

Electronic Supplementary Information

# All solution-processed organic photocathodes with increased efficiency and stability via the tuning of the hole-extracting layer

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Tiphaine Bourgeteau,<sup>a</sup> Denis Tondelier,<sup>b</sup> Bernard Geffroy,<sup>a,b</sup> Romain Brisse,<sup>a</sup> Stéphane Campidelli,<sup>a</sup> Renaud Cornut,<sup>a</sup> and Bruno Jusselme<sup>a</sup>

<sup>a</sup> Laboratory of Innovation in Surface Chemistry and Nanosciences (LICSEN), NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette Cedex, France.

Email: [bruno.jusselme@cea.fr](mailto:bruno.jusselme@cea.fr)

Fax: +33 169086462 ; Tel.: +33 169089191

<sup>b</sup> Laboratoire de Physique des Interfaces et Couches Minces, Ecole Polytechnique, CNRS, 91128 Palaiseau, France

## S-1. Details of experimental procedures

### S-1-A. Materials

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 Stylus.

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 3.5 M) 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), which is the electrochemical potential of the solution under conditions of hydrogen evolution at the photocathode. The potential of the Reversible Hydrogen Electrode (RHE) is defined as  $E_{RHE} = -0.059 \text{ pH}$ . Thus potentials measured versus the Ag/AgCl electrode can be converted versus the RHE by using the following formula:  $E_{vs \text{ RHE}} = E_{vs \text{ Ag/AgCl}} + E^{\circ}_{\text{Ag/AgCl}} + 0.059 \text{ pH}$ . With a pH of 0, the formula becomes:  $E_{vs \text{ RHE}} = E_{vs \text{ Ag/AgCl}} + 0.205 \text{ (V)}$ . The  $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$  couple ( $E^0 = 0.56 \text{ V vs. SHE in HCl } 0.1 \text{ M}$ )<sup>1</sup> has then been used for the standardization of the measurements.

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 (85 °C).

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.

The samples were illuminated with a 200 W mercury-xenon lamp (Oriel, ozone free) operated at 101 W coupled with a Spectra-Physics 59472 UV cut-off filter ( $\lambda > 400 \text{ nm}$ ). Irradiance at the substrate surface was measured to  $\sim 100 \text{ mW.cm}^{-2}$  thanks to a Coherent PowerMax-USB PM150-50C Power Sensor.

## S-1-B. Methods

- a. Cleaning procedure for ITO-coated glass substrates
- b. Preparation of rGO thin films
- c. Synthesis and deposition of NiO<sub>x</sub> thin films
- d. Synthesis and deposition of MoO<sub>x</sub> thin films
- e. Fabrication of organic solar cells
- f. Synthesis and deposition of MoS<sub>3</sub> nanoparticles
- g. Fabrication of the photocathodes

### a. Cleaning procedure for ITO-coated glass substrates

ITO substrates were placed in a sample holder, and sonicated in DI water, acetone and isopropanol, ending by 15 min in a UV-ozone cleaner.

### b. Preparation of rGO thin films

First, graphene oxide (GO) was prepared using the standard Hummers<sup>2,3</sup> method followed by spontaneous exfoliation in water using successive centrifugation steps. The GO film was formed through the bubble deposition method, which is described in a previous report.<sup>4</sup> Substrates with deposited GO were dried in a nitrogen flow and thermally annealed under high vacuum at 350 °C for 90 min to give rGO.

### c. Synthesis and deposition of NiO<sub>x</sub> thin films

**Synthesis.** NiO<sub>x</sub> precursor was synthesized according to a reported procedure.<sup>5</sup> Nickel acetate (1.245 g, 5 mmol, 1.00 eq.) was dissolved in absolute ethanol (50 mL) with monoethanolamine (305 mg, 5 mmol, 1.00 eq.). The solution was stirred for 4 h in a closed vial at 70 °C until complete dissolution. After cooling down, it was stored in a refrigerator (4 °C).

**Deposition.** Prior to deposition, the precursor was diluted by 4 in absolute ethanol in a 4 mL glass vial. It was then spin-coated at 4000 rpm / 5 s ramp / 90 s (5 s ramp to 4000 rpm, during 90 s) in air or in the glovebox using an Eppendorf pipette (80 μL) followed by immediate annealing at 110 °C for 10 s. Contacts were cleaned with a cotton bud with ethanol. The substrates were then annealed at 320 °C in air for 30 min. After removing the dust particles with N<sub>2</sub> stream, they were submitted to UV-ozone treatment for 15 min, after which they had a grey color, disappearing quickly. Again, a short N<sub>2</sub> flux was used to remove dust. They were transferred as quickly as possible in the glovebox and immediately used for P3HT:PCBM deposition.

