Supporting Information

Cu_2O/CuO photocathode with improved stability for photoelectrochemical water reduction

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Experimental details:

Materials

The copper foil with a purity of 99.9% was ultrasonic cleaned with ethanol and deionized water for 5 min in sequence prior to use. All chemicals were analytical grade and were used as purchased without further purification. Solutions were prepared using high purity water (Millipore Milli-Q purification system, resistivity > 18 MΩ cm).

Preparation of Cu_2O/CuO electrodes

The Cu_2O/CuO electrode was prepared by heat treatment of copper foil (15 mm* 15 mm* 2 mm) in a H_2-O_2 flame at *ca.* 1300 K for 2 s (HT-2S), 5 s (HT-5S), 10 s (HT-10S), and 15 s (HT-15S) respectively as shown in Scheme 1. The temperature of the flame was controlled by tuning the ratio of hydrogen and oxygen and measured by a thermoelectric couple. After heating the film for the intended duration, the films were allowed to cool down to room temperature in air naturally.

Characterizations of the electrodes

The morphologies analysis of the photocathodes was examined by a Quanta 200 FEG scanning electron microscope (SEM) equipped with an energy dispersive spectrometer at an accelerating voltage of 20 kV. The prepared photocathodes were characterized by XRD on an X'pert Powder diffractometer using Cu Kα radiation with an operating voltage of 40 kV and an operating current of 40 mA. A scan rate of 12 °/min was applied to record the patterns in the range of 20~70 °. Raman spectra were measured on Renishaw raman spectrometer with spectral resolution of 2 cm^{-1}. The laser line at 532 nm of a solid laser was used as an exciting source. The power of laser line, measured at the samples, was about 0.3 mw. The spectra of all samples were recorded at room temperature. XPS was performed using a monochromatized Al Kα source (hν = 1486.6 eV), operated at 225 W, on a Kratos Axis Ultra DLD system at a takeoff angle of 0 ° relative to the surface normal and a pass energy for narrow scan spectra of 20 eV, corresponding to an instrument resolution of approximately 600 meV. Survey spectra were collected with a pass energy of 80 eV. Spectral positions were corrected by shifting the primary C 1s core level position to 285 eV. The UV-vis diffuse reflectance spectra of the photocathodes were examined on JASCO-V650 spectroscopy in the range of 300-900 nm. The high resolution transmission electron microscopy (HRTEM) and the electron diffraction of HT-10S photocathode are conducted on the FEI tecnai F30 instrument.

Photoelectrochemical measurements

The PEC performances of Cu_2O/CuO electrodes were measured in a three-electrode setup with Pt counter electrode and SCE reference electrode in 0.5 M Na_2SO_4 electrolyte with Ar bubbling or air bubbling. Before measurement, the areas of electrodes were fixed by insulating cement. Linear sweep voltammetry (LSV) with a scanning rate of 20 mV s^{-1} was performed using an Ivium electrochemical station and a Newport Oriel sol3A light source under 100 mW cm^{-2} illumination. Current-time (i-t) curve was performed using the same electrochemical station and light source at 0 V vs. RHE.

