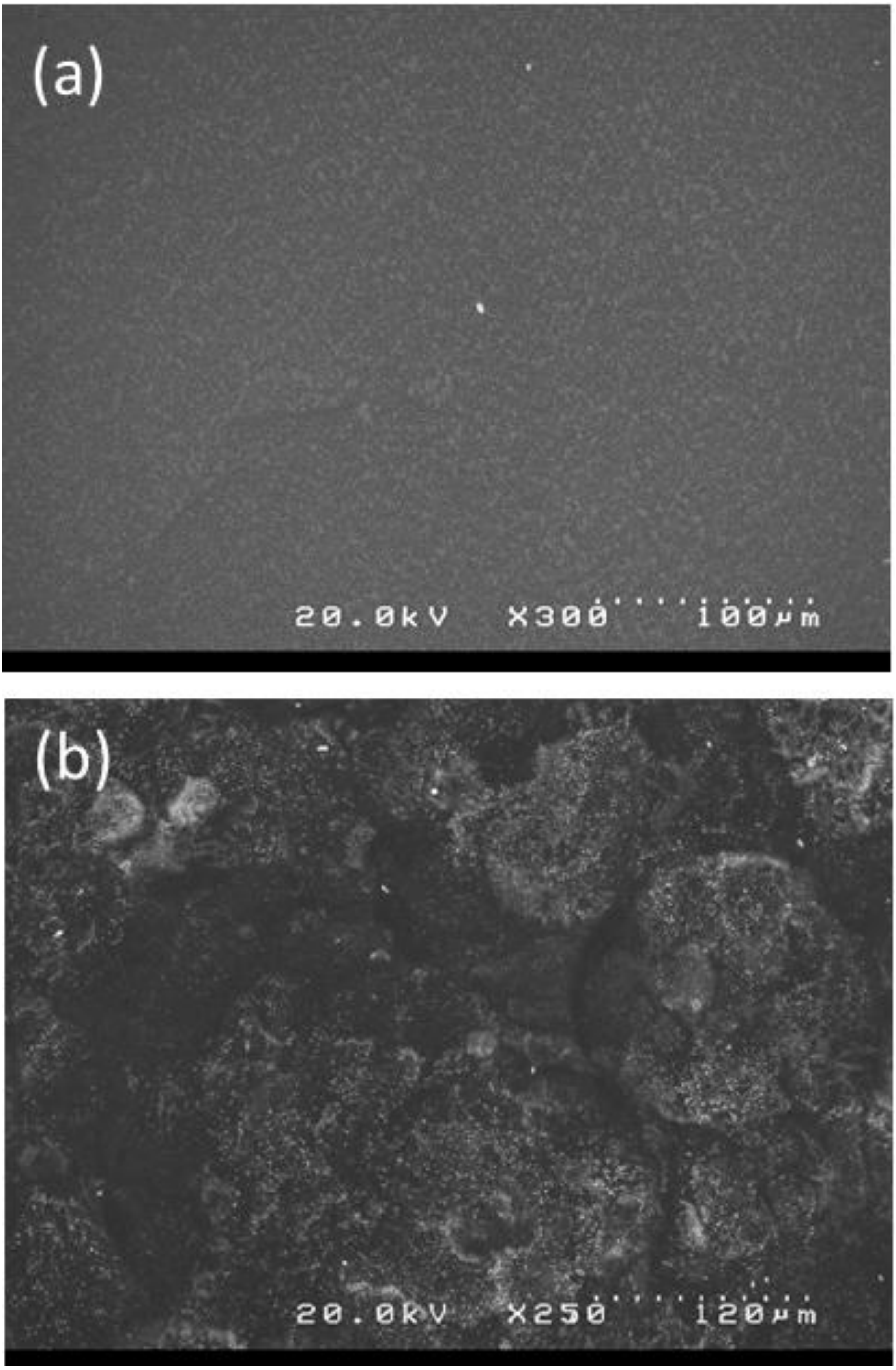

**Fig. S4** SEM images taken from a (a) spin-coated and (b) spray-cast film of $MoS_3$ deposited on ITO-coated glass substrates.

