

Supporting Information

All solution-processed, hybrid organic-inorganic photocathode for hydrogen evolution

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EXPERIMENTAL METHODS

Materials and photocathode fabrication

Photocathodes were fabricated on commercial fluorine-doped tin oxide (FTO) coated soda-lime glass substrates (Dyesol Italia SRL, dimensions 20 x 12 x 2.1 mm, FTO thickness 250 nm and sheet resistance 15 Ohm/sq). Substrates were cleaned by subsequent ultrasonic baths lasting 20 minutes each (alkaline detergent HELLMANEX 3%, ultrapure water, acetone, isopropyl alcohol). After each step the substrates were dried under a nitrogen flow. A subsequent overnight drying at 130° C allowed full solvent evaporation. An oxygen inductively coupled plasma treatment (DIENER, 40 Pa, 300 W for 20 minutes) completed the substrate preparation procedure.

Cuprous iodide (CuI, Sigma Aldrich, 97% purity) was dissolved in acetonitrile (Sigma Aldrich, ACS grade) at 10 g/L concentration. CuI deposition was carried out by means of spin coating in one single step (3000 rpm rotation speed for 60 sec). Poly(3-hexylthiophene-2,5-diyl) (rr-P3HT, purchased from Sigma Aldrich and used without further purification, molecular weight MW 15000 - 45000, purity 99.995%) and fullerene derivative [6,6]-Phenyl C61 butyric acid methyl ester (PCBM, purchased from Nano-C Inc.) were individually dissolved in chlorobenzene (Sigma Aldrich, ACS grade) and then mixed at 1:1 wt. ratio and 25 g/L on a polymer basis. Blend solution was stirred overnight at 50° C. The active layer was spin-coated on top of the CuI layer in a two-step process (800 rpm for 3 sec, followed by 1600 rpm for 60 sec).

Organic-based TiO_x nanoparticles (TiO_{x(org)}) were synthesized according to ref.¹. Titanium tetraisopropoxide (TTIP 97%, Sigma-Aldrich) was dissolved in a mixture ethanol/isopropanol (5:5 mL) to provide a concentration of 0.05 mol/L. The solution was stirred for 5 minutes and then concentrated HCl was added as acid catalyst. The water present in the concentrated HCl initial solution results in a H₂O/TTIP molar ratio of 0.82. The precursor solution was stirred for 72 hours at room temperature in a sealed vial. This solution was spin coated on top of BHJ surface at 1000 rpm

¹ Haro, M.; Solis, C.; Molina, G.; Otero, L.; Bisquert, J.; Gimenez, S.; Guerrero, A. Toward Stable Solar Hydrogen Generation Using Organic Photoelectrochemical Cells. *J. Phys. Chem. C* 2015, 119, 6488-6494

for 1 min and kept a Petri dish in ambient conditions for 2 h to enhance hydrolysis of TiO_x network.

A thermal treatment at 85 °C for 10 min in air was finally applied.

Aqueous-based TiO_2 nanoparticles ($\text{TiO}_{2(\text{aq})}$) were synthesized according to a modified sol-gel protocol.² A mixture of 15 mL of TTIP (97%, Sigma-Aldrich) and 2.5 ml of ethanol was added drop wise to 90 ml of distilled water in a three-necks, round-bottom flask to obtain a TTIP/ethanol/ H_2O molar ratio of 1:0.75:83. Then, 1 mL of concentrated hydrochloric acid was added as acid catalyst and the resulting solution was refluxed under vigorous stirring for 8 h at 80° C. Finally, a stable milky dispersion of TiO_2 nanoparticles was obtained at 15 wt. % concentration, under a Ti-basis. A 30 seconds, 60 W power plasma treatment (plasma 1) was applied to the surface of the BHJ to enhance the wettability of the $\text{TiO}_{2(\text{aq})}$ dispersion. A three step-spin coating protocol was employed starting from 3 seconds at 200 rpm, 60 seconds at 1000 rpm and 30 seconds at 5000 rpm. Samples were stored in a Petri dish in ambient conditions for 1 day to enhance hydrolysis and condensation of the TiO_2 nanoparticles network. Afterwards, a thermal annealing under inert atmosphere at 130° C for 10 minutes was applied followed by a second plasma treatment (plasma 2, with the same parameters used for plasma 1), just prior to catalyst deposition.

