

Electronic Supplementary Information

Room temperature synthesis of highly active Cu/Cu₂O photocathode for photoelectrochemical water splitting

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Experimental procedure

Materials: Stock solutions of sodium hydroxide (3.0 M) and copper acetate (0.03 M) were prepared by dissolving NaOH (99%) and copper acetate (Farco Chemical Supplies, 99%) in deionized water respectively, and stored in glass bottles. Copper mesh (100 mesh with the wire diameter of 0.1mm, 99%) and copper foil (1.27 mm in thickness, 99.9%; Alfa Aesar) were used as received.

Preparation of Cu mesh/Cu₂O electrodes: A typical fabrication process was performed as follows. A blue solution was prepared in a 15 mL glass bottle by mixing 4 mL of the NaOH solution (3.0 M) and 1 mL of copper acetate solution (0.03 M). The Cu mesh (10 mm × 20 mm) was sequentially cleaned in 0.5 M HCl solution, acetone

and ethanol with ultrasonication for 15 min. The cleaned Cu mesh was then immersed into the solution, and the temperature was maintained at 25 °C using a water bath. After a certain time, the copper mesh with a dark red color was taken out from the solution, rinsed with deionized water and ethanol, and dried in air.

To prepare Cu foil/Cu₂O electrode, a common Cu foil (10 mm × 20 mm) was used as the substrate. The cleaning process and reaction condition was the same as previous description for Cu mesh. The reaction time was optimized to 12 h.

Cu mesh/Cu₂O NWs was prepared using the method reported in literature.¹

Atomic layer deposition of protective layers: Protective layers of Al:ZnO (AZO) and TiO₂ were deposited on the surface of the Cu mesh/Cu₂O electrodes using a thermal ALD system (PICOSUN, R-200 Advanced). The ALD of Al:ZnO was carried out at a substrate temperature of 120 °C using diethylzinc, trimethylaluminum and H₂O as the Zn, Al and O precursors, respectively. All the precursors were maintained at room temperature. Each precursor was held in the chamber for 2.0 s, followed by a 15.0 s nitrogen purge. Al:ZnO was deposited by running 20 cycles of diethylzinc and water followed by 2 cycles of trimethylaluminum and water. The growth rate per cycle (GPC) was 2.0 Å for ZnO and 1 Å for Al₂O₃. Such process was repeated for 5 times, and the overall thickness of Al:ZnO layer was 22 nm. TiO₂ was deposited at a substrate temperature of 150 °C using tetrakis(dimethylamino)titanium (TDMAT) at a precursor temperature of 75 °C, and water at room temperature. Each precursor was held in the chamber for 2.0 s, followed by a 15.0 s nitrogen purge. The overall thickness of TiO₂

layer was about 100 nm.

Cocatalyst deposition: To enhance the kinetics of the hydrogen evolution reaction on the TiO₂ surface, Pt nanoparticles were deposited onto Cu mesh /Cu₂O-20/AZO/TiO₂ by a sputter coater (Polaron, SC502) with a plasma current of 3 mA for 90 s.

Characterization

X-Ray diffraction (XRD) was performed on a Rigaku SmartLab X-ray diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The morphology of the products was investigated by transmission electron microscopy (TEM) on a CM120 microscope (Philips, 120kV) and by scanning electron microscopy (SEM) on a FEI Quanta 400 microscope. The EDX line-scanning measurement was carried out on another TEM instrument (Tecnai Model F20; FEI). X-Ray photoelectron spectroscopy (XPS) was acquired on a Sengyang SKL-12 spectrometer equipped with a VG CLAM 4 MCD electron energy analyzer and twin anode Mg K α radiation (1253.6 eV). The chemical state of copper being difficult to determine using Cu 2p binding energy, the Auger Cu LMM signal was also recorded. UV–vis diffuse reflectance spectra (DRS) were achieved using a UV–vis spectrophotometer (Cary 100, Agilent).

Photoelectrochemical measurement

The PEC performance of the prepared electrodes was evaluated in a three-electrode cell using the prepared sample as the working electrode, Ag/AgCl (saturated KCl) electrode as the reference electrode and Pt foil as the counter electrode. The electrolyte used was 0.1 M Na₂SO₄ solution (pH 7.0) or 0.1 M KH₂PO₄-0.5 M Na₂SO₄ (pH 5.0). The photoresponse was measured under a chopped irradiation from a solar simulator (Oriel Sol3A standard) with an air mass 1.5 G filter. Light intensity was calibrated to 1 sun (100 mW cm⁻²) using a Si diode. The backside of the photoelectrode was attached with vinyl tape (VINI-TAPE[®], Denka) for isolation. The scan rate for the linear sweep voltammetry was 10 mV s⁻¹ in cathodic direction. Photocurrent stability tests were carried out by measuring the photocurrent under chopped light irradiation at a fixed potential of 0 V *vs.* RHE. Before PEC measurement, the electrolyte was continuously bubbled with N₂ to remove oxygen and thus eliminate erroneous signals arising from oxygen reduction.