#### d. Synthesis and deposition of MoO<sub>x</sub> thin films

**Synthesis.** A solution of molybdenum tricarbonyl trispropionitrile [Mo(CO)<sub>3</sub>(EtCN)<sub>3</sub>] was prepared in acetonitrile at a concentration of 0.05 M.<sup>6</sup> The solution was stirred for 24 h in a closed vial in the glovebox and was left to settle.

**Deposition.** The supernatant was taken with a syringe, and a PVDF filter (0.45 μm) was used to remove undissolved material. It was deposited by spin-coating in the glovebox at 5000 rpm / 5 s ramp / 60 s. After contact cleaning (cotton bud with acetone), the samples were annealed in air at 150 °C for 20 min to remove the organic part.

#### e. Fabrication of organic solar cells.

**PEDOT:PSS.** ITO-coated glass substrates are cleaned as described before, ending by 15 min of UV-ozone. A short N<sub>2</sub> stream is applied to remove dust particles and PEDOT:PSS is deposited by spin-coating in air at 3000 rpm / 5 s ramp / 30 s + 5000/5/30 resulting in a 40 nm thick layer. A PVDF syringe filter (45 μm) is used to remove undesired particles from the PEDOT:PSS suspension. Gold contact pads previously deposited on the substrate are cleaned with a cotton bud and DI water.

PEDOT:PSS is then heated at 150°C for 10 min in air, and transferred immediately in the glovebox.

**P3HT:PC<sub>60</sub>BM.** P3HT and PC<sub>60</sub>BM are weighed in the same brown vial in air. The P3HT:PC<sub>60</sub>BM weight ratio is 1:1 for a concentration of 25 mg mL<sup>-1</sup> of each material. Anhydrous *ortho*-dichlorobenzene is added in the glovebox. The solution is stirred 2 h at 55 °C, then overnight at room temperature, and 1 h at 55 °C prior to deposition. The solution is spin-coated in the glovebox at 1500 rpm / 5 s ramp / 60 s, using a PVDF filter (45 μm, 13 mm diameter). Contacts are cleaned with a cotton bud and *ortho*-DCB. Annealing is carried out before evaporating the metallic cathode. When photocathodes are prepared, annealing is carried out after the deposition of the catalyst.

**Cathode evaporation.** LiF (1.2 nm) and Al (100 nm) were evaporated in a Joule evaporator under vacuum (< 10<sup>-6</sup> mbar). The electrode area was 0.28 cm<sup>2</sup>.

#### f. Synthesis and deposition of MoS<sub>3</sub> nanoparticles

MoS<sub>3</sub> particles were synthesized according to a procedure reported by Merki et al.<sup>7</sup> In a typical preparation, molybdenum trioxide (MoO<sub>3</sub>, 0.51 g, 3.48 mmol) was added to an aqueous solution of sodium sulfide (1.34 g, 17.37 mmol of anhydrous Na<sub>2</sub>S in 125 mL of water) to form a bright yellow solution. This solution was then kept under vigorous stirring

while 6.0 M aqueous HCl was added slowly (10 minutes) until the pH was below 3. At first, darkening of the solution was observed. After the addition of acid, the solution was boiled for 30 minutes, resulting in an increase of the pH by 1 unit. After being cooled to ambient temperature, the suspension was centrifuged, the supernatant liquid was thrown away and particles were dispersed in DI water. This process was repeated twice to wash the particles. Then it was repeated twice in ethanol, and once in ether, to remove as much water as possible. Finally, without drying the precipitate, the particles were dispersed in acetone and sonicated for 10 minutes using an ultrasonic horn at 20 kHz.

The MoS<sub>3</sub> sol was deposited by spray casting (vertical holder heated at 80 °C, in air).

#### **g. Fabrication of the photocathodes.**

Each layer has been deposited as described in the previous sections, but some processes have been slightly changed so that the processes of all successive depositions are compatible.

A masking tape (electroplating tape) is used to define the electrochemical area (a disc of a specific area). This tape is chemically resistant and was applied onto the substrate before spray-coating MoS<sub>3</sub>, with gentle pressing with pliers all around the disc to ensure the adhesion of the tape.

