Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Polymer-based photocathodes with a solution-processable cuprous iodide anode layer and a polyethyleneimine protective coating

Hansel Comas Rojas,[a] Sebastiano Bellani,[a,b] Francesco Fumagalli,[a] Gabriele Tullii,[a] Silvia Leonardi,[a] Matthew T. Mayer,[c] Marcel Schreier,[c] Michael Grätzel,[c] Guglielmo Lanzani,[a,b] Fabio Di Fonzo,[a,*] and Maria Rosa Antognazza[a,*]

[a]Center for Nano Science and Technology @PoliMi, Istituto Italiano di Tecnologia, Via Pascoli 70/3, 20133 Milano, Italy.
[b]Politecnico di Milano, Dip.to di Fisica, P.zza L. da Vinci 32, 20133 Milano, Italy.
[c]Laboratory of Photonics and Interfaces, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

* E-mail: fabio.difonzo@iit.it ; mariarosa.antognazza@iit

Electronic supporting information

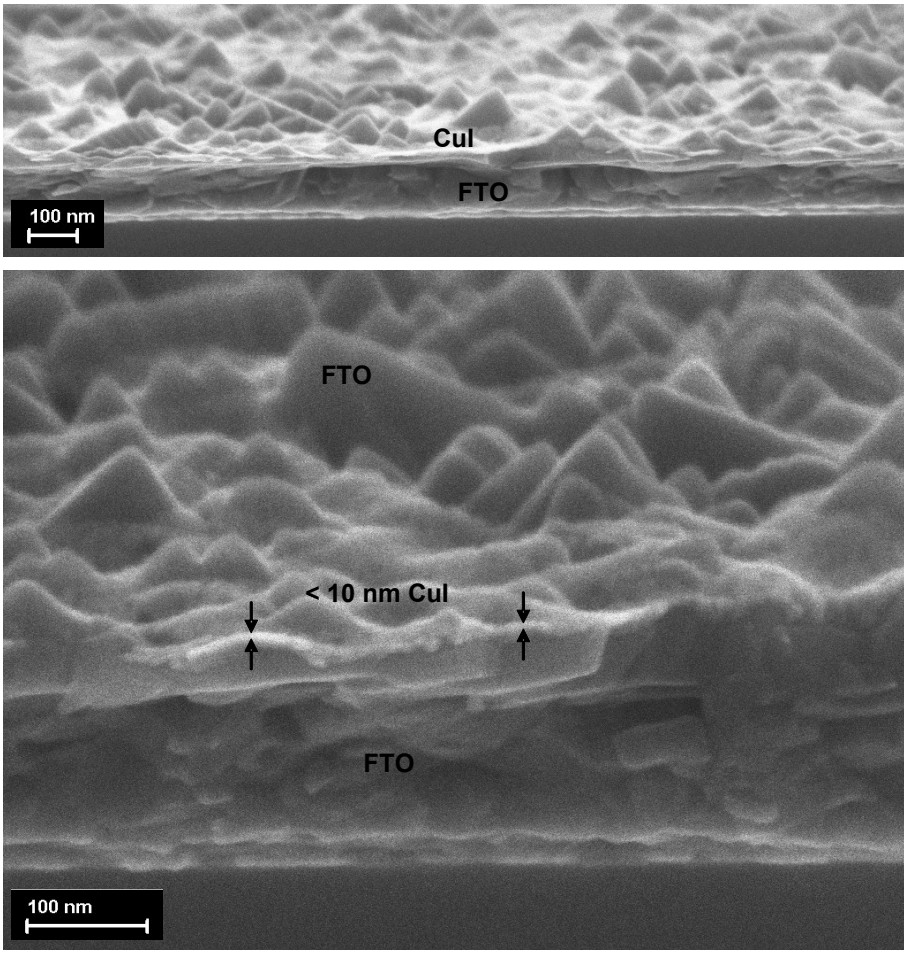

Fig. S1. Cross-sectional SEM of a CuI layer deposited over the rough FTO substrate. Top: Long scale view (scale bar, 100 nm). Bottom: High resolution image showing the thin layer of CuI (thickness around or below 10 nm) and the big FTO crystals (scale bar, 100 nm).