IPCE measurement

The incident photon to current efficiency (IPCE) was carried out on the same 3-electrode cell using a 250 W Hg lamp with a monochromator (Oriel) with a bandwidth of 10 nm. IPCE was calculated according to the following equation:

$$IPCE = (1240 \times I) / (\lambda \times J_{light}) \times 100$$

where I is the photocurrent (mA), λ is the incident light wavelength (nm), and J_{light} is the intensity of incident monochromatic light at a specific wavelength (mW).

Electrochemical measurement

Electrochemical impedance measurements were carried out in the same system with an excitation AC signal of 10 mV amplitude under dark conditions. Mott–Schottky plots were acquired by sweeping the potential at fixed frequencies. Bode phase plots were measured in a frequency range between 100 kHz and 0.1 Hz at open-circuit voltage.

Hydrogen production measurement

Hydrogen production measurement was conducted in a PEC cell connected to a closed gas circulation and evacuation system. The electrolyte was 0.1 M KH_2PO_4 -0.5 M Na_2SO_4 (pH 5.0). PEC hydrogen production was performed at 0 V vs. RHE under AM 1.5G illumination. The amount of evolved hydrogen was determined using on-line gas chromatography (Techcomp GC7900; MS-5A column, TCD). High purity argon gas was used as the carrier gas. The Faradaic efficiency was calculated using the equation:

$$\text{Faradaic efficiency} = \frac{n(\text{H}_2)}{Q/2F}$$

where $n(\text{H}_2)$ is the total amount of hydrogen produced (mol); Q is the total amount of charge passed through the cell (C), which can be calculated from the integration of the measured photocurrent with time; and F is the Faraday constant (96485 C mol^{-1}). For the reduction of protons, two electrons are needed to reduce two protons and produce one H_2 molecule.

Table S1. Summary of PEC performances under AM 1.5G light illumination for bare Cu₂O photocathodes reported in literature.

Substrate	Fabrication Method	Electrolyte	Maximum photocurrent density [mA cm ⁻²]	Ref.
Au-Cr coated FTO	Electrodeposition	1.0 M Na ₂ SO ₄	2.4	24
Cu foil	Thermal oxidation	0.2 M K ₂ HPO ₄	0.47	27
FTO	Electrodeposition	0.5 M Na ₂ SO ₄	0.3	22
FTO	Electrodeposition	1.0 M Na ₂ SO ₄	0.37	25
Cu mesh	Anodization followed by annealing in N ₂	1.0 M Na ₂ SO ₄	2.28	14
Cu foil	Chemical oxidation followed by annealing in a vacuum	0.5 M Na ₂ SO ₄	4.07	29
Cu mesh	Redox reaction in Cu(OAc) ₂ -NaOH	0.1 M Na ₂ SO ₄	4.8	Present work
Cu foil	Redox reaction in Cu(OAc) ₂ -NaOH	0.1 M Na ₂ SO ₄	4.0	Present work

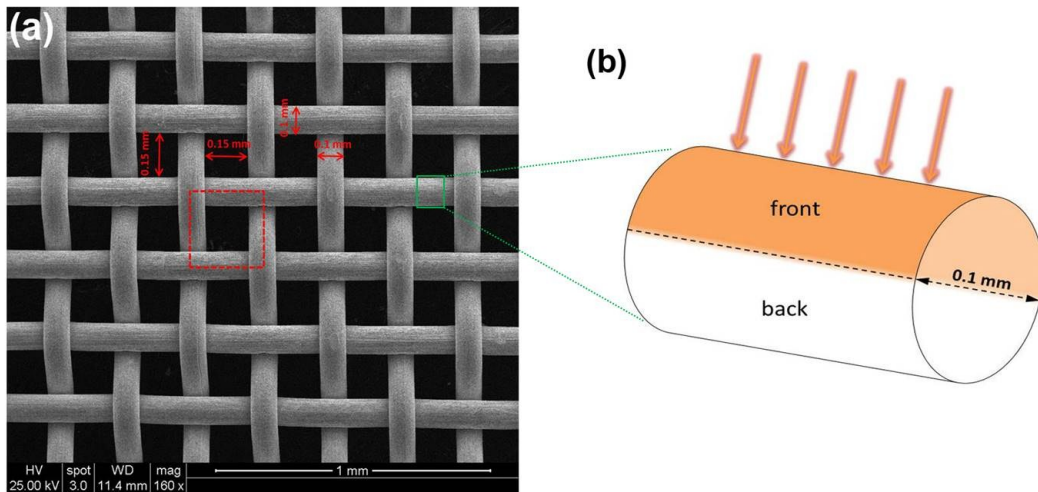


Fig. S1 (a) Low-magnification SEM image of the Cu mesh/Cu₂O, the red dash square represents a repeating unit for the mesh configuration; (b) Schematic diagram showing the 3D view of the copper wire.