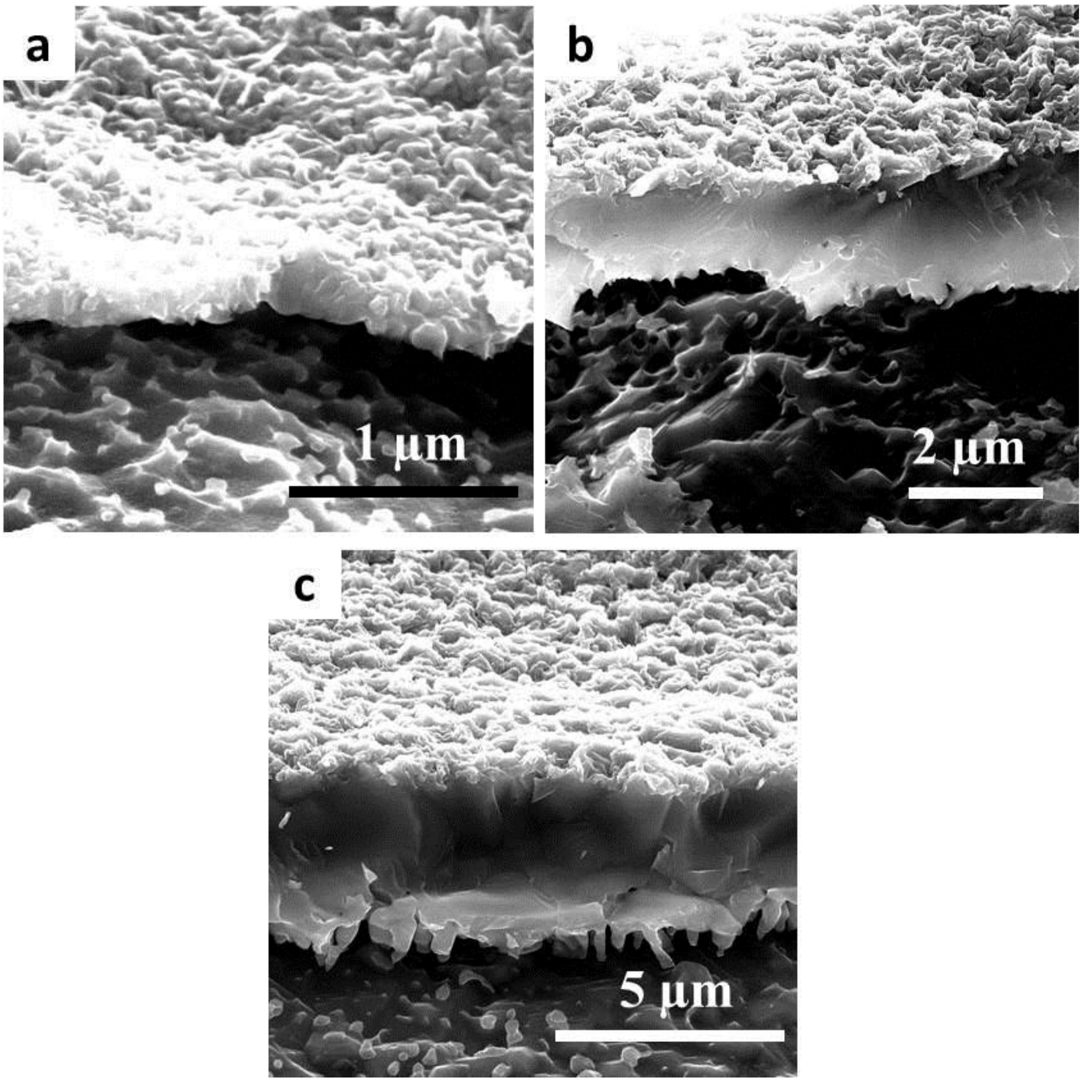

Fig. S1 Cross-sectional SEM images of HT-5S (a), HT-10S (b) and HT-15S (c).