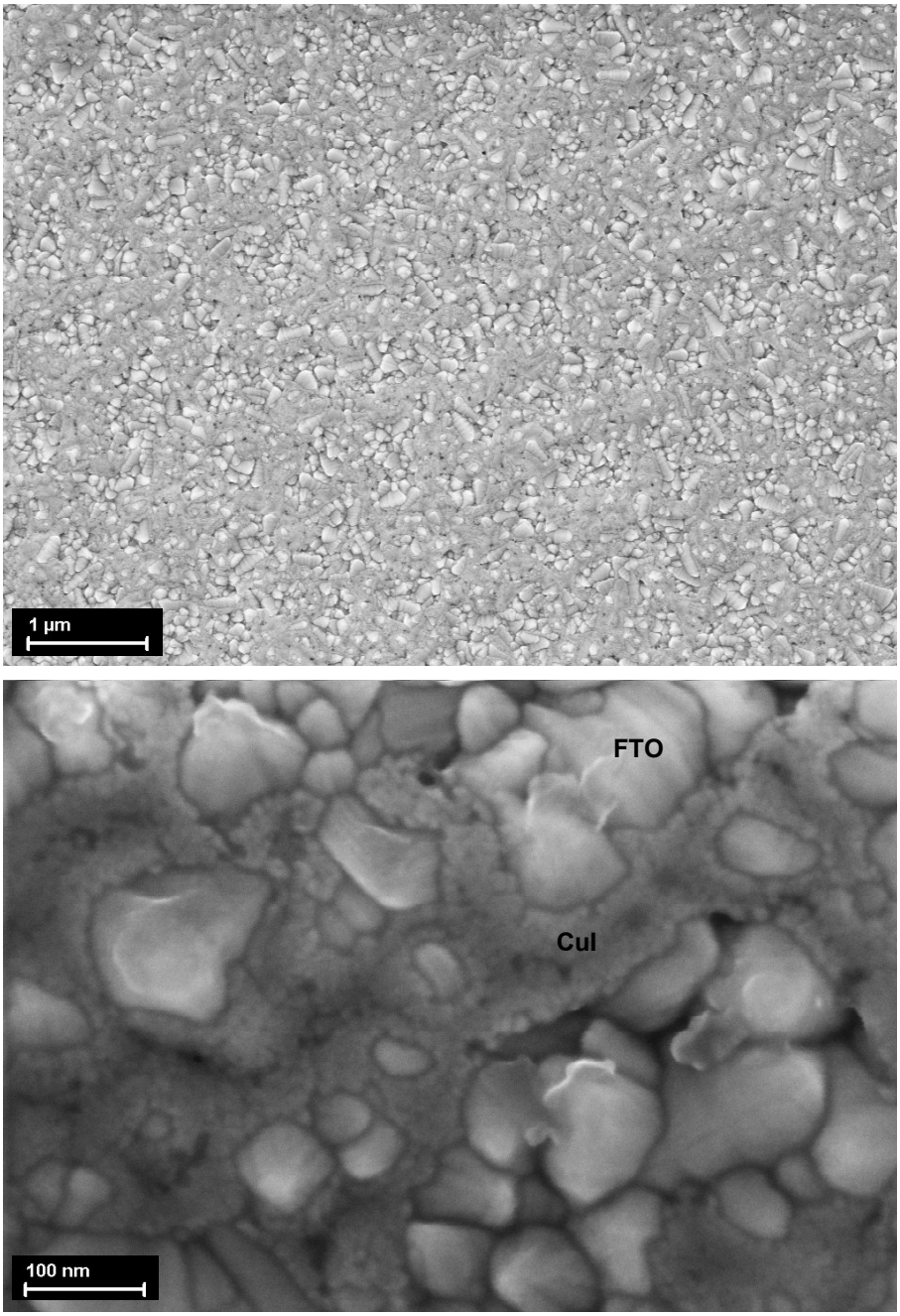

Fig. S2. SEM micrographs of a CuI layer (darker gray) deposited over the rough FTO substrate (brighter big crystals). Top: Long scale view of the surface (scale bar, 1 µm). Bottom: High resolution image showing a granular morphology with nanoparticles around 10 nm in size (scale bar, 100 nm).

