Hydrophobic polymer stabilized p-Cu₂O nanocrystal photocathode for highly efficient solar water splitting

Yang Li,^{a†*} Xiaolan Zhong,^{b†} Kai Luo^a and Zongping Shao^{a, c*}

^{a.} School of Energy and Power, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu, 212003, P. R. China.

^{b.} School of Physics, Beihang University, Beijing, 100191, P. R. China.

^{c.} Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), State Key Laboratory of Materials-Oriented Chemical Engineering College of Energy, Nanjing Tech University, No. 5 Xin Mofan Road, Nanjing 210009, P. R. China.

[†] These authors contributed equally to this work.

Experimental details:

Material preparation

The fluorine-doped tin oxide (FTO) substrates were washed thoroughly with acetone and ethanol under ultrasonic cleaning for 10 min, respectively. Afterwards, the FTO substrates coated with 50 nm of Ag and 100 nm of Au by DC magnetron sputtering under identical conditions using a 50 mm diameter Ag target (99.99%), and the evaporation chamber was pumped to a base pressure of 1.0×10^{-4} Pa before deposition. Film growth was carried out in high purity argon as working gas and at a constant working pressure of 0.3-0.5 Pa. The sputtering current was 75 mA for all the samples. For Cu₂O preparation, the films were deposited by electrodeposition from solutions of lactate-stabilized copper sulphate. The plating bath was 0.2 M CuSO₄ (ALADDIN) and 1.2 M sodium lactate (ALADDIN) solution in deionized water. The bath pH was adjusted to 12 by adding an amount of NaOH. The temperature of the bath was maintained at 30 °C using a water bath with an in situ temperature probe. The Cu₂O thin films were deposited at biasing of 1.5 V for 300 min using a potentiostat (HM-PS100) in a two-electrode configuration with a Pt plate counter electrode.

Before coating polyurethane acrylate (PUA), the Cu₂O thin films were conditioned for 5 min under plasma in a Plasma Cleaner (HM-Plasma5L, 13.56 MHz) in low pressure Ar atmosphere. Viscous urethane acrylate (UA) monomer dipped on the Cu₂O nanocrystal surface followed by a high-speed spinning coating (> 10000 rmp), which resulted in an ultra-thin UA film on the Cu₂O electrodes. Afterwards, the resultant monomer film was polymerized under the induction of high power ultraviolet light (500 W Mercury lamp) to form a solid polyurethane acrylate (PUA) film, before the process of the polymerization 1 wt.% of 2-hydroxy-2methylpropiophenone (HMPF, also called 1173) was added as the photoinitiator.

TiO₂ thin films were deposited by reactive DC magnetron sputtering with a thickness of ~50 nm. The base pressure in the coating chamber was less than 1.0×10^{-4} Pa, while pure argon was used as sputter gas, oxygen as reactive gas. The oxygen partial pressure and sputtering pressure were 0.2-0.3 Pa and 0.5 Pa, respectively. The target was a titanium metal (purity 99.9%) of 50 mm diameter. The deposition rate of the film was controlled as 4 nm/min. The TiO₂ thin films were also prepared by a solgel method. Titanium n-butoxide [Ti(OC₄H₉)₄, TBT] was used as a precursor. TBT was dissolved in ethanol and acetylacetone. The Cu₂O was coated with the gel by the spin-coating process and then heated at 150 °C for 30 min in an electric furnace.

Platinum nanoparticles were potentiostatically electrodeposited in the dark from a solution of 1 mM H_2PtCl_6 in deionized water at a constant current density of -10 μ A/cm² (Galvanostatic mode) for a certain time using a source meter. The amount of

catalyst deposited is calculated from the amount of electricity, $0.001 \ \mu mol/cm^2$ of Pt atoms were deposited on the surface of cuprous oxide every 60 seconds. The Pt catalyst was deposited for 5 min.