As shown in the SEM image, the Cu mesh consists of many Cu wires intersecting perpendicularly with each other. The diameter of each Cu wire is 0.1 mm, and the length of a side of the open (empty) area is 0.15 mm. During the PEC test, only one side of the photoelectrode was exposed to the incident light, and the other side was covered by vinyl tape to block light and electrolyte. To estimate the surface area of the mesh electrode, a repeating unit (the red dash square in the SEM image) was considered. The area of this square (denoted as illumination area) was found to be 0.0625 mm². While in this unit region, the total surface area of the wires is calculated to be 0.126 mm². Since only the front side is exposed, the effective surface area for light absorption is about half of 0.126 mm², which is close to the illumination area of 0.0625 mm². This means for every illumination area of 1 cm², the effective surface area of the mesh electrode is also about 1 cm², suggesting that the working area of a Cu mesh is comparable to that of a flat solid substrate like a copper foil.

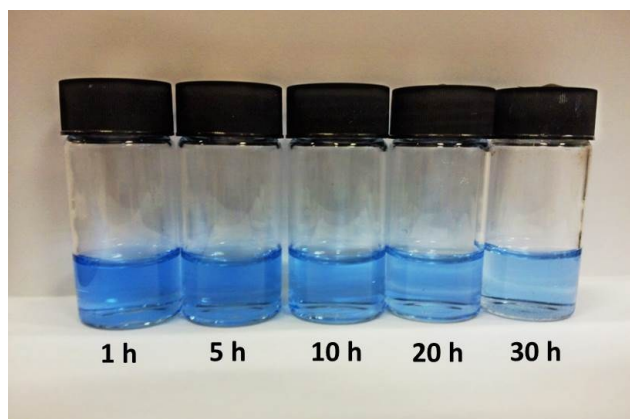


Fig. S2 Photograph of the remaining reaction solution after a certain time.

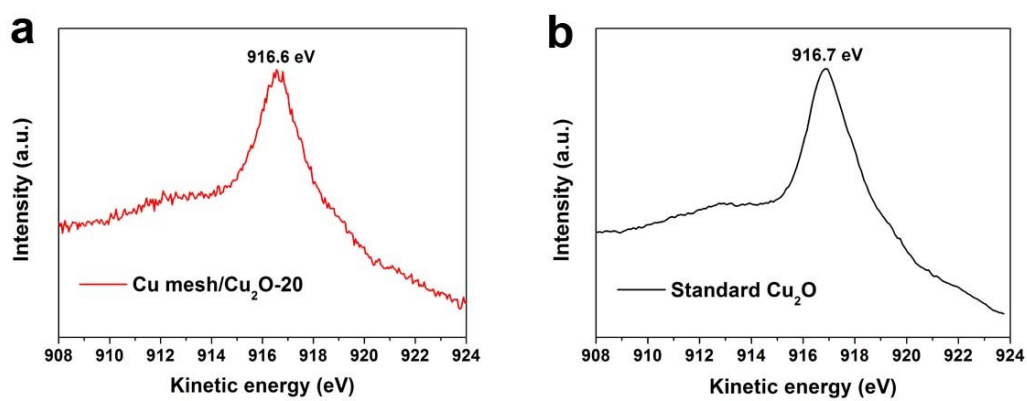


Fig. S3 Auger Cu LMM spectra of (a) Cu mesh/Cu₂O-20 and (b) standard Cu₂O.