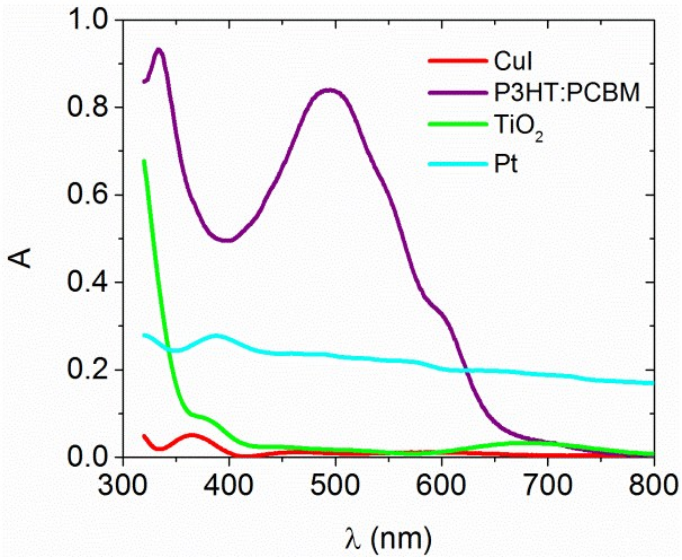

Fig. S3. Neat UV-visible absorption spectra of every layer present in the hybrid photocathode according to the architecture FTO/CuI/P3HT:PCBM/TiO_2/Pt.

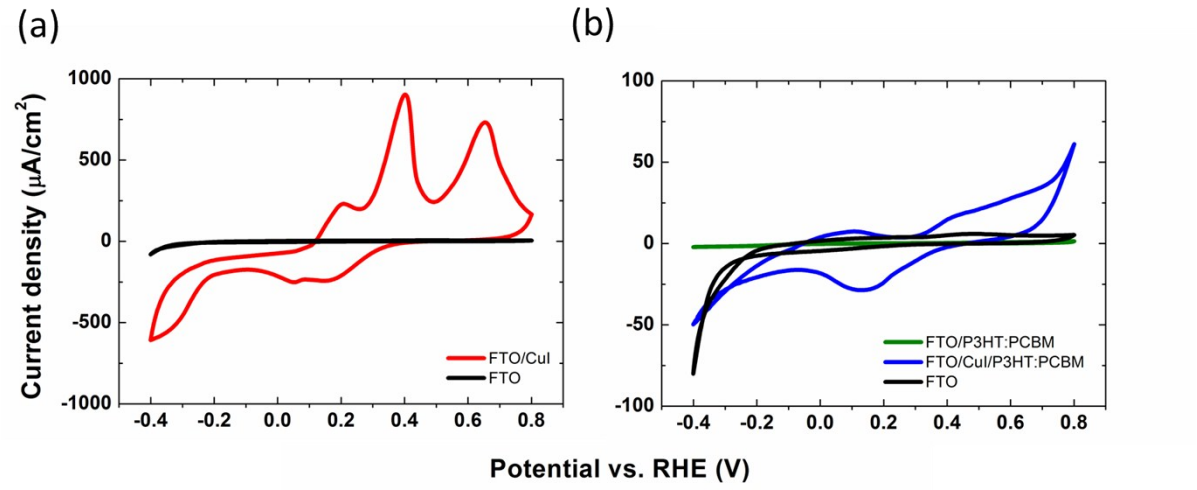

Fig. S4. Cyclic voltammetry measurements on CuI deposited on top of FTO substrates and directly exposed to the electrolyte solution (panel a, red line), as compared to FTO/CuI/P3HT:PCBM samples (panel b, blue line). Control bare FTO and FTO/P3HT:PCBM devices (black and green solid lines, respectively) show almost no electrochemical activity within the considered potential range. Scan rate, 200 mV/s.

