

Stabilizing organic photocathodes by low-temperature atomic layer deposition of TiO₂

Ludmilla Steier,^{‡*a} Sebastiano Bellani,^{‡b} Hansel Comas Rojas,^{‡b} Linfeng Pan,^a Mikko Laitinen,^c Timo Sajavaara,^c Fabio Di Fonzo,^b Michael Grätzel,^a Maria Rosa Antognazza,^b Matthew T. Mayer^{‡*a}

^a Institute of Chemical Sciences and Engineering, Ecole polytechnique fédérale de Lausanne, Station 6, 1015 Lausanne, Switzerland.

^b Center for Nano Science and Technology @PoliMi, Istituto Italiano di Tecnologia, via Pascoli 70/3, 20133 Milano, Italy

^c Dept. of Physics, P.O. Box 35, 40014 University of Jyväskylä, Finland

[‡] Present affiliations: L.S.: Department of Chemistry, Imperial College London, London SW7 2AZ, UK; S.B.: Graphene Labs, Istituto Italiano di Tecnologia, via Morego 30, 16163 Genova, Italy; H.C.R.: Higher Institute for Applied Sciences and Technologies (INSTEC), Salvador Allende y Luaces, 6163, La Habana, Cuba; M.T.M.: Helmholtz-Zentrum-Berlin für Materialien und Energie, 14109 Berlin, DE