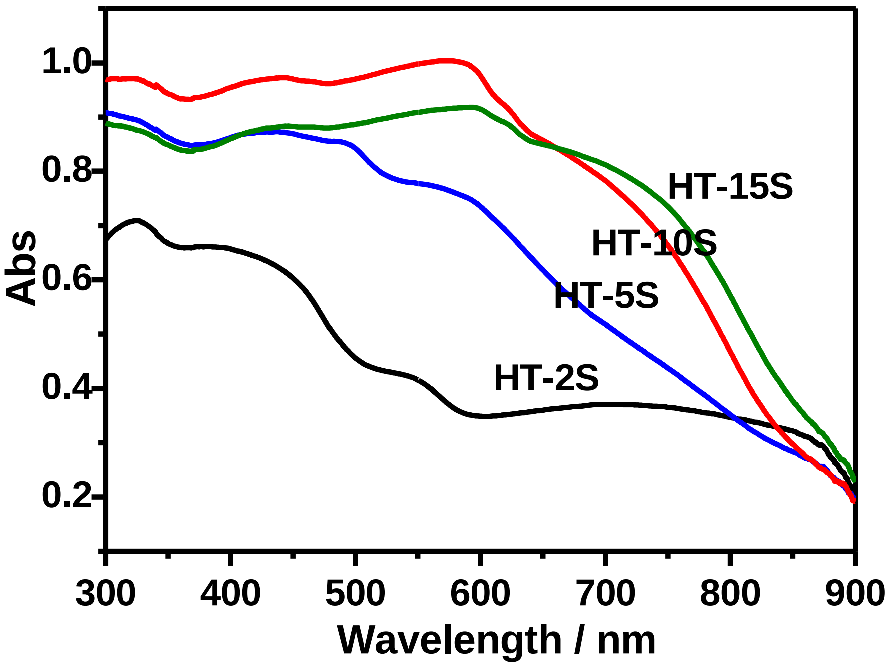

Fig. S2 UV-visible diffuse reflectance spectra of composite Cu_2O/CuO photocathodes.

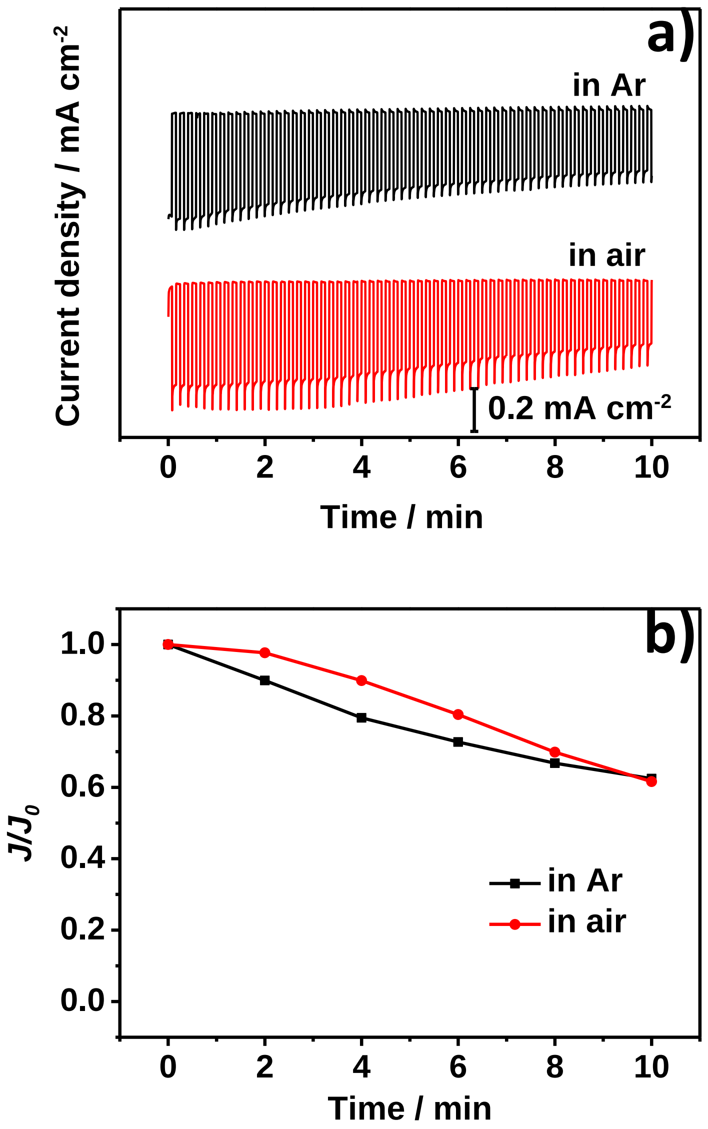

Fig. S3 Current-time curves (a) and current decay curves (b) of HT-15S elecrodes in Ar (black line) and air atmosphere (red line). Electrolyte, 0.5 M Na_2SO_4 aqueous solution with Ar or air bubbling; Light source, AM 1.5 G (100 mW cm^{-2}) with a chopping frequency of 0.2 Hz; The potential applied for current-time test, 0 V vs. RHE.

