

Platinum-free photoelectrochromic devices working with copper-based electrolytes for ultrastable smart windows

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Electronic Supplementary Information

Experimental Details

WO₃ powder (99.99%), nitric acid (HNO₃), Triton X-100, chenodeoxycholic acid (CDCA), ethanol, 4-tert-butylpyridine (TBP), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), poly(ethylene oxide) (PEO, average M_w : 400000), *tert*-butanol, acetonitrile (ACN) were purchased from Sigma-Aldrich. TiO₂ nanopowder (Degussa P25) was kindly provided by Evonik. Conductive glasses (FTO, sheet resistance 12–14 Ω sq⁻¹, 82%–84% transmittance in the visible) were purchased from Dyesol. 3-{6-[4-[bis(2',4'-dihexyloxybiphenyl-4-yl)amino-]phenyl]-4,4-dihexyl-cyclopenta-[2,1-b:3,4-b']dithiophene-2-yl}-2-cyanoacrylic acid (Y123 dye), bis-(2,9-dimethyl-1,10-phenanthroline)copper(I) bis(trifluoromethanesulfonyl)imide (Cu(dmp)₂TFSI) and bis-(2,9-dimethyl-1,10-phenanthroline)copper(II) bis(bis(trifluoromethanesulfonyl)imide) (Cu(dmp)₂(TFSI)₂) were purchased from Dyenamo AB. Graphene nanoplatelets (GNPs) Grade 4 were produced by Cheaptubes, with a plane dimension of 1 to 2 mm and thickness <4 nm when exposed to high shear or sonication.

WO₃ films were prepared onto FTO glasses (previously washed following the procedure described)¹ by electron beam gun evaporation, at a pressure of 10⁻⁵ mbar in a vacuum system (evacuated by turbomolecular and mechanical pumps) and at room temperature. The desired film thickness was adjusted by means of a quartz thickness controller.

A TiO₂ film was later deposited by doctor blading the TiO₂ paste onto the 15% of the WO₃ area, *i.e.* on the bottom part of the FTO glass, by using a mask. The TiO₂ paste was prepared as described in a previous work from our groups.² The as-obtained WO₃/TiO₂ films were placed onto a hot plate at 100 °C for 45 min and then sensitized by dipping the TiO₂ side into a Y123 dye solution (0.10 mM, solvent: *tert*-butanol/ACN 1:1 v/v; additive: CDCA 0.40 mM) for 16 h. Then, the samples were thoroughly rinsed with ACN to remove the excess of dye.

For counter electrodes preparation, 20 mg of GNPs were dispersed in 50 mL of ethanol with a Vibra-Cell ultrasonic tip for 15 min at 100 W. The suspension was then slowly dispensed with a Pasteur pipette onto the FTO glass, and ethanol evaporation was done in a fume hood. Standard platinum counter electrode were not tested due to their poor performance in the presence of copper-based redox shuttles.³

The electrolyte was prepared starting from a solution consisting of Cu(dmp)₂TFSI 0.10 M, Cu(dmp)₂(TFSI)₂ 0.03 M, LiTFSI 0.20 M and TBP 0.20 M in ACN. Then, the solution was jellified by adding PEO 45 wt% under vigorous magnetic stirring at 40 °C. The resulting gel was easily spread onto the TiO₂/WO₃ electrode by doctor blade.

The PECD (dimensions: 3.0×4.0 cm²) was sealed with a 25 µm-thick thermoplastic film by Greatcell Solar Materials, activated by a 1 min heating step at 120 °C.