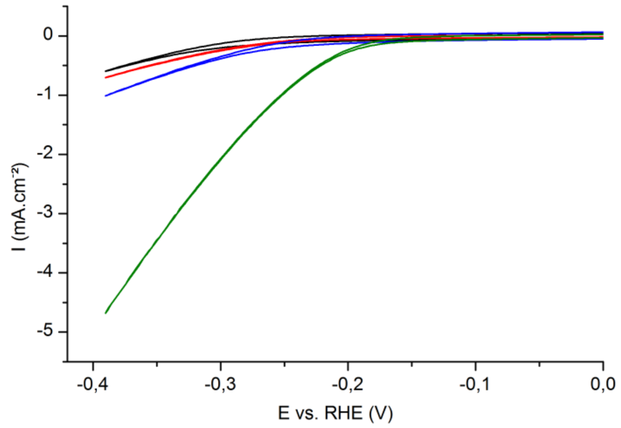

**Fig. S5** Cyclic voltammetry (50 mV.s$^{-1}$) of $MoS_3$ films (spin-coating, 30 nm, on ITO-coated glass substrates), in electrolyte with decreasing $H_2SO_4$ concentration by dilution in $Na_2SO_4$ 0.1 M (green: 0.5 M, blue: 0.1 M, red: 0.05 M, black: 0.01 M). Electrode area: 0.5 cm².

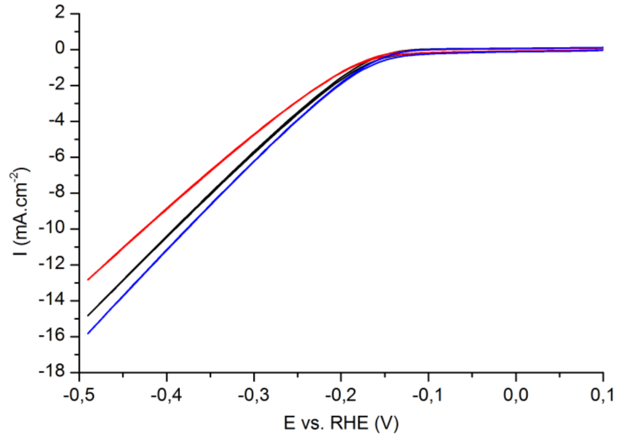

**Fig. S6** Cyclic voltammetry at 50 mV.s$^{-1}$ in $H_2SO_4$ 0.5 M of $MoS_3$ films (30 nm, deposition by spin coating on an ITO-coated glass substrate) for a synthesis ending at pH 2 (black), 2.7 (red) and 3.5 (blue). Electrode area: 0.5 cm².

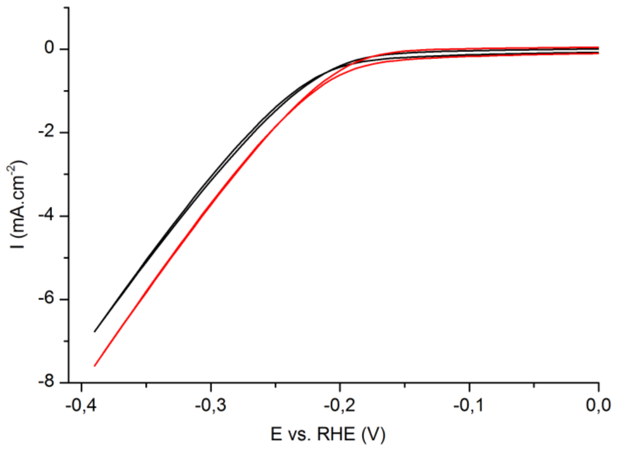

**Fig. S7** Cyclic voltammetry (50 mV.s$^{-1}$), second cycle, of $MoS_3$ films deposited by spray (black line, 30nm) and spin-coating (red line, 30nm), in $H_2SO_4$ 0.5 M. Electrode area: 0.5 cm².