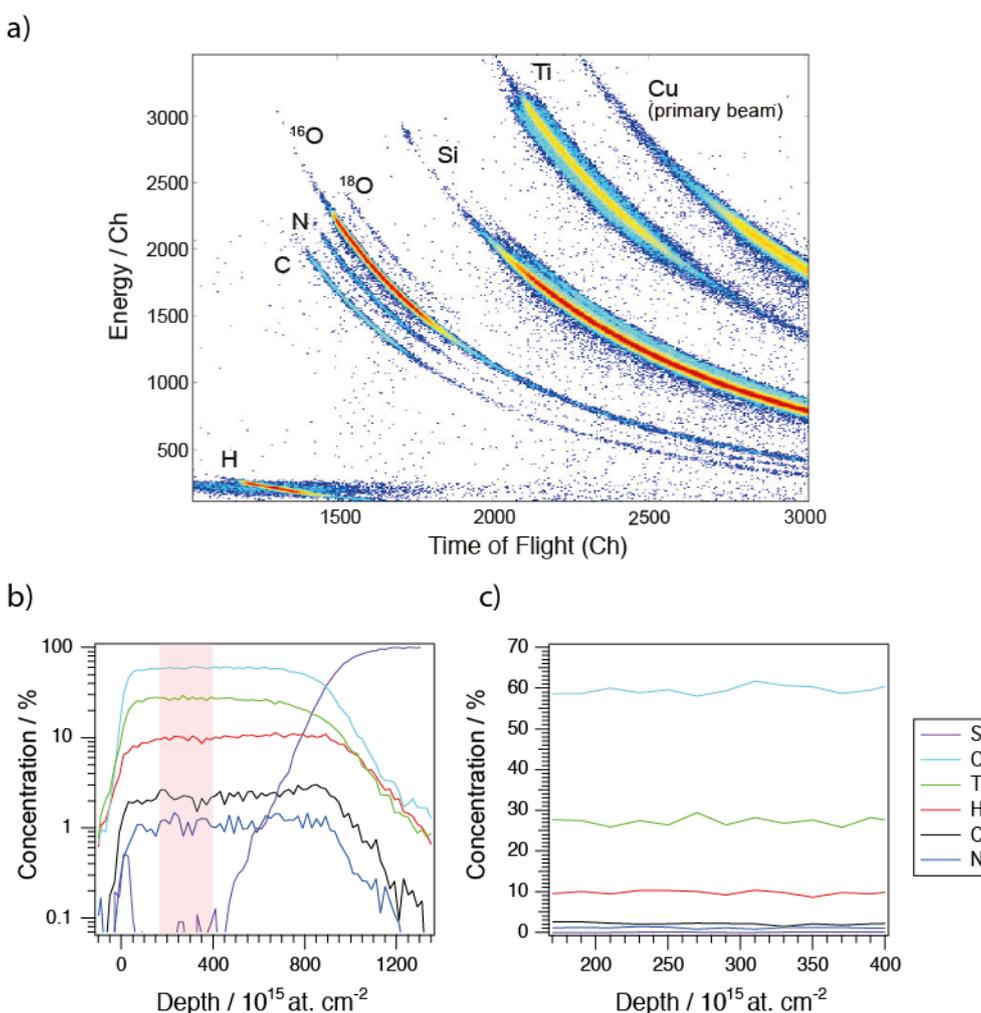


Figure S1. a) Histogram of coincident time-of-flight and energy events for ALD TiO₂ grown at 80 °C with TDMAT and H₂O on silicon wafers showing hydrogen, carbon, nitrogen, both isotopes of oxygen, silicon and titanium as well as copper from the primary beam for a 90 nm thick TiO₂ film on Si. b) Concentration depth profiles for the 90 nm thick TiO₂ samples from a). Values in Table 1 were averaged from the pink marked region that is presented in a linear plot in c). No elemental losses were observed during the measurements. Hydrogen, carbon and nitrogen concentrations increase slightly towards the interface.

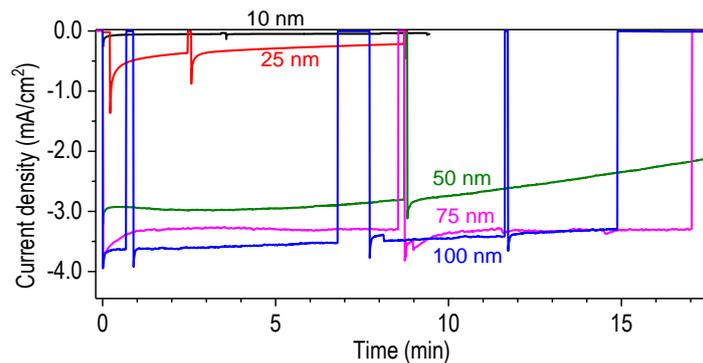


Figure S2. Constant potential (0 V vs RHE) measurements of CuI/P3HT:PCBM/TiO₂/RuO_x photocathodes with varied ALD TiO₂ thicknesses as labeled, under steady illumination that was periodically blocked to observe the current in dark. All measurements were performed in pH 5 electrolyte under simulated one-sun illumination.

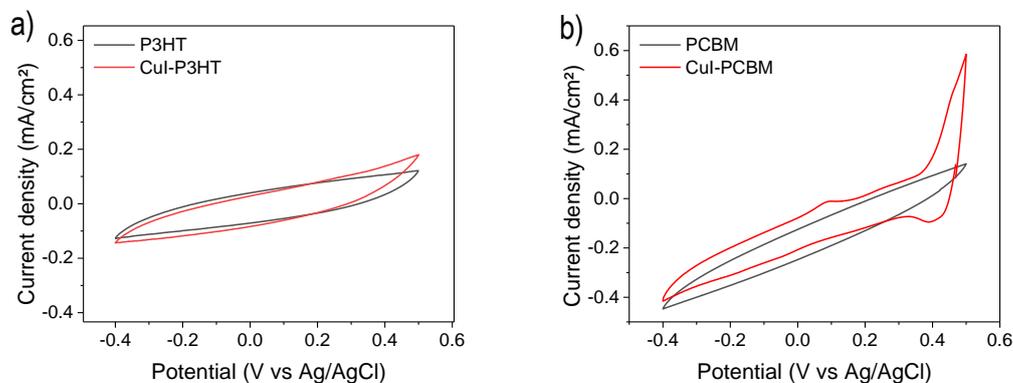


Figure S3. Cyclic voltammetry scans of films of a) P3HT and b) PCBM deposited onto bare FTO substrates (black) and onto CuI-coated FTO (red). Scan rates = 100 mV/s, electrolyte pH = 5. Around 5-10 repeated scan cycles were performed for each, and the data presented here are representative behaviours observed during this period.