The coloration of the devices was performed under open circuit conditions, by exposing the PECD to an AM1.5G simulated sunlight with an intensity equal to 1000 W m⁻², produced by a VeraSol-2 LED solar simulator (class AAA, by Oriel), calibrated with an Oriel PV reference cell system (model 91150V). Transmittance (*T*) spectra were recorded with a Lambda 35 spectrophotometer (PerkinElmer). Photocoloration efficiency (PhCE) values were calculated with the equation

$$PhCE = \frac{\Delta OD}{I \cdot t}, \text{ where } I \text{ is the incident light intensity, } t \text{ is the exposure time and}$$

$$\Delta OD = \log \frac{T_{bleached}}{T_{colored}}.$$

J–V curves to determine DSSC figures of merit were recorded by a Keithley Source Measure Unit, starting 60 s after switching on the sun simulator.

To characterize GNPs-based counter electrodes, Raman spectra were recorded by a Horiba Jobin-Yvon LabRAM HR800 instrument equipped with an Olympus BX41 microscope. The samples were excited with a red He-Ne laser ($\lambda = 633$ nm, power = 20 mW) and a Nd solid state green laser ($\lambda = 532$ nm, power = 250 mW); a magnification ratio of 50× with 30 acquisition of 30 s was fixed. The hydrodynamic size and zeta potential of GNPs were determined by a DLS Zetasizer Nano Series ZS90 (Malvern Instruments). To this purpose, samples were prepared by dispersing the powders in distilled water and the measurements were carried out at 25.0 ± 0.1 °C in a thermostatic cell; analyses

were done in triplicate and the average value was considered. Field-emission scanning electron microscopy (FESEM) was carried out by an Auriga Zeiss instrument (Carl Zeiss). Thermogravimetric analysis (TGA) was carried out with a thermobalance (SDT Q600, TA Instruments) in the range 25-1000 °C with a heating rate of 10 °C min⁻¹ under air flow (50 mL min⁻¹).

Supplementary TGA

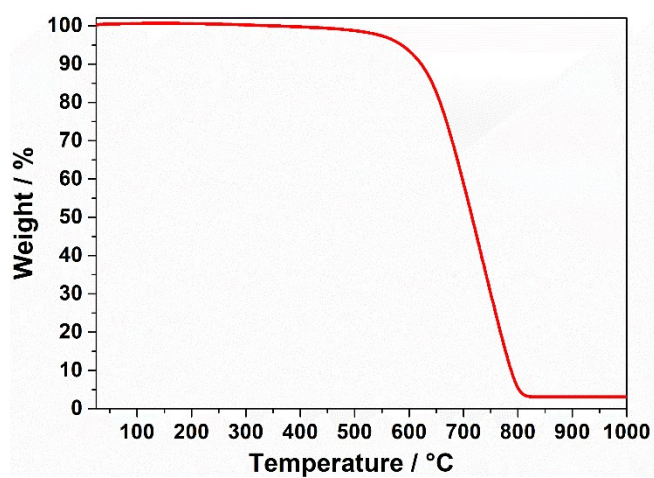


Figure S1. TGA profile for GNPs. The measurement was carried out under air flow and at a scan rate equal to $10\text{ }^{\circ}\text{C min}^{-1}$.

