Electronic Supplementary Material (ESI) for ChemComm.

Performance improvement of p-Cu_2O nanocrystal photocathode with ultra-thin silver protective layer

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 20 nm of Cr and 100 nm of Au by thermal evaporation, and the evaporation chamber was pumped to a base pressure of 1.0×10^{-4} Pa before deposition. The temperatures of the tungsten boats for Cr and Au deposition were around 2000 and 1200 °C, respectively. For Cu_2O preparation, the films were deposited by electrodeposition from solutions of lactate-stabilized copper sulphate. The plating bath was 0.2 M $CuSO_4$ (ALADDIN) and 1.2 M sodium lactate (ALADDIN) solution in deionized water. The bath pH was adjusted to 12 by adding an amount of KOH. The temperature of the bath was maintained at 30 ºC using a water bath with an in situ temperature probe. The Cu_2O thin films were deposited at biasing of 2.0 V for 300 min using a potentiostat (HM-PS100) in a two-electrode configuration with a Pt plate counter electrode.

Before Ag deposition, the Cu_2O thin films were conditioned for 5 min under plasma in a Plasma Cleaner (HM-Plasma5L, 13.56 MHz) in low pressure Ar atmosphere. A series of Ag films with different thickness were deposited on Cu_2O by high power impulse magnetron sputtering (HiPIMS) under identical conditions using a 50 mm diameter Ag target (99.99%). The pulse frequency was 50 Hz, and the pulse-on time was 50 μs. A stainless steel vacuum chamber equipped with a turbomolecular pump backed up with a mechanical pump. To guarantee the uniformity in the lateral direction and the thickness of the films, all the Cu_2O thin films were set on the fixture with the same radius of the circle, and rotated about the center of the fixture. The target-to-substrate distance was 10 cm. The Ag target was mounted on a water-cooled copper plate. The 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 0.15 Pa. The sputtering peak current was 7.5 A for all the samples. The film thickness was in-situ detected by a crystal thin film deposition controller (MorningTech) equipped with quartz crystal resonators.

For comparison, a thermal evaporator (HM-V160, Changzhou Hongming Instrument Technology Co., LTD.) was used for Ag thermal evaporation, the vacuum chamber was pumped to a base pressure of 1.0×10^{-4} Pa before deposition. The temperature of the tungsten boat was set as 1000 °C. The electrodeposited Ag film was carried out in a two-electrode cell with a mixed solution of 100 mM $AgNO_3$ and 100 mM $NaNO_3$. The Cu_2O cathode and a Pt sheet acted as the working electrode and the auxiliary electrode, respectively, while the current density was $-10\ mA\cdot cm^{-2}$.

After the deposition, the film was rinsed by deionized water. For DC magnetron sputtering (DCMS), the sputtering current was 75 mA for all the samples, and the process steps were the same as the above HiPIMS.

Characterization

X-ray diffraction (XRD) patterns were measured with a XRD-6000 (Shimadzu) diffractometer, with a Cu Kα X-Ray source. The surface morphologies were observed with a field-emission scanning electron microscopy (SEM; HITACHI, S-4800), and energy-dispersive X-ray (EDX) analysis obtained with a Noran System 7 (THERMO). UV-Visible (UV-VIS) spectra were recorded with a 722S (JINGHUA) Spectrometer. The atomic force microscope (AFM) images were obtained with tapping mode AFM in air. The temperature and humidity during the test were 25 °C and 57%, respectively. A CSPM5500A cantilever probe (Being Nano-Instruments) was used for characterizing.

Photoelectrochemical response measurements were carried out using a three-electrode 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:

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

The photocurrent stability tests were monitored in 1 M Na_2SO_4 with a HM-PS100 potentiostat (HONGMING) at a fixed electrode potential of 0 V_{RHE}, 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 electrolyte was continuously bubbled with Ar to remove oxygen and thus eliminate errors arising from oxygen reduction. The scan rate for the linear sweep voltammetry was 10 $mV \cdot s^{-1}$.

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

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

Here I is the photocurrent density ($mA \cdot cm^{-2}$), P is the power of monochromatic light irradiated on the electrode ($mW \cdot cm^{-2}$) 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 (Pacific Silicon Sensor, PS13-5b) allowed the calculation of the incident photons.