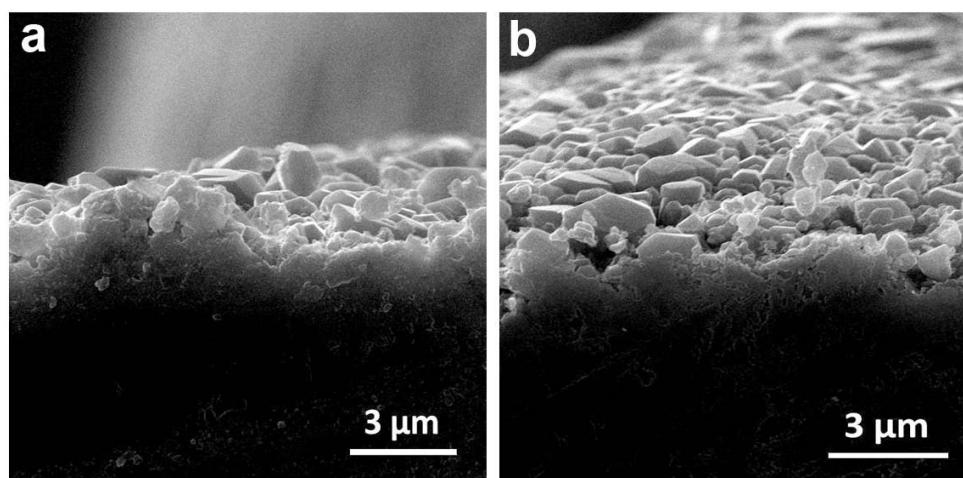


Fig. S4 SEM cross-sectional images of Cu mesh/Cu₂O-20.

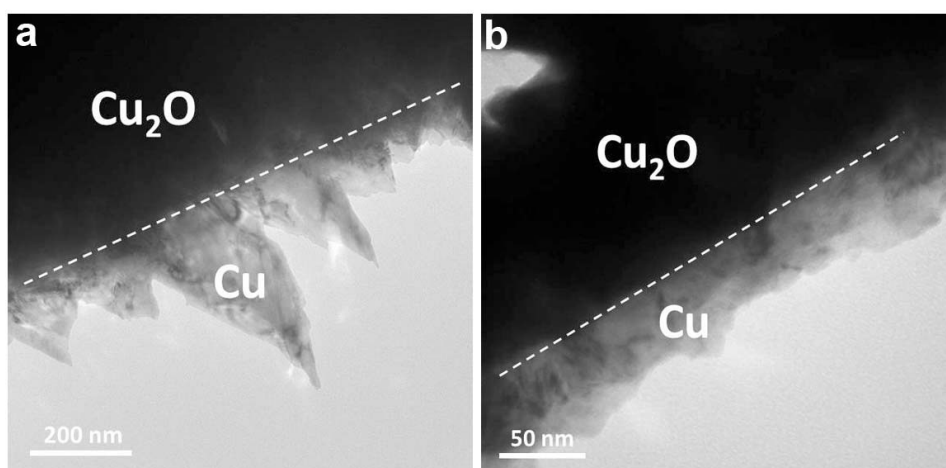


Fig. S5 TEM images of Cu/Cu₂O flakes scraped from Cu mesh/Cu₂O-20.

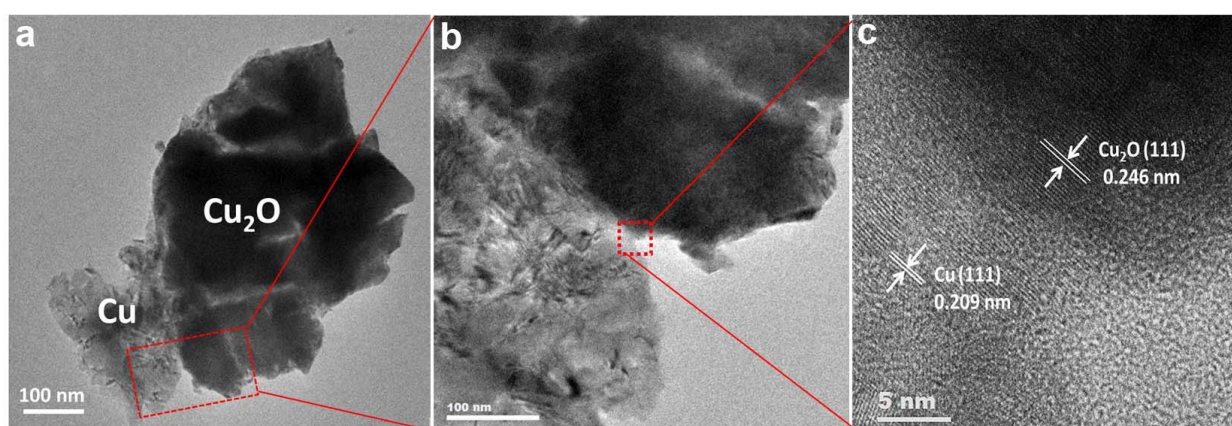


Fig. S6 TEM (a,b) and HRTEM (c) images of a flake of Cu/Cu₂O.