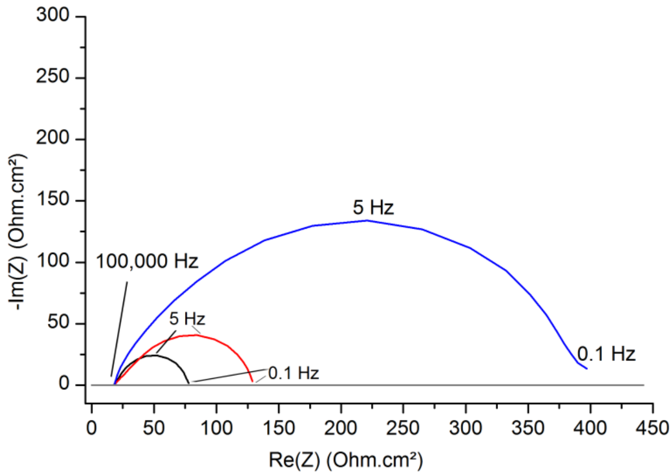

**Fig. S8** Impedance spectra for three spray-cast films of $MoS_3$ with different thicknesses, at a bias voltage of –0.4 V vs. Ag/AgCl. Black line: 40 ± 20 nm; red line: 100 ± 30 nm; blue line: 300 ± 100 nm. Electrode surface area: 0.5 cm².

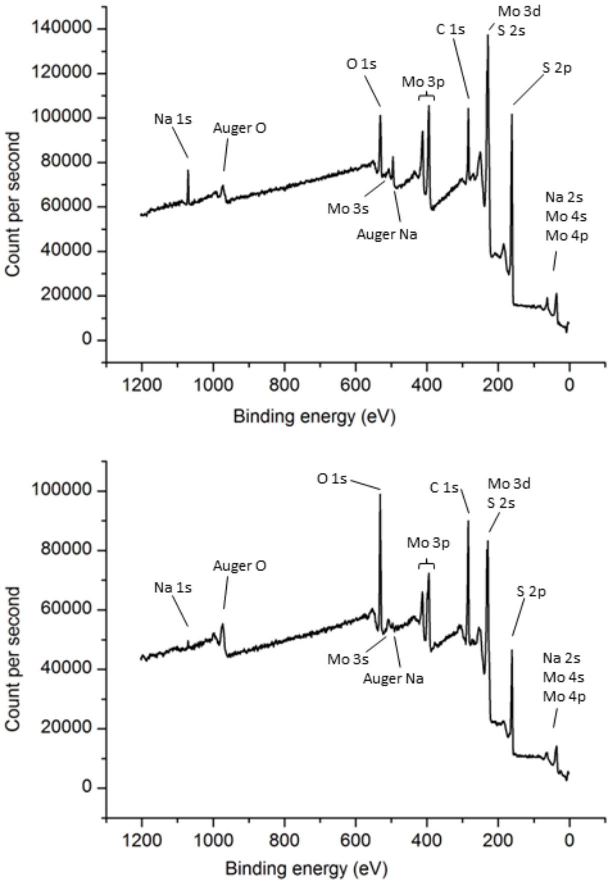

**Fig. S9** X-ray photoelectron survey spectra of spin-coated $MoS_3$ films (final pH = 3) before (top) and after (down) cyclic voltammetry (2 cycles at 50 $mV.s^{-1}$, from 0 to -0.4 V vs. RHE).