Characterization

X-ray diffraction (XRD) patterns were measured with a XRD-6000 (Shimadzu) diffractometer, with a Cu K α X-Ray source. The surface morphologies were observed with a field-emission scanning electron microscopy (FESEM, FEI, XL30 S-FEG). UV-Visible-Near infrared (UV-VIS-NIR) spectra were recorded with a UV1800 (JINGHUA) Spectrometer. The film growth rates and the film thicknesses were measured by both profilometer (Veeco Dektak 6M) and cross-sectional SEM (FESEM, FEI, XL30 S-FEG) on FTO substrates. The oxidation states were analyzed with an X-ray photoelectron spectroscopy (XPS, Perkinelmer, PHI1600 ESCA). The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference. Transmission electron microscope (TEM) analysis was carried out on a JEOL JEM 2100PLUS instrument. Electrochemical impedance spectra (EIS) experiments were performed in the dark and under illumination at a frequency range of 10 mHz to 0.1 MHz by using a CHI600C potentiostat.

Photoelectrochemical response measurements were carried out using a threeelectrode setup, with a platinum counter-electrode and a Ag/AgCl/KCl(sat.) reference electrode (E = 0.197 V vs. SHE). All the potentials in this work are converted using the reversible hydrogen electrode (RHE) as the reference electrode, according to the following equation:

 $E(RHE) = E(Ag/AgCl) + 0.197 + 0.059 \times pH$ (1)

The electrochemical behaviour was monitored with a HM-PS100 potentiostat (HONGMING), while the light was provided by a HONGMING Xenon-arc lamp, calibrated to provide 1 sun (100 mW \cdot cm⁻²) of AM 1.5 illumination to the sample.

The incident-photon-to-current-efficiency (IPCE) is defined as:

$$IPCE (\%) = \frac{I}{P} \times \frac{1240}{\lambda} \times 100$$
(2)

Here *I* is the photocurrent density (mA·cm⁻²), *P* is the power of monochromatic light irradiated on the electrode (mW·cm⁻²) and λ is the wavelength (nm). IPCE measurements were performed under light from a 500 W xenon lamp (OSRAM) passing through a monochromator (HM-ISW151). Comparison with a calibrated Si photodiode allowed the calculation of the incident photons (Figure S4).

The Faraday efficiency measurements were performed by using an auto-analysis system (Figure S5), employing bias 0 V_{RHE} , aqueous 1 M Na₂SO₄ as electrolyte and an exposed electrode area of 1 cm². The produced hydrogen and oxygen were circulated in a sealed system (HM-A300) and analyzed with a gas chromatograph

(TCD detector; Carrier gas: Ar; Flow rate: 36 mL·min; Oven temperature: 50 °C; Detector temperature: 120 °C; 5A molecular sieve packed column), beforehand, the sealed system was vacuumed to evacuate the air and the dissolved oxygen in the electrolyte.



Figure S1. (a) XRD patterns of the FTO substrate and the as-prepared Cu_2O photocathode; (b) X-ray photoelectron spectrum (XPS) of Cu LMM in the Cu_2O photocathode; SEM images of (c) the FTO substrate and (d) the Cu_2O photocathode, respectively; (e) Cross-section SEM image of the Cu_2O photocathode.



Figure S2. (a) The TEM image of the PUA coated Cu_2O nanocube. (b) The UV-VIS-NIR transmission spectrum of the PUA film. The current-voltage (I-V) curves of (c) the FTO substrates and (d) the PUA film.



Figure S3. Cyclic voltammetry of the bare and the PUA protected Cu_2O electrodes (a) in dark and (b) under illumination. Nyquist impedance plots of (c) the bare Cu_2O photocathode, (d) the PUA| Cu_2O photocathode, (e) the Pt| TiO_2 |PUA| Cu_2O photocathode and (f) the Pt| TiO_2 |PUA| Cu_2O |Ag photocathode in dark and under illumination, respectively.



Figure S4. The automatic IPCE analysis system in this work.



Figure S5. The automatic analysis system for the gas detection in this work.