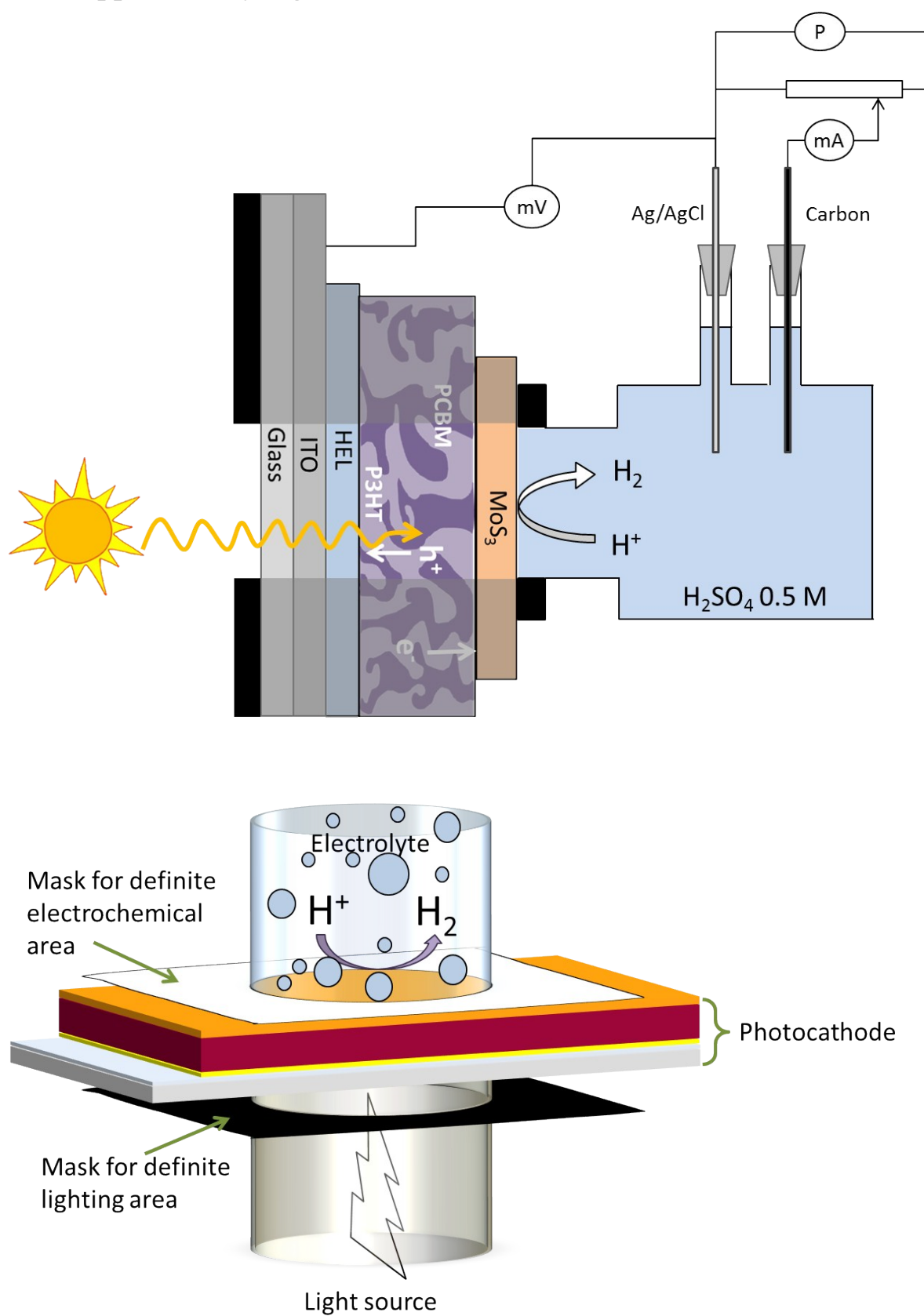
**ITO/PEDOT:PSS/P3HT:PCBM/MoS<sub>3</sub>.** PEDOT:PSS and P3HT:PCBM are deposited as described previously, without annealing. The electroplating tape is pasted and MoS<sub>3</sub> is deposited by spray-coating in air. The devices are finally annealed in the glovebox at 130 °C for 20 min.

**ITO/rGO/P3HT:PCBM/MoS<sub>3</sub>.** rGO as described before, P3HT:PCBM (without annealing), MoS<sub>3</sub> by spray in air, annealing 20 min at 140 °C.