Supplementary FESEM

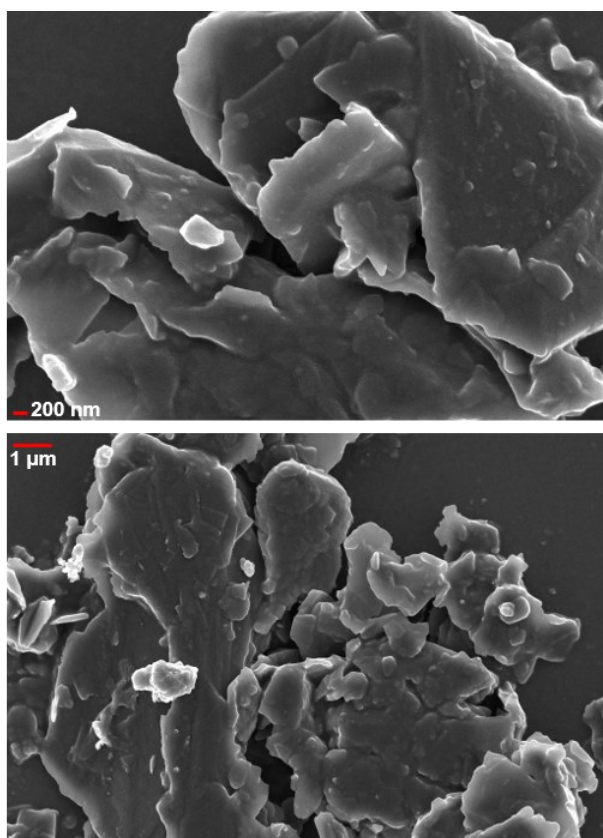


Figure S2. FESEM micrographs of GNPs-based counter electrodes, for a PECD disassembled after 400 days of ageing.

Supplementary FESEM

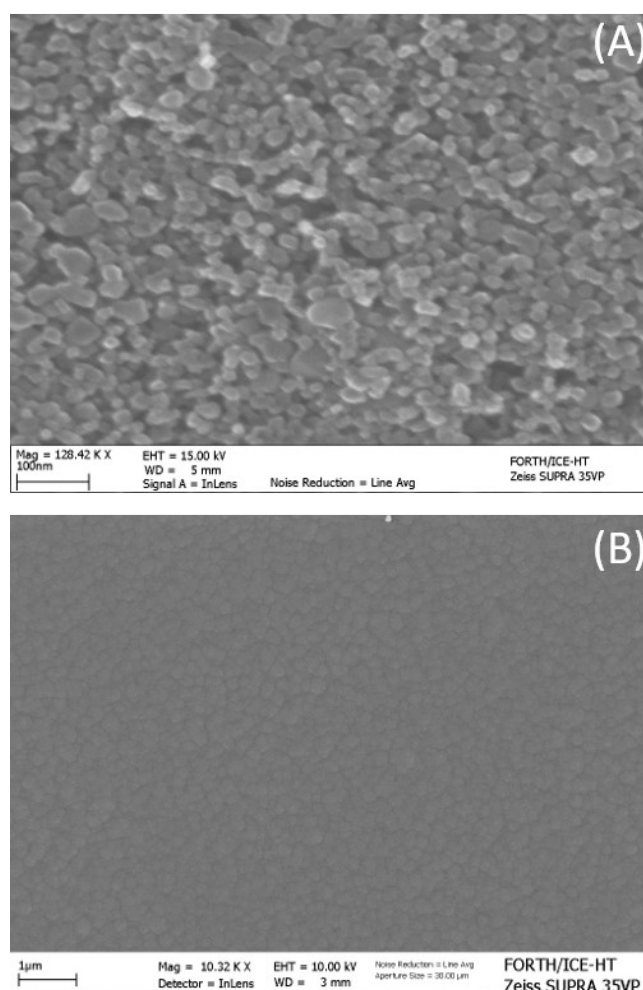


Figure S3. FESEM micrographs of (A) TiO_2 and (B) WO_3 electrodes used for PECD fabrication. Other micrographs were published in our previous works.^{4,5}

Supplementary XRD

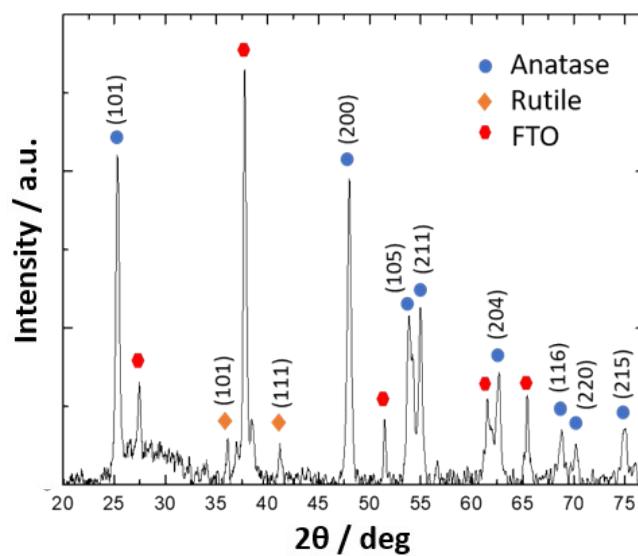


Figure S4. XRD patterns of TiO_2 electrodes used for PECVD fabrication, adapted and reprinted with permission from our previous publication.⁶ XRD data for WO_3 electrodes used for PECVD fabrication appeared in our previous work.⁵