Commercial platinum nanopowder (Sigma Aldrich) was dissolved in water at 1 g/L concentration in weight and sonicated for 30 minutes. Commercial catalyst Vulcan XC-72 (20% loading platinum on graphitized-carbon powder, Sigma Aldrich) was dissolved in isopropanol at 1 g/L concentration

in weight and sonicated for 30 minutes. Commercial MoS_3 powder (Thermo Fisher Scientific) was dissolved in a water:acetone mixture at volume ratio 1:2 in the presence of NaOH 1 M to a mass concentration of 3.8 g/L. The dispersion was stirred at 70° C for 2 hour and later on sonicated for 30 minutes. The three catalyst dispersions were spin coated at 2000 rpm for 60 sec each. Branched polyethyleneimine (PEI, MW 25000 g/mol, Sigma Aldrich) was dissolved in ethanol at 0.1% concentration and spin coated on top of full devices at 3000 rpm for 60 seconds.

² Yun, Y.J.; Chung, J.S.; Kim, S.; Hahn, S.H.; Kim, E.-J. Low-temperature coating of sol-gel anatase thin films. *Materials Letters* 2004, 58, 3703– 3706.

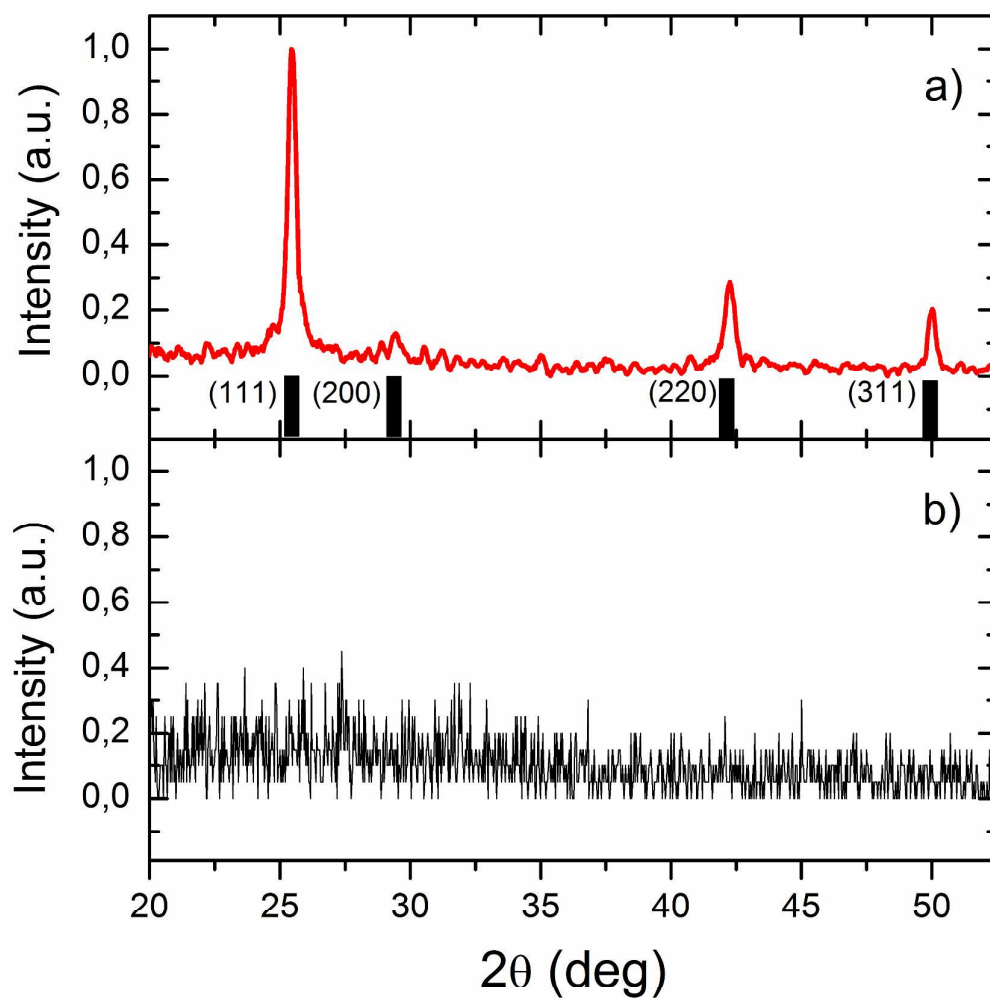


Figure S1. Photocathodes layers structural analysis. X-ray diffraction spectra of (a) CuI and (b) MoS₃ thin films spin coated over a glass substrate. Reference reflections of CuI γ -phase are shown as black lines for comparison.