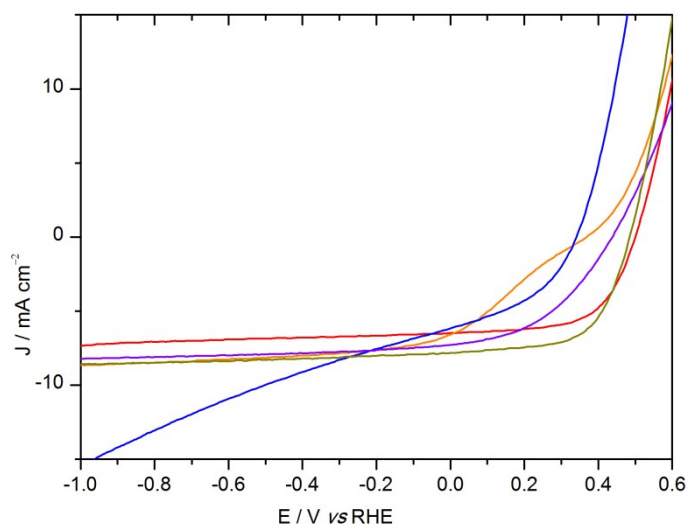
**ITO/NiO<sub>x</sub>/P3HT:PCBM/MoS<sub>3</sub>.** NiO<sub>x</sub> as described before, P3HT:PCBM (without annealing), MoS<sub>3</sub> by spray in air, annealing 20 min at 140 °C.

**ITO/MoO<sub>x</sub>/P3HT:PCBM/MoS<sub>3</sub>.** MoO<sub>x</sub> as described before, P3HT:PCBM (without annealing), MoS<sub>3</sub> by spray in air, annealing 20 min at 140 °C.

## S-2. Supplementary Figures



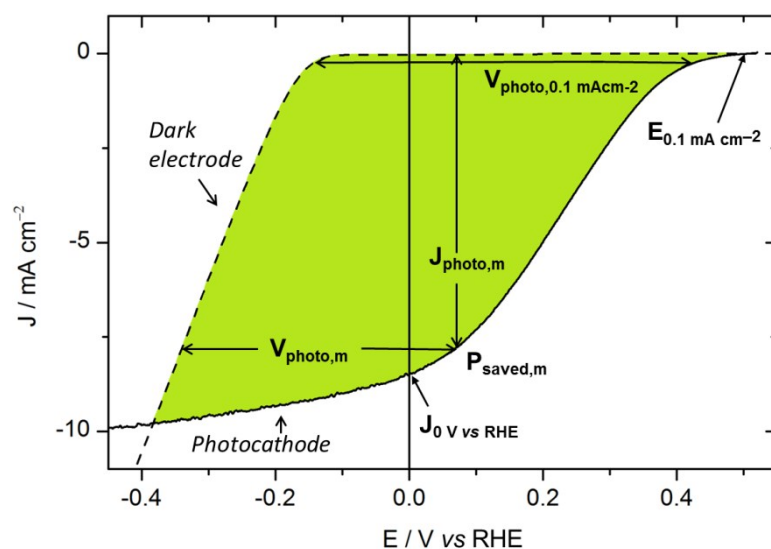
**Fig. S1.** Architecture of the MoS<sub>3</sub>/P3HT:PCBM H<sub>2</sub>-evolving photocathode inserted in the cell used in this study for photo-electrochemical measurements.



**Fig. S2.** Current density – voltage curves of:

- ITO \ P3HT:PCBM \ LiF \ Al
- ITO \ PEDOT:PSS \ P3HT:PCBM \ LiF \ Al
- ITO \ rGO \ P3HT:PCBM \ LiF \ Al
- ITO \ NiO<sub>x</sub> \ P3HT:PCBM \ LiF \ Al
- ITO \ MoO<sub>x</sub> \ P3HT:PCBM \ LiF \ Al

Electrode area: 0.28 cm<sup>2</sup>.



**Fig. S3.** Current-voltage characteristic of a photocathode under illumination (black line) and of a dark cathode (black dashed line) made of the same electrocatalyst used for the photocathode.  $J_{0V \text{ vs RHE}}$  is the current density at 0 V vs RHE,  $E_{0.1 \text{ mA cm}^{-2}}$  the onset potential taken at a current density of 0.1 mA cm<sup>-2</sup>,  $V_{\text{photo},0.1 \text{ mA cm}^{-2}}$  the photovoltage taken at 0.1 mA cm<sup>-2</sup>, and  $P_{\text{saved},m}$  the maximum power of the photocathode compared to the dark electrode with the corresponding  $V_{\text{photo},m}$  and  $J_{\text{photo},m}$ .