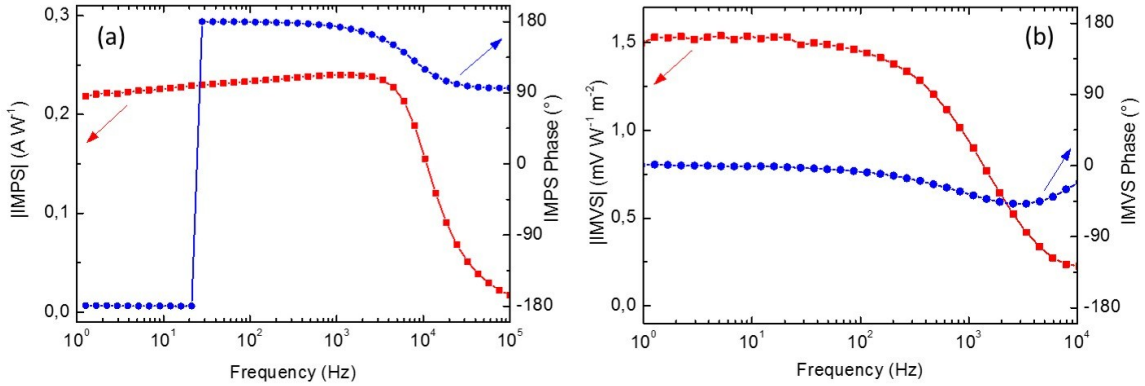

Fig. S5 IMPS (a) and IMVS (b) Bode diagrams recorded at 0 V vs. RHE and at open circuit condition, respectively. A red and blue color traces represent module and phase, respectively.

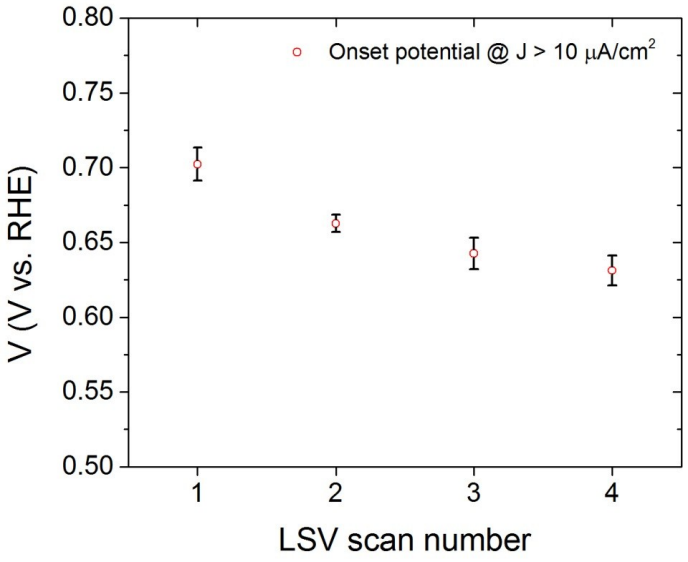

Fig. S6. Onset potentials (OP) for cathodic photocurrents higher than 10 μA/cm^2 during subsequent LSV scans of hybrid photocathodes at pH 1 and 1 sun illumination. Error bars represent the standard deviation of measurements over six different devices.

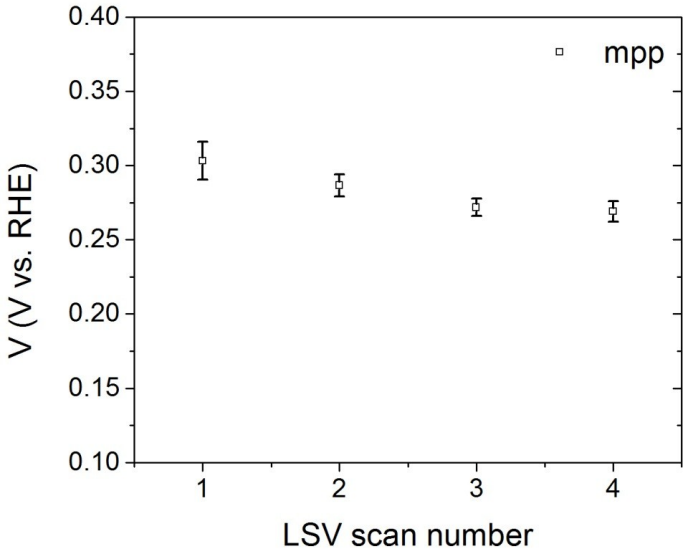

Fig. S7. Maximum power points (mpp) during subsequent LSV scans of hybrid photocathodes at pH 1 and 1 sun illumination. Error bars represent the standard deviation of measurements over six different devices.