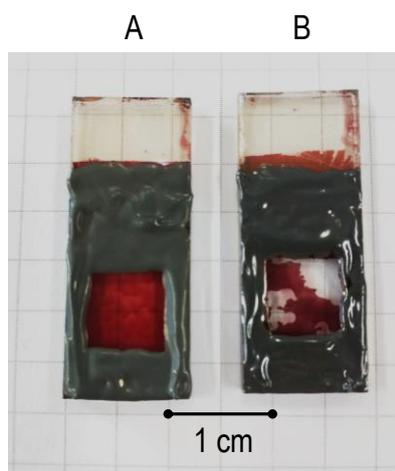


Figure S4. Photographs of photocathodes after extended testing. Devices with 75 nm TiO₂ tested for (A) 90 min. and (B) 300 min. in pH 5 electrolyte at 0 V vs RHE. Sample degradation initiates at the edge of the epoxy, suggesting that the encapsulation strategy may stress the TiO₂ overlayer and cause defects through which electrolyte can penetrate. The purple P3HT:PCBM film gradually delaminates from the FTO surface, indicative of dissolution of the CuI underlayer.

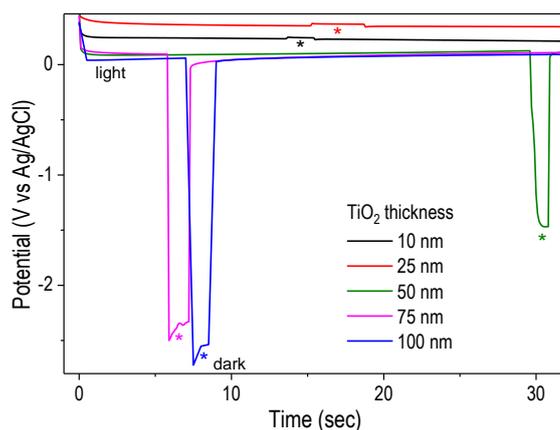


Figure S5. Potential measurement during RuO_x catalyst photo-electrodeposition on devices of varied TiO_2 thickness. A reducing galvanostatic current density of $-36 \mu\text{A}/\text{cm}^2$ was fixed for 900 s total, and simulated one-sun illumination was applied constantly except when briefly blocked during the moments labeled by asterisks (*).

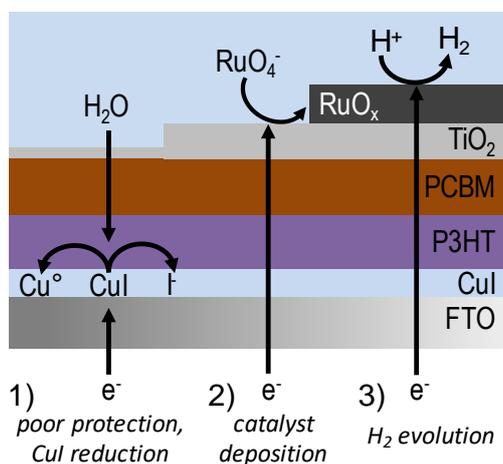


Figure S6. Schematic illustration of charge transport and transfer processes which are sensitive to TiO_2 overlayer thickness. 1) When TiO_2 is thin or absent, H_2O can penetrate the blend, and red-ox behaviours attributable to CuI reduction can be seen in the CVs. This corrosion process also inhibits catalyst electrodeposition. 2) With a TiO_2 overlayer, electrons are efficiently collected from the blend and transported to the surface where they drive the catalyst electrodeposition, forming a RuO_x film. 3) The full device with catalyst drives photoelectrochemical hydrogen evolution. Note that photoexcitation of electrons in P3HT is not depicted here, and the illustration is not to scale.