The Faraday efficiency measurements were performed by using an auto-analysis system, employing bias 0 V_{RHE}, aqueous 1 M Na_2SO_4 as electrolyte and an exposed electrode area of 1 cm^{-2}. 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 ^{o}C; Detector temperature: 120 ^{o}C; 5A molecular sieve packed column), beforehand, the sealed system was vacuumed to evacuate the air and the dissolved oxygen in the electrolyte.

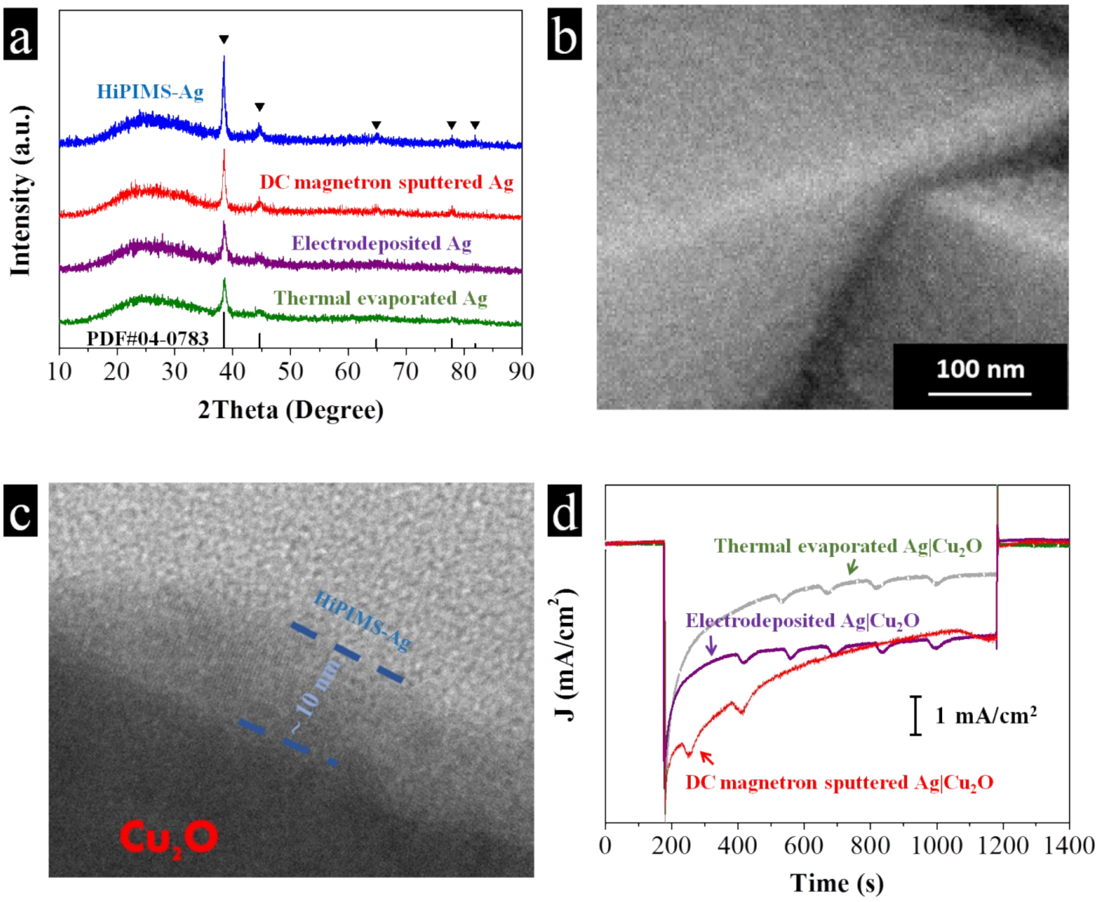

Figure S1. (a) The XRD patterns of the Ag films deposited by different methods; (b) The SEM image of the HiPIMS-Ag coated Cu_2O photocathode; (c) The TEM image of the HiPIMS-Ag coated Cu_2O nanocube; (d) J-t curves of the different Ag film coated Cu_2O photocathodes held at 0 V_{RHE} in 1 M Na_2SO_4 solution electrolyte with Ar bubbling, under 100 mW/cm^2 of AM1.5 illumination.