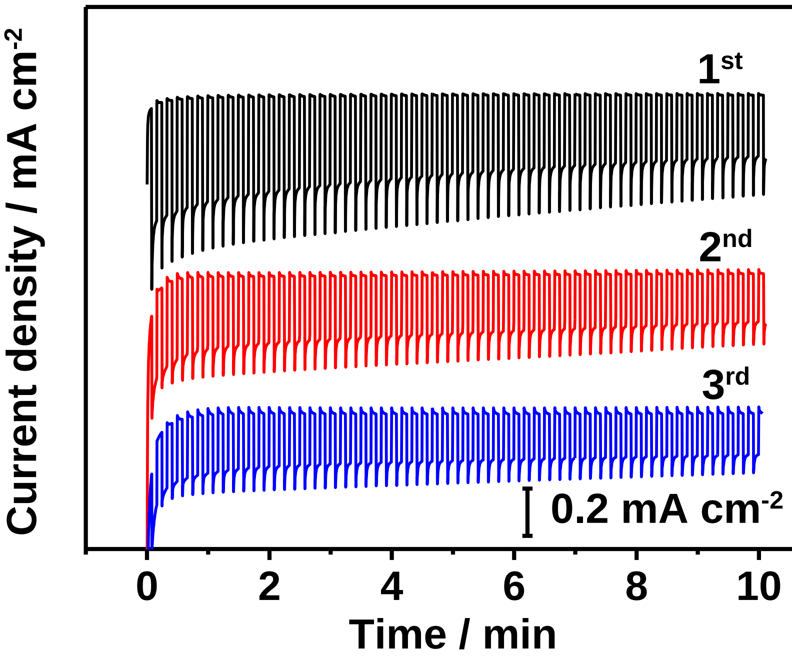

Fig. S4 Current-time curves of HT-15S electrode for three times. Electrolyte, 0.5 M Na_2SO_4 aqueous solution with Ar bubbling (pH 6.82); Light source, AM 1.5 G (100 mW cm^{-2}) with a chopping frequency of 0.2 Hz; The potential applied for current-time test is 0 V vs. RHE.

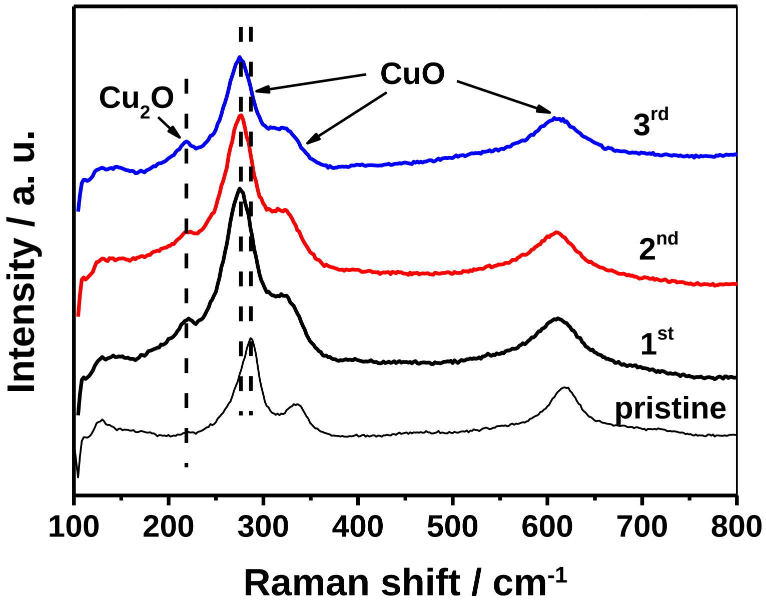

Fig. S5 The Raman spectra of the pristine HT-15S electrode and these after repeated PEC tests.