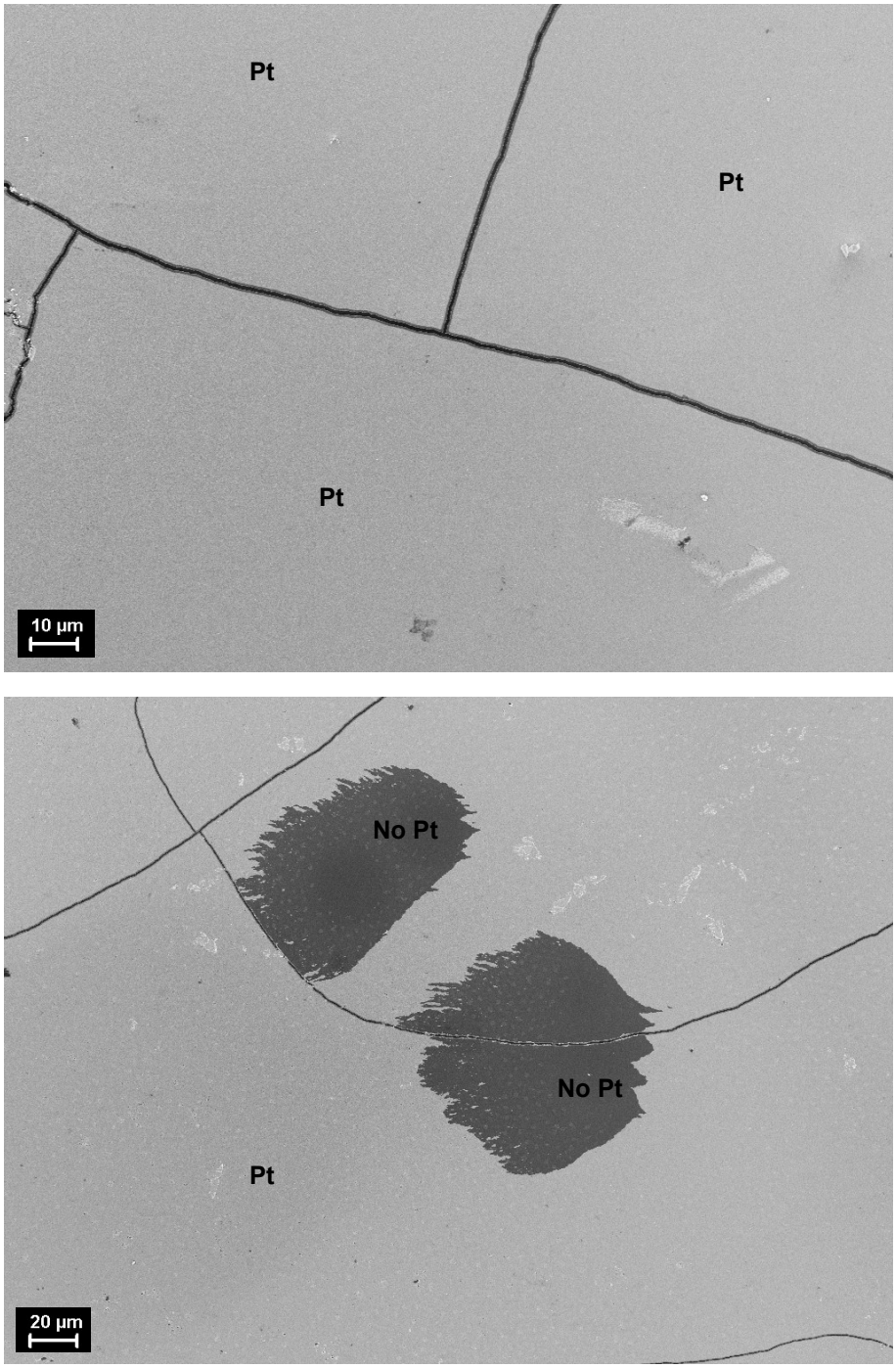

Fig. S8. SEM micrographs of the surface (capping Pt layer on top of the nanostructured TiO_2) of a hybrid photocathode. View of the surface after thermal annealing (scale bar 10 µm, top). View of the surface after one hour operation at 0 V vs. RHE, pH 1 and 1 sun illumination (scale bar 20 µm, bottom).