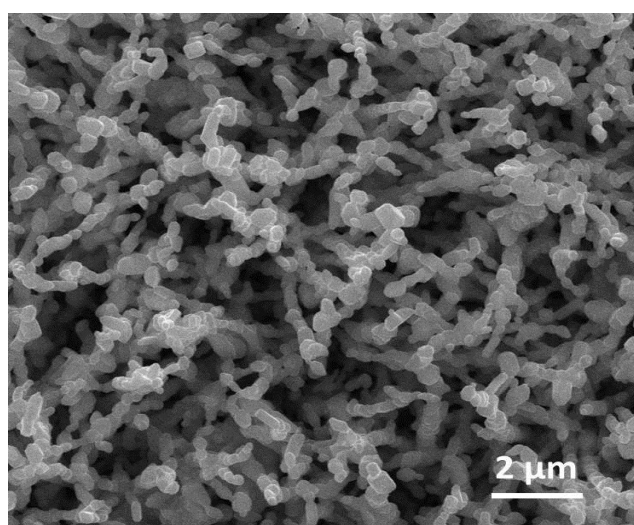


Fig. S7 SEM image of the as-prepared Cu mesh/Cu₂O NWs

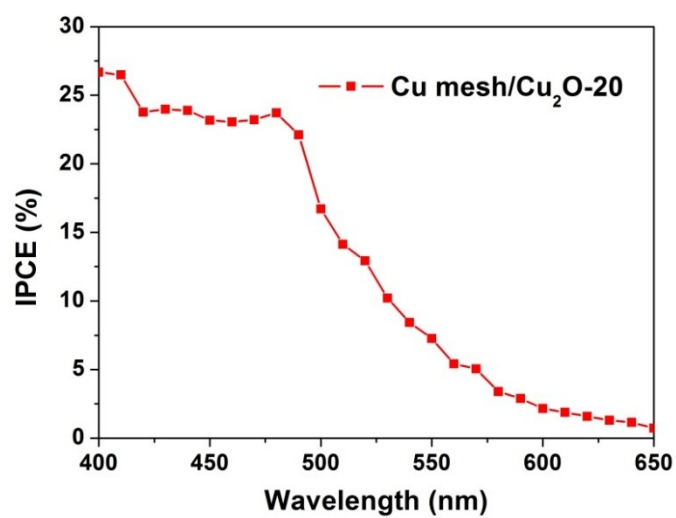


Fig. S8 IPCE of Cu mesh/Cu₂O-20 as photocathode.

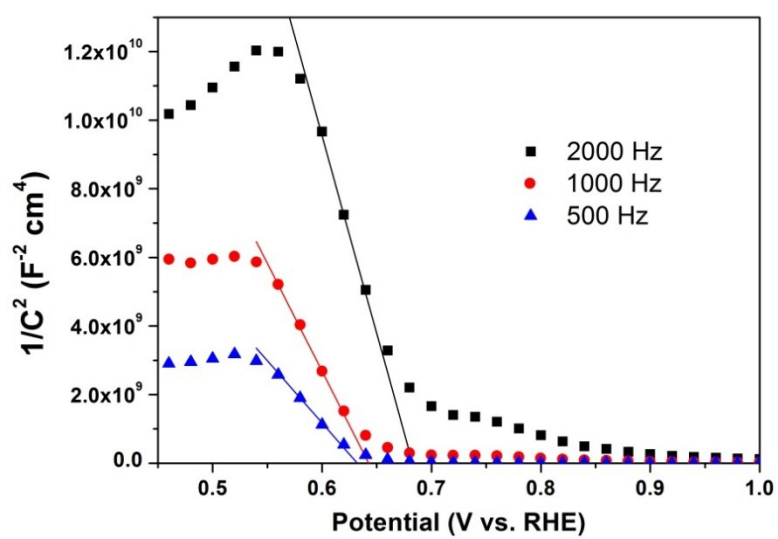


Fig. S9 Mott-Schottky plots of Cu mesh/Cu₂O-20 at different fixed frequencies.

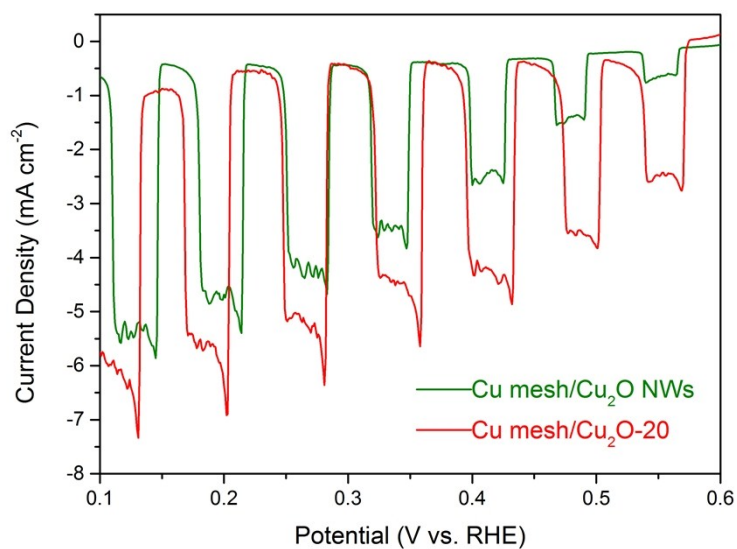


Fig. S10 J-V (Current–potential) curves of Cu mesh/Cu₂O-20 and Cu mesh/Cu₂O NWs in 0.1 M Na₂SO₄ electrolyte saturated with O₂ under chopped AM 1.5G illumination. The electrolyte was bubbled consecutively with O₂ during the PEC test.