Materials	Work function (eV)	Standard Deviation (eV)
FTO	5.10	0.01
CuI	4.87	0.01
TiO ₂	4.71	0.01
TiO ₂ annealed	4.70	0.01
MoS ₃	5.06	0.01

Table S1. Work function measurements. Work function (WF) values of materials used as photocathodes layers as measured by Kelvin probe (in air). Mean values and standard deviation values are obtained over a statistical sample of $n = 6$ independent measurements.

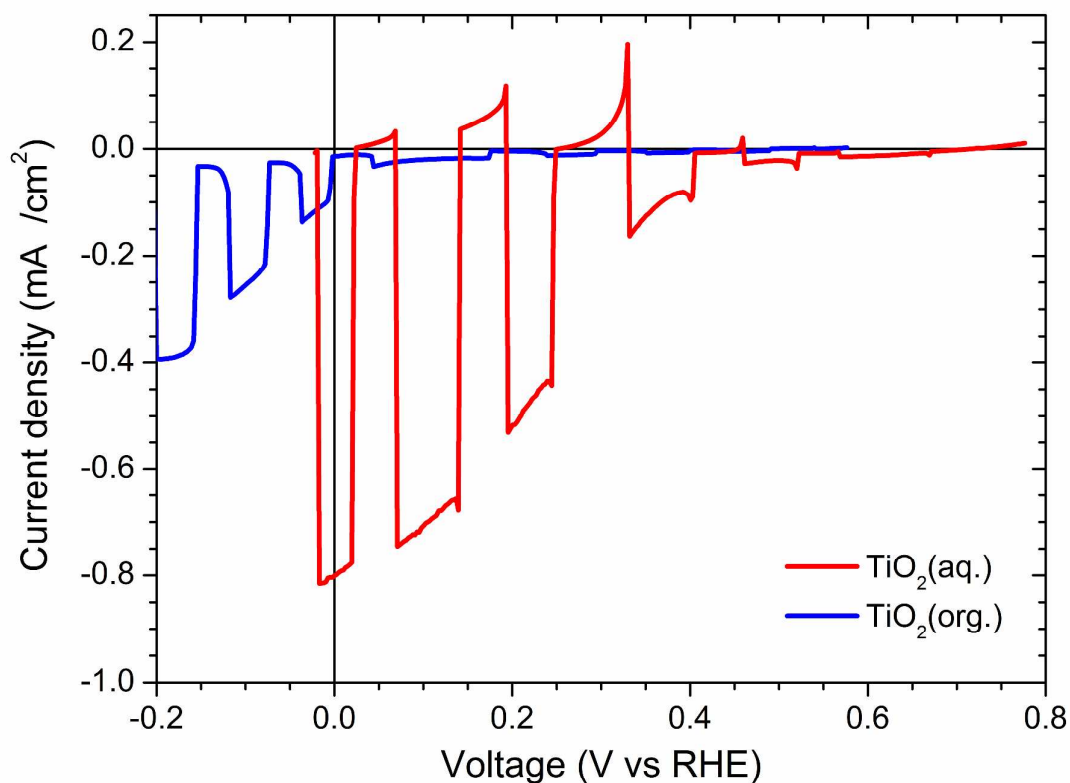


Figure S2. Photo-electrochemical performance of photocathode architectures with different ESL layers preparation. Current–potential characteristics of different all solution-processed photocathode architectures (FTO/CuI/P3HT:PCBM/TiO₂/VC-Pt) measured at pH 1 under simulated AM 1.5G illumination and using commercial Vulcan XC-72 (VC-Pt, platinum on graphitized-carbon powder) as an electrocatalyst. The two curves show the effect of different ESL layer preparation, TiO₂(org)/VC-Pt (blue solid line) and TiO₂(aq)/VC-Pt (red solid line). In the latter case, the BHJ surface was treated by oxygen plasma, to facilitate the subsequent deposition of the TiO₂(aq) layer.