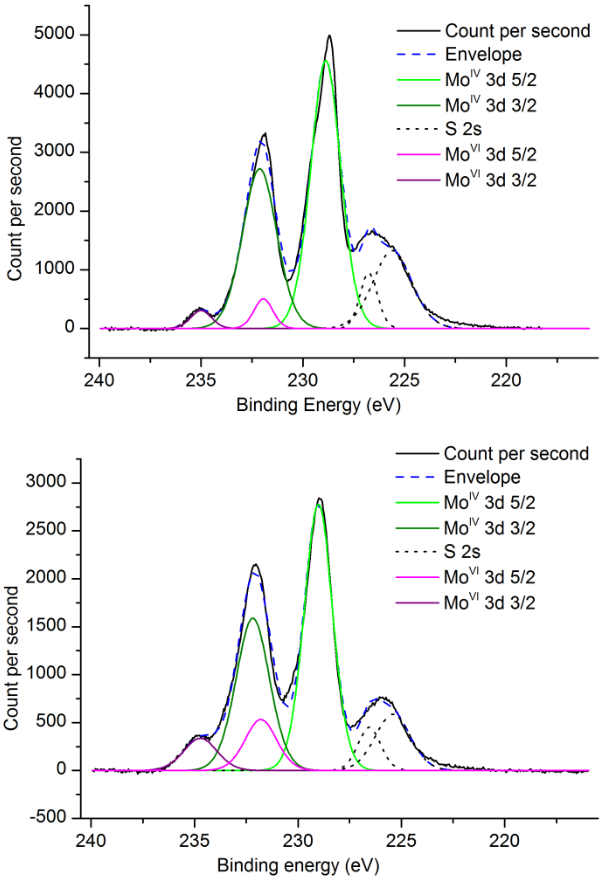

**Fig. S10** XPS spectra of Mo 3d (same sample as survey), before (up) and after (down) cyclic voltammetry as in Figure S8 (black solid line). $Mo^{IV}$ 3d 5/2 (light green line), $Mo^{IV}$ 3d 3/2 (dark green line), $Mo^{VI}$ 3d 5/2 (light purple line), $Mo^{VI}$ 3d 3/2 (dark purple line), S 2s (black dots), and envelope (blue dashes). After CV, the area of $Mo^{IV}$ and $Mo^{VI}$ signals both decreased, indicating that Mo is released in aqueous media which may be the reason for the observed decrease in activity. In the same time, the $Mo^{IV}$ to $Mo^{VI}$ ratio decreases from 16 to 5, and the S:Mo ratio varies from 2.85 to 2.1.