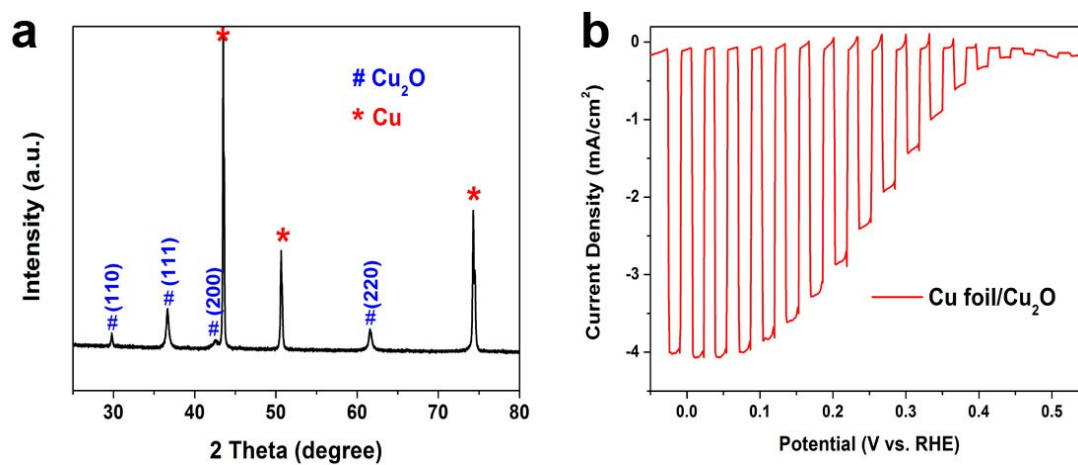


Fig. S11 (a) XRD pattern of Cu foil/Cu₂O; (b) Current–potential characteristics of Cu foil/Cu₂O in 0.1 M Na₂SO₄ saturated with N₂ under chopped AM 1.5G illumination.

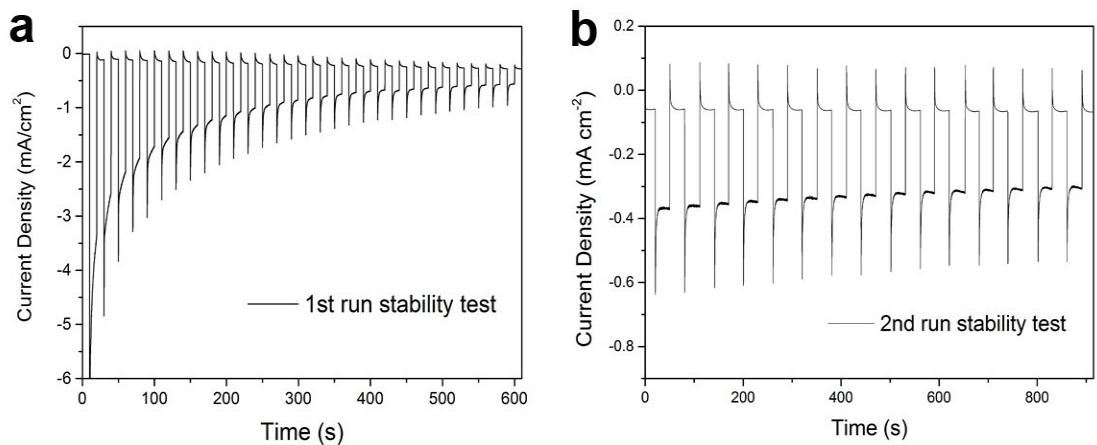


Fig. S12 PEC stability test of Cu mesh/ Cu_2O -20 in 0.1 M Na_2SO_4 at 0 V vs. RHE under chopped AM1.5G illumination: (a) 1st run stability test; (b) 2nd run stability test (after 10 min of 1st run test).

