Supporting Information

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

Hansel Comas Rojas, a,b,* Sebastiano Bellani, a,c Eduardo Aluicio Sarduy, a,b Francesco Fumagalli, a Matthew T. Mayer, e Marcel Schreier, e Michael Grätzel, e Fabio Di Fonzo, a Maria Rosa Antognazza, a,*

a Center for Nano Science and Technology @PoliMi, Istituto Italiano di Tecnologia, Via Pascoli 70/3, 20133 Milano, Italy.
b Instituto Superior de Tecnologías y Ciencias Aplicadas (INSTEC), Salvador Allende y Luaces, AP6163 Havana, Cuba.
c Graphene Labs, Istituto Italiano di Tecnologia, via Morego 30, 16163 Genova, Italy.
d Laboratory of Photonics and Interfaces, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

*Corresponding authors: hcomas@instec.cu; mariarosa.antognazza@iit.it
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 TiOx nanoparticles (TiOx(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 TiO₂ network. A thermal treatment at 85 °C for 10 min in air was finally applied.

Aqueous-based TiO₂ nanoparticles (TiO₂(aq)) were synthesized according to a modified sol-gel protocol. 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/H₂O 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 TiO₂ 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 TiO₂(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 TiO₂ 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 MoS₂ 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) MoS$_3$ thin films spin coated over a glass substrate. Reference reflections of CuI $\gamma$-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<sub>2</sub> | 4.71               | 0.01                    |
| TiO<sub>2</sub> annealed | 4.70               | 0.01                    |
| MoS<sub>3</sub> | 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/TiO$_2$/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, TiO$_2$(org)/VC-Pt (blue solid line) and TiO$_2$(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 TiO$_2$(aq) layer.
Figure S3. SEM images (top tilted views) of the all solution-processed photocathodes: 
FTO/CuI/P3HT:PCBM/TiO\textsubscript{2(aq.)}/Pt (upper panel, a) and FTO/CuI/P3HT:PCBM/TiO\textsubscript{2(aq.)}/MoS\textsubscript{3} (bottom panel, b). Arrows indicate the positions of Pt (black) and MoS\textsubscript{3} (grey) agglomerates while the TiO\textsubscript{2} 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/TiO$_2$ (aq.)/catalyst. The effect of different electrocatalysts layers is shown, Pt in red circles and MoS$_3$ 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), MoS$_3$ (in red) and the combination Pt/PEI (in blue). At certain times the illumination was chopped to show the corresponding dark current.