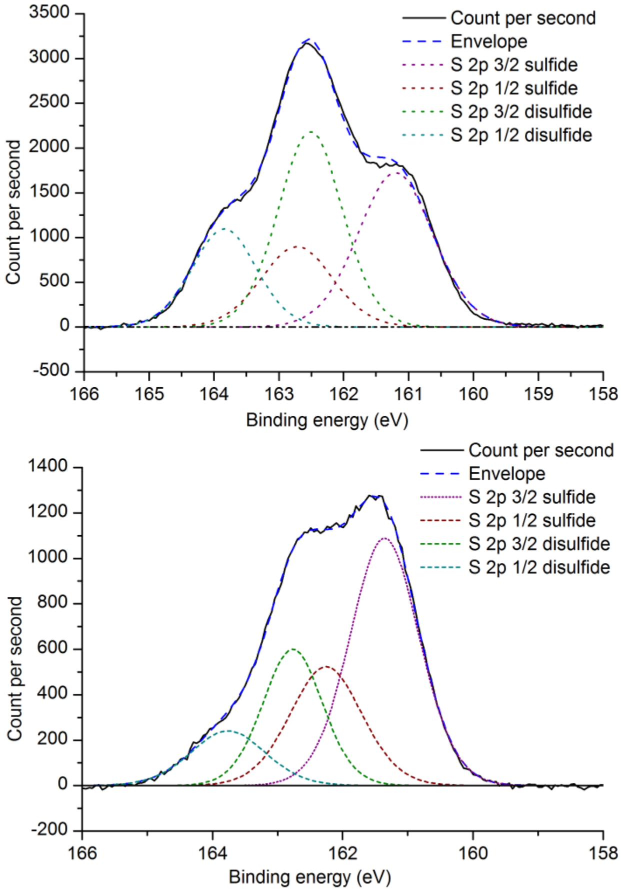

**Fig. S11** XPS spectra of S 2p (same sample as survey), before (up) and after (down) cyclic voltammetry as in Figure S8 (black solid line). S 2p 3/2 of sulfide $S^{2-}$ (pink dots), S 2p ½ of sulfide $S^{2-}$ (red dots), S 2p 3/2 of disulfide$S_2^{2-}$ (green dots), S 2p ½ of disulfide $S_2^{2-}$ (light blue dots), and envelope (blue dashes). After CV, the sulfide to disulfide ratio increases from 1.1 to 2.1

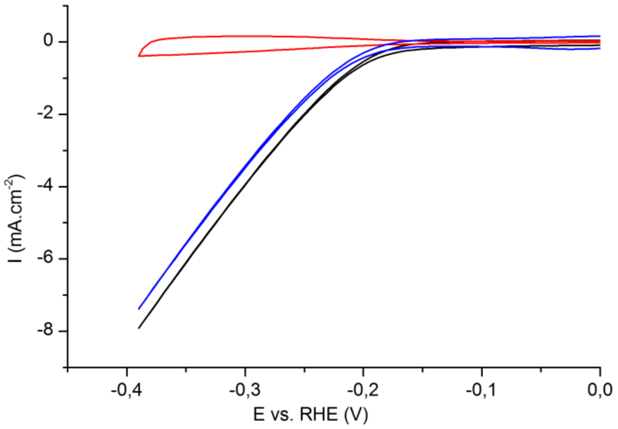

**Fig. S12** Cyclic voltammetry (50 mV.s$^{-1}$) of spin coated films of $MoS_3$ (20 nm, black), $TiO_2$ (80 nm, red) and mixed $MoS_3$: $TiO_2$ (100 ± 20 nm, blue). Electrode area: 0.5 cm².

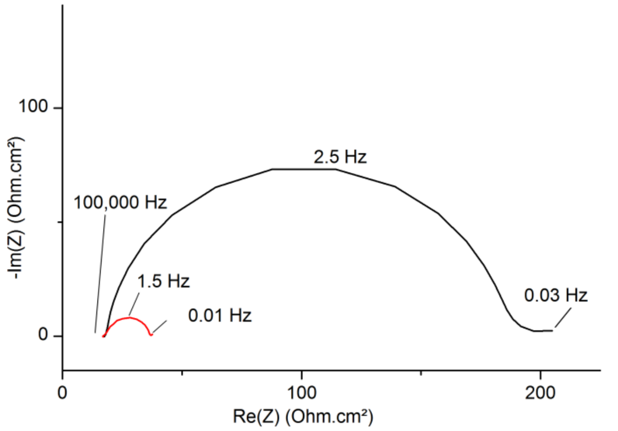

**Fig. S13** Impedance spectra of spin coated films of $MoS_3$ (thickness = 30 nm, black line) and mixed $TiO_2$:$MoS_3$ (thickness = 80 nm, red line), at a bias voltage of –0.4 V vs. Ag/AgCl. Electrode area: 0.5 cm².

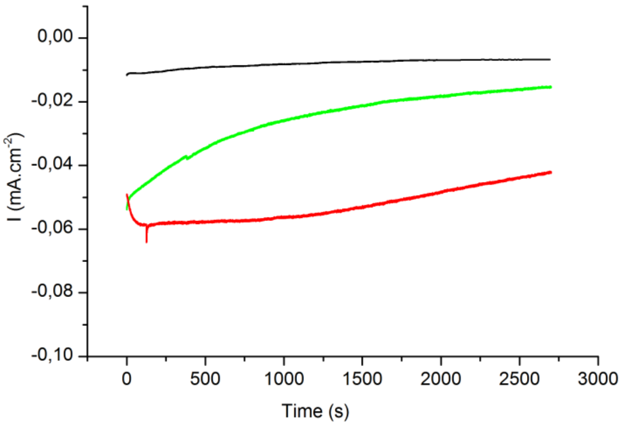

**Fig. S14** Electrolysis at +0.16 V vs. RHE of photocathodes in $H_2SO_4$ 0.5 M, under illumination. Black line: P3HT:PCBM; green line: $MoS_3$ / P3HT:PCBM ; red line : $MoS_3$:$TiO_2$ / P3HT/PCBM. Electrode area: 0.5 cm².