## Evaluation of the photocathode performance:

The solar-to-hydrogen conversion efficiency is usually calculated in a two-electrode configuration in which the whole water splitting reaction is performed, without the support of external bias, according to equ. (1).<sup>8,9</sup>

$$STH = \left[ \eta_F \times \frac{|J_{SC} (mA cm^{-2})| \times 1.23 (V)}{P_{in} (mA cm^{-2})} \right]_{AM 1.5 G} \quad (1)$$

where  $J_{SC}$  is the short-circuit photocurrent density,  $\eta_F$  the Faradaic efficiency for hydrogen evolution, and  $P_{in}$  the incident illumination power density. However, to evaluate the properties of a single photoelectrode performing one of the two half-reactions, without the losses arising from the other components of the cell (overpotential requirement, mass transport limitations at the counter electrode, solution Ohmic losses between the working and counter electrode, etc.), the photoelectrode is tested in a three-electrode configuration. In this configuration, the polarization to drive the counter reaction at the counter electrode is not taken into account, and the current in the working photoelectrode is measured as a function of the photoelectrode potential against the third electrode (reference electrode). In this case, the ratiometric power-saved metric is an adapted figure-of-merit. It is defined as the ratio between  $P_{saved}$  and the input solar power  $P_{in}$ . At any current  $I$ ,  $P_{saved}$  is the product of the current  $I$  and the difference between the potential required to drive a half-reaction at a selected working electrode at this current in the dark,  $E_{dark}(I)$ , and the potential required to drive the same half reaction at the photoactive electrode in the light,  $E_{light}(I)$ .<sup>9</sup>

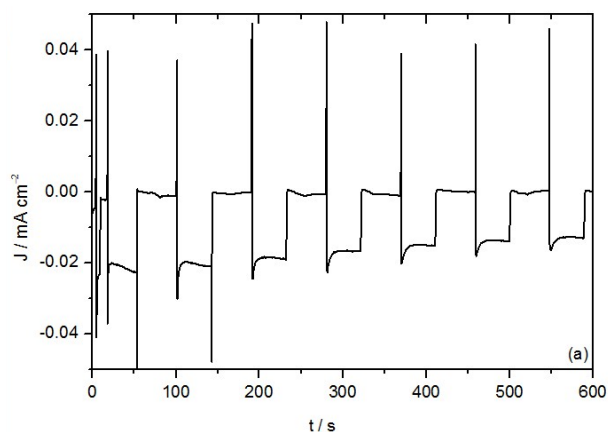
The power-saved metric relative to a non-photoactive dark electrode with an identical catalyst is measured in an three-electrode electrochemical cell. The photovoltage at a given current is thus evaluated from the potential under illumination compared to that of the same catalyst directly deposited on ITO, as presented in Fig. 8.  $\Phi_{saved, NPAC}$  (NPAC = non-photoactive, identical catalyst) is calculated following equ. (2):

$$\Phi_{saved, NPAC} = \eta_F \times \frac{|J_{photo, m}| \times [E_{light}(J_{photo, m}) - E_{dark}(J_{photo, m})]}{P_{in}} = \eta_F \times \frac{|J_{photo, m}| \times V_{photo, m}}{P_{in}} \quad (2)$$

where  $\eta_F$  is the Faradaic efficiency assumed to be 100 % again,  $P_{in}$  is the power of the incident illumination, and  $J_{photo, m}$  and  $V_{photo, m}$  are the photocurrent and photovoltage at the maximum power point.

In equ. (2),  $J_{photo}$  is obtained by calculating the difference between the current under illumination for a photocathode ( $J_{light}$ ) and the current of the corresponding catalyst ( $J_{dark}$ ). The photovoltage  $V_{photo}$  is the difference of the potential for the photocathode under illumination ( $E_{light}$ ) and the potential of the catalyst ( $E_{dark}$ ) to obtain the same current density. The maximum value is taken at this maximum power point which is referred to the activity of the catalyst in the dark.  $\Phi_{saved, NPAC}$  reflects the photovoltage and photocurrent of a photocathode independently from the overpotential requirement of the catalyst.





**Fig. S4.** Chronoamperometry at 0 V vs RHE in 0.5 M H<sub>2</sub>SO<sub>4</sub> with chopped visible light for an ITO/PEDOT:PSS/P3HT:PCBM/MoS<sub>3</sub> photocathode, cf. Fig. 6a. Electrode area: 0.28 cm<sup>2</sup>.

### References

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