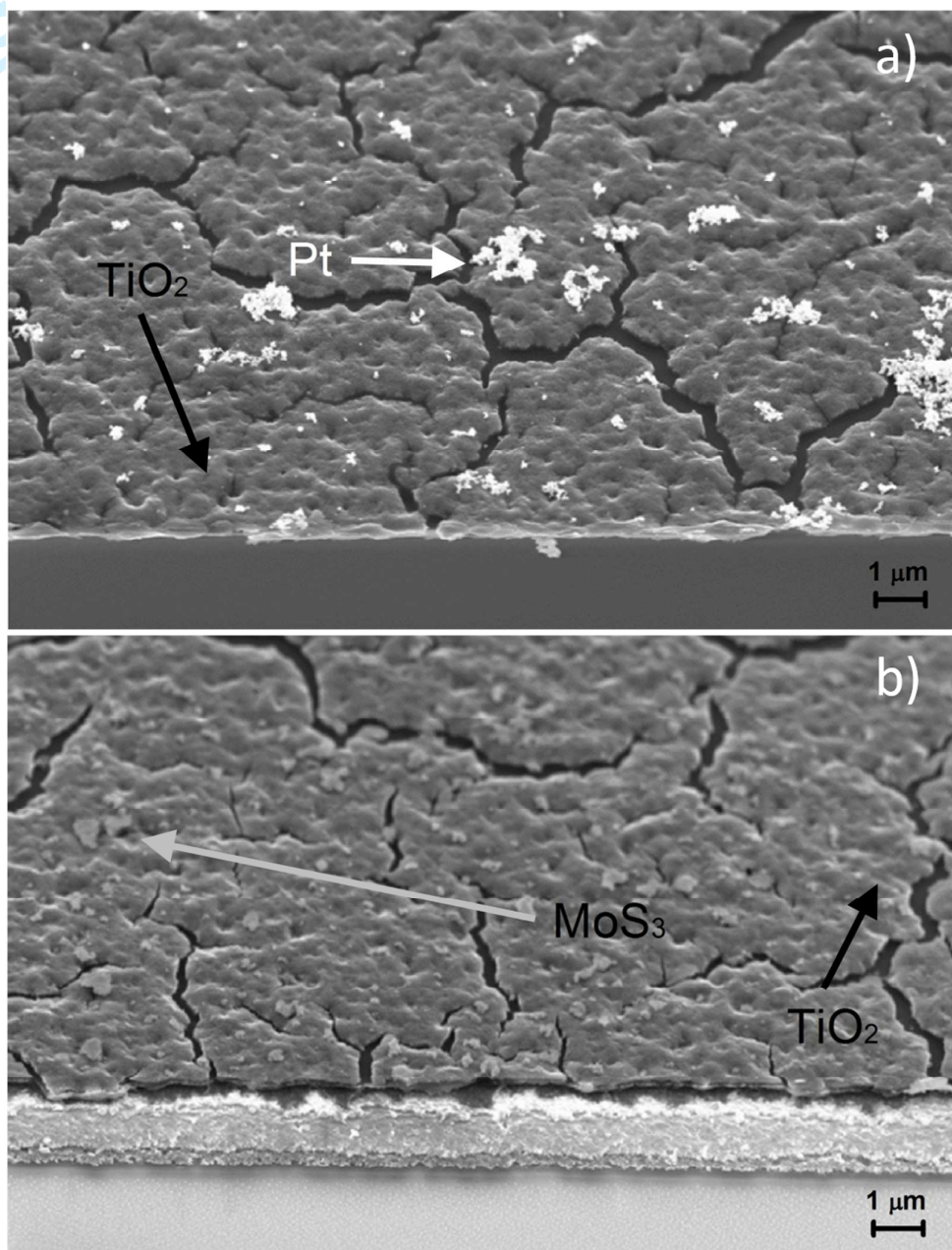


Figure S3. SEM images (top tilted views) of the all solution-processed photocathodes: FTO/CuI/P3HT:PCBM/TiO_{2(aq.)}/Pt (upper panel, a) and FTO/CuI/P3HT:PCBM/TiO_{2(aq.)}/MoS₃ (bottom panel, b). Arrows indicate the positions of Pt (black) and MoS₃ (grey) agglomerates while the TiO₂ ESL layer is indicated by white arrows in both panels.