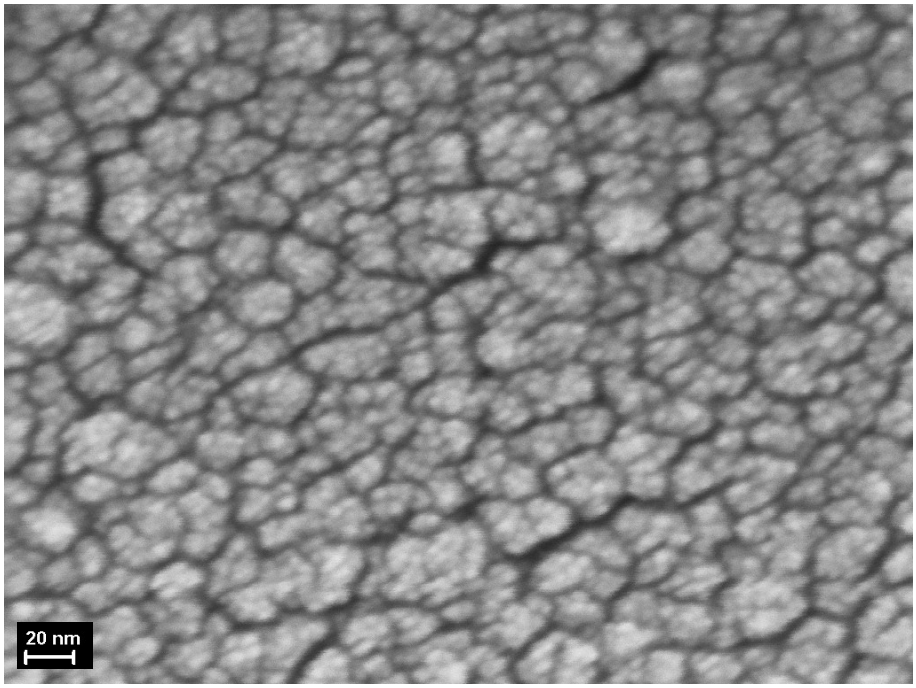

Fig. S9. HR-SEM of the surface (capping Pt layer on top of the nanostructured TiO_2) of a hybrid photocathode after thermal annealing. The granular morphology at the top of TiO_2 layer are clearly visible (scale bar 20 nm).

Impact of a second platinum deposition on photocurrent recovery after one hour operation

The fraction of photocurrent lost after one hour operation under CA at 0 V, pH 1 electrolyte, amounts approximately at 75%. The stressed device was removed from the electrolyte, rinsed with DI water and dried under inert atmosphere flux. Then, it was subjected to a second catalyst deposition and thermal annealing at the end, under identical conditions to the original ones. Afterwards, a LSV scan was performed.

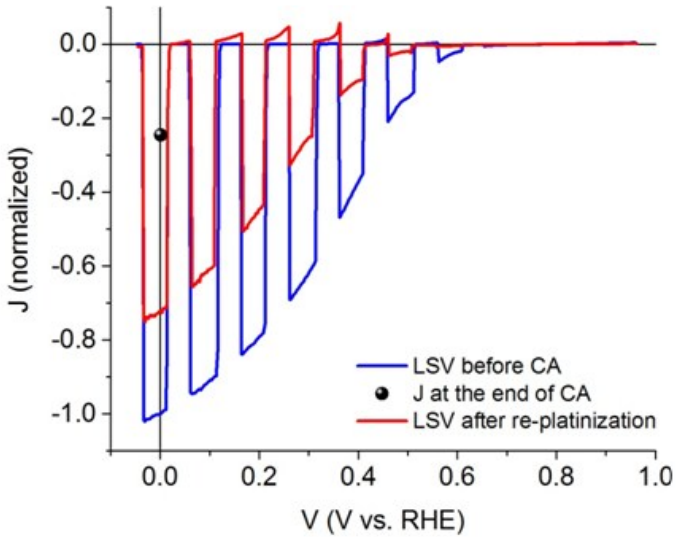

Fig. S10. Comparison between LSV scans before and after a second platinum deposition, on a photocathode undergoing one hour operation at 0 V and pH 1 electrolyte. The final photocurrent value at the end of the CA is identified by the black dot.

A high fraction of the initial photocurrent was recovered after re-platinization amounting at 72%, representing more than 200% increment with respect to the photocurrent produced by the device after one hour operation. One should notice that no special care was taken to clean the surface of the photocathode. Notably, the onset potential (0.67 V), the mpp (0.23 V) and the fill factor were also recovered to a greater extent, which further supports the Pt loss as the main source of degradation.