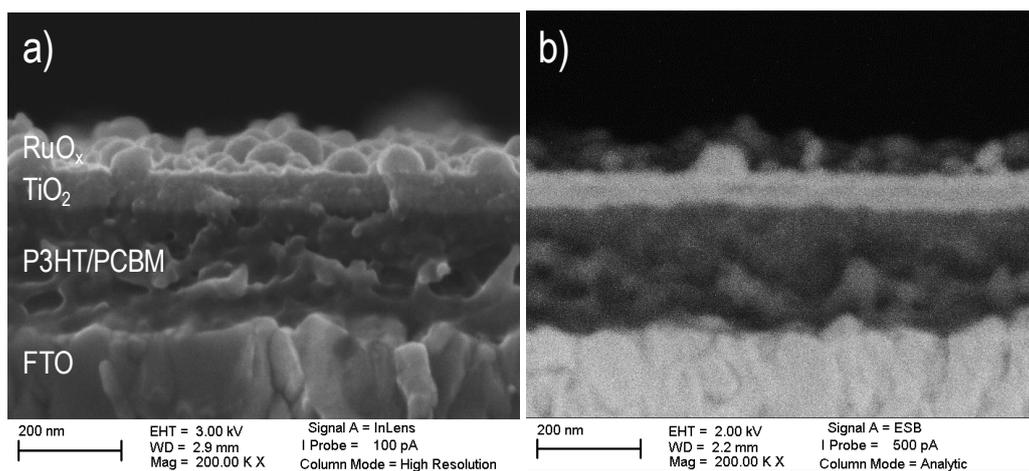


Figure S7. Scanning electron microscopy imaging of cleaved photocathode cross-sections for a CuI/P3HT:PCBM/TiO₂/RuO_x device with 75 nm ALD TiO₂. a) Secondary electron imaging. b) Electron backscatter imaging. The bright areas in the backscatter image arise from the enhanced scattering from heavy atoms such as metals (Ti, Ru, and Sn). There is no clear evidence of TiO₂ penetration into the polymer film.

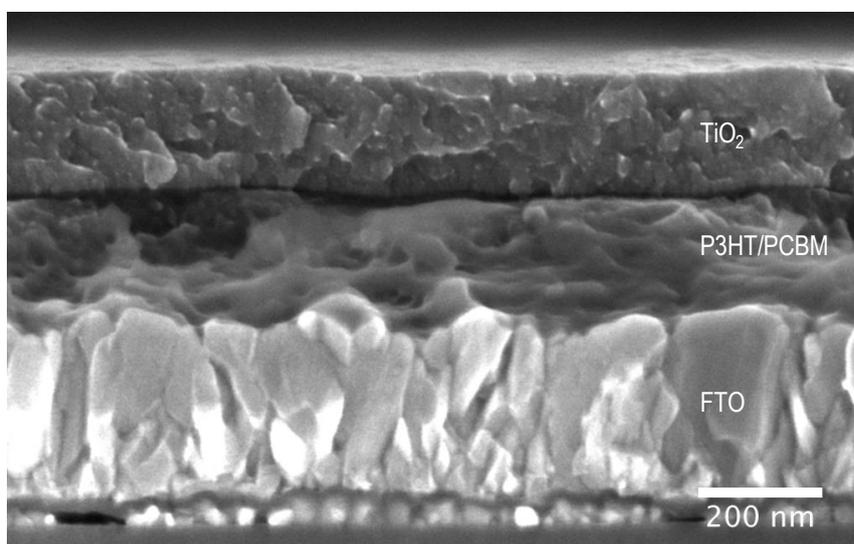


Figure S8. High-resolution SEM cross-section image of a CuI/P3HT:PCBM/TiO₂ device.