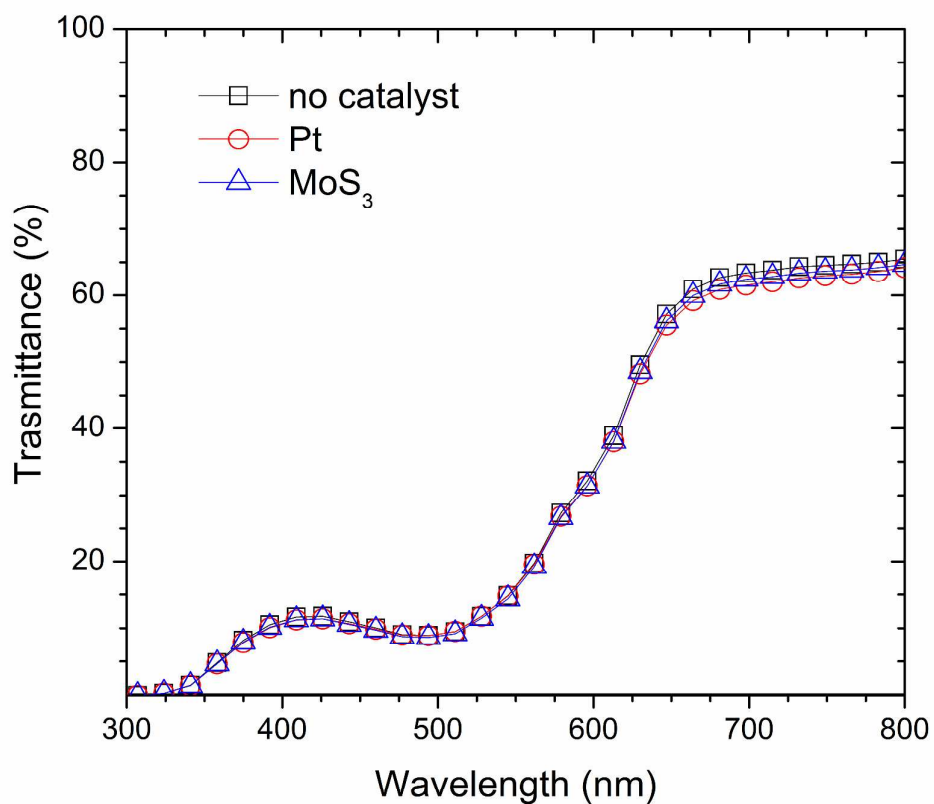


Figure S4. Photocathodes optical characterization. UV-visible transmission spectra of all solution- processed photocathodes fabricated with the architecture FTO/CuI/P3HT:PCBM/TiO₂ (aq.)/catalyst. The effect of different electrocatalysts layers is shown, Pt in red circles and MoS₃ in blue triangles. The transmittance of a device fabricated omitting the catalyst layer is also shown for comparison (black squares).

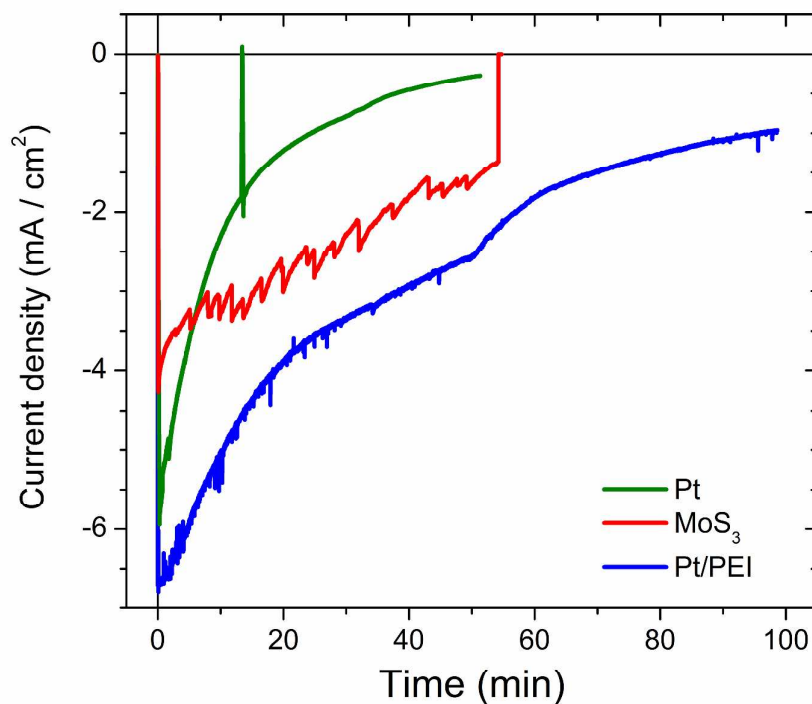


Figure S5. Photocathodes chrono-amperometric photo-electrochemical characterization. Photocurrent density in potentiostatic operation for the solution-processed hybrid photocathodes measured at 0 V vs. RHE and pH 1, under simulated AM 1.5G illumination. The devices were fabricated with the architecture FTO/CuI/P3HT:PCBM/TiO_{2(aq.)}/catalyst. The catalyst layers used were Pt (in green), MoS₃ (in red) and the combination Pt/PEI (in blue). At certain times the illumination was chopped to show the corresponding dark current.