Supplementary PECD test

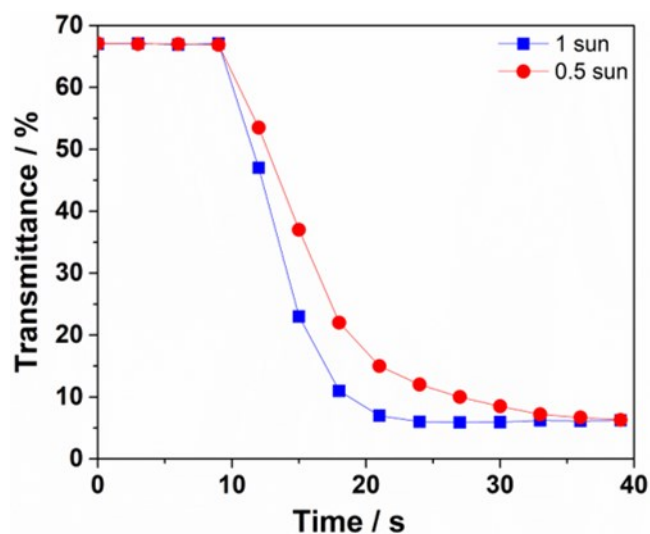


Figure S5. Transient transmittance response time for the PECD under different irradiation intensity values, *i.e.* 0.5 and 1.0 sun. The coloration kinetics was slightly lowered when halving the sun simulator power output, but the PECD was able to reach the same colored state with a rather low delay, *i.e.* 9 s.

Supplementary literature survey

Table S1. Literature studies reporting stability studies of PECDs.

Investigated PECd component	Stability study	Ref.
Addition of Pt catalyst in WO ₃ layer	300 h under thermal stress	[7]
Incorporation of carbon-based perovskite solar cells	40 cycles	[8]
Salicylic acid attached to the TiO ₂ photoactive layer	150 cycles	[9]
Optimized thermal annealing of TiO ₂	20 days in OC or SC conditions	[10]
Cobalt redox electrolytes	157 days in OC in a dark room	[11]
Gel electrolytes	36 weeks under SC	[12]
Carbon quantum dots sensitized photoanode	400 cycles	[13]
ZnS barrier to block loss reactions at the WO ₃ /electrolyte interface	339 days in OC in the dark	[14]
Polymer electrolyte membrane + External perfluoropolymeric coating	90 days under real outdoor conditions	[15]
Br ⁻ /Br ₃ ⁻ electrolyte	4 h of illumination	[16]
Preparation of WO ₃ thin film by successive dip coating	1000 cycles	[17]
Electrochemical treatment of the WO ₃ films + Tuning the electrolyte composition	10 months at OC conditions	[18]
Optimization of electrochromic film thickness	70 days in OC in the dark	[19]
Prussian blue counter electrode	1000 cycles under 100 mW/cm ² illumination	[20]
Poly(3,4-(2,2-dimethylpropylenedioxy)thiophene) thin film as coloring layer	1500 cycles	[21]
N3 ruthenium dye	2 months	[22]
WO ₃ /TiO ₂ layers optimization	100 cycles	[4]
PEDOT/PSS as solid-state electrolyte	100 cycles	[23]
Pt catalyst	60 min	[24]
Solid Li ⁺ ion conductor	90 h under dark	[25]

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