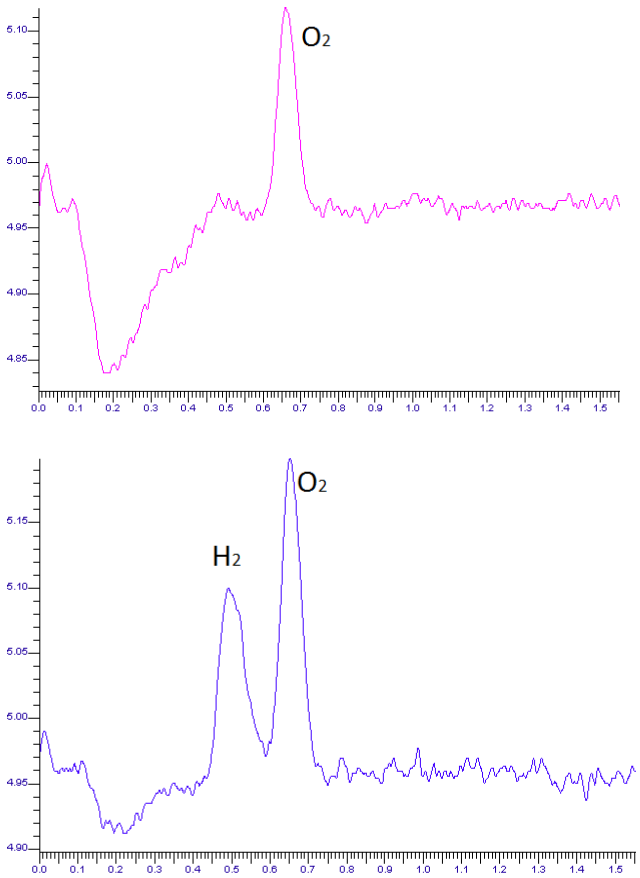

**Fig. S15** $H_2$ detection (gas chromatography) before and after electrolysis during 30 min at +0.16 V vs. RHE. The sample of gas was taken from the gas above the electrolyte in the test cell.

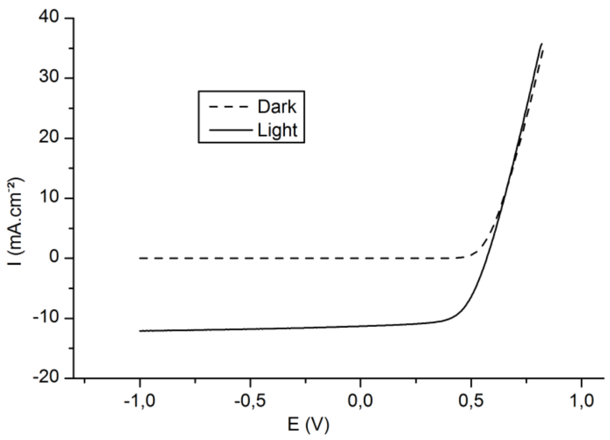

**Fig. S16** Current-voltage curves of P3HT:PCBM solar cells used in our photocathodes. The current–voltage characteristics are measured with a Keithley 2635 system Source Meter under nitrogen atmosphere. Solar cell performances are characterized under various light intensity of AM 1.5 illumination with an Atlas Solar Constant 575PV simulator. The sample is illuminated through glass substrate. Exposed area: 0.28 cm².

1. Allen J. Bard and Larry R. Faulkner, *Electrochemical methods, Fundamentals and Applications*, John Wiley & Sons, Inc., 2nd edition, 2001