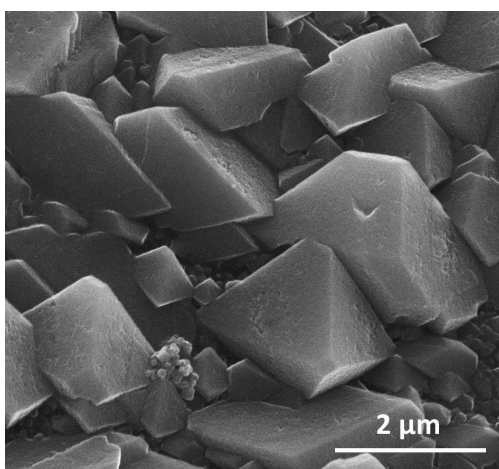


Fig. S13 SEM image of Cu mesh/ Cu_2O -20 after 10 min of PEC stability test.

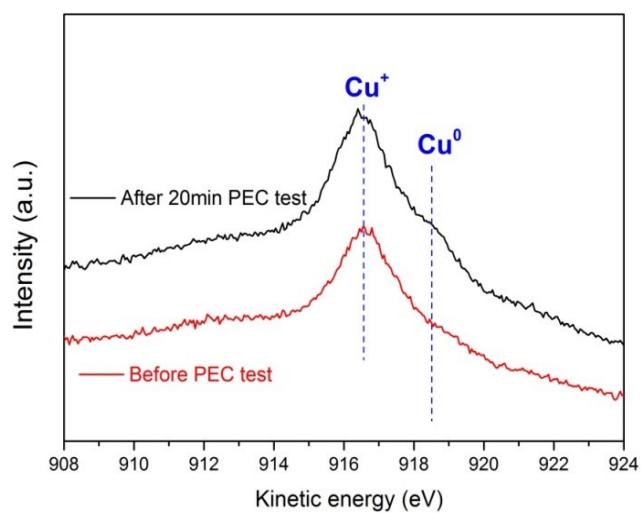


Fig. S14 Auger Cu LMM spectra of Cu mesh/Cu₂O-20 before and after the stability test.

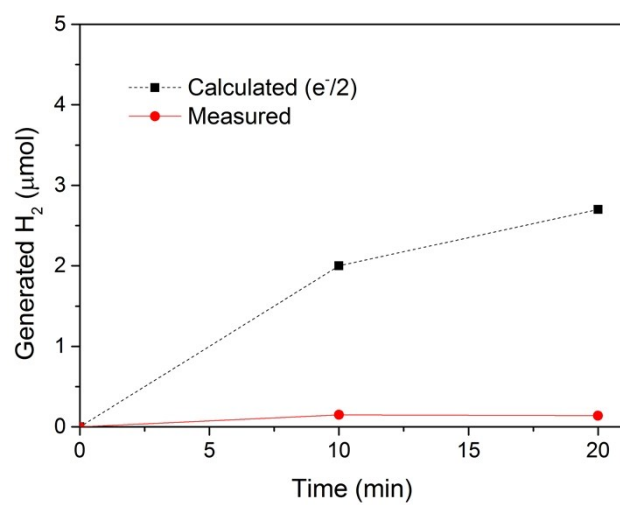


Fig. S15 H₂ evolution from the Cu mesh/Cu₂O-20 photocathode in 0.1 M Na₂SO₄ biased at 0 V vs. RHE under AM 1.5G illumination.

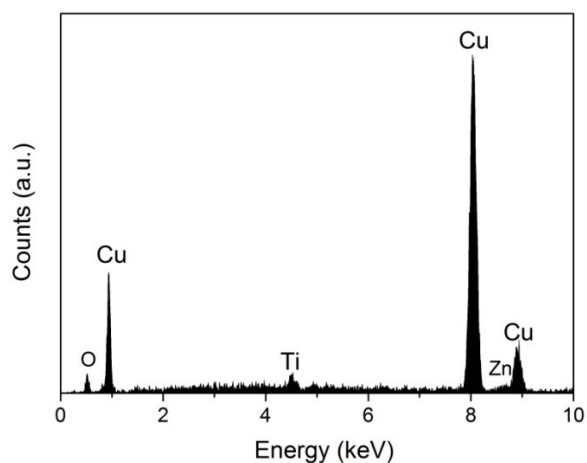


Fig. S16 EDX spectrum of Cu mesh/Cu₂O-20/AZO/TiO₂.

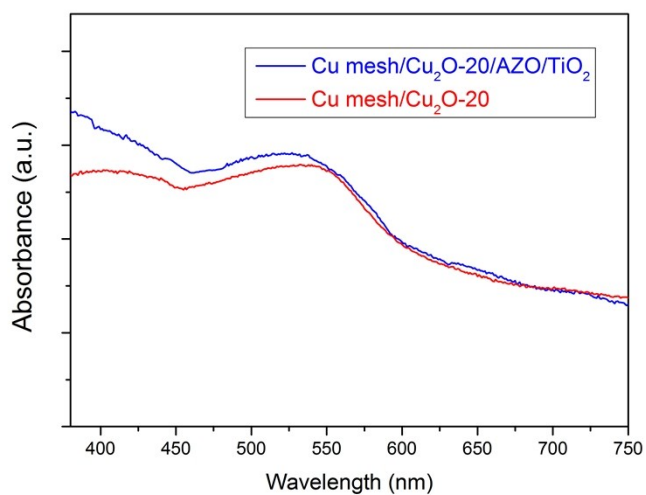


Fig. S17 Absorption spectra of Cu mesh/Cu₂O-20 and Cu mesh/Cu₂O-20/AZO/TiO₂.

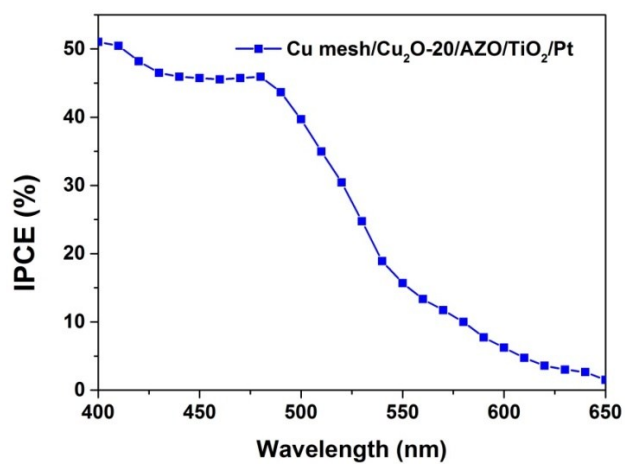


Fig. S18 IPCE of Cu mesh/Cu₂O-20/AZO/TiO₂/Pt photocathode at 0 V vs. RHE in pH 5.0 electrolyte (0.1 M KH₂PO₄-0.5 M Na₂SO₄).

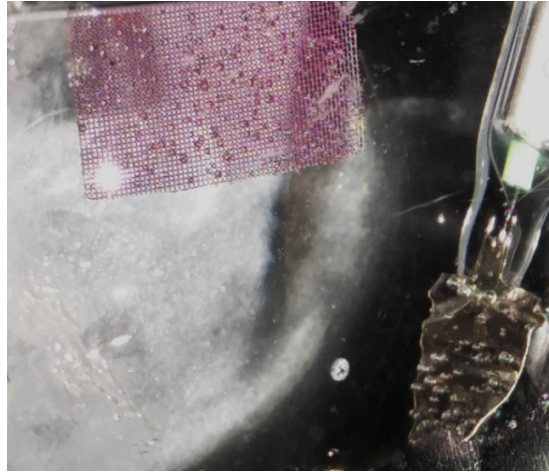


Fig. S19 Digital photograph of hydrogen gas bubbles generated on Cu mesh/Cu₂O-20/AZO/TiO₂/Pt photocathode and oxygen gas bubbles on Pt anode during stability test.

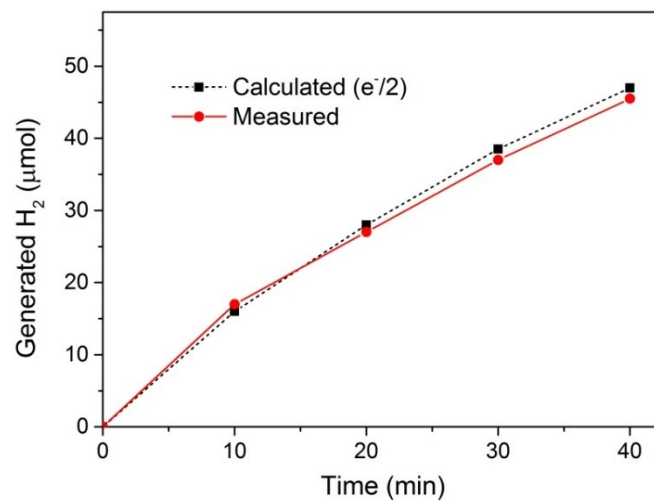


Fig. S20 H₂ evolution from the Cu mesh/Cu₂O-20/AZO/TiO₂/Pt photocathode biased at 0 V vs. RHE in pH 5.0 electrolyte (0.1 M KH₂PO₄-0.5 M Na₂SO₄) under AM 1.5G illumination.

Reference:

1. Z. Zhang, R. Dua, L. Zhang, H. Zhu, H. Zhang and P. Wang, *ACS Nano*, 2013, **7**, 1709-1717.