Supporting information

A Robust and Highly Active Copper-Based Electrocatalyst for Hydrogen Production at Low Overpotential in Neutral Water

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Experimental section

Materials. copper(II) ethylenediamine (1 M, water solution), $CuCl_2{\cdot}2H_2O$ (99.0%), NaCl (99.5%), NaOH (96.0%), potassium hydroxide (KOH, 85.0%), sulfuric acid (H_2SO_4, ~70%), and potassium phosphate (99.0%) were purchased from Aldrich or Acros. All chemicals were used without further purification unless otherwise noted. Electrolyte solutions were prepared with Millipore water (resistivity: 18 MΩ·cm).

Electrochemical methods. All electrochemical experiments were carried out with a CHI720E potentiostat (Shanghai Chenhua Instrument Co., Ltd.) at room temperature. The Ag/AgCl electrode (3 M KCl, 0.21 V vs NHE) was used as the reference electrode, Pt wire was used as the counter electrode, and fluorine doped tin oxide (FTO) electrode was used as the working electrode. Bulk electrolysis was performed at variable current densities with *iR* compensation without stirring. All cyclic voltammograms (CV) and linear sweep voltammograms (LSV) were measured with 80 % *iR* compensations, and no stirring was performed.

Hydrogen production reaction. The hydrogen production experiments were performed in a gas-tight electrochemical cell, and the solution was 0.1 M KPi solution at pH 7.0 with the deposited Cu(0) materials coated on FTO as the working electrode obtained from **Cu-EA.** Before the test, air was excluded of air by bubbling with high purity N_2 for 20 minutes with vigorous stirring. Hydrogen gas evolution was measured by gas chromatography (SP-6890, nitrogen as a carrier gas) with thermal conductivity detection (TCD) and methane as the internal standard.[1]

Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX). The morphology and EDX spectra of the deposited copper based materials were studied by a

SIRION200 Schottky field emission scanning electron microscope (SFE-SEM) equipped with a Rontec EDX system. Before the experiment, the detected samples were rinsed at least three times by degassed ethanol or deionized water and dried under N_2 unless noted otherwise. After being coated with Au or Pt, the samples were loaded into the instrument and the SEM images were obtained with an acceleration voltage of 5 kV or 10 kV.

X-ray photoelectron spectroscopy (XPS). The elemental composition and the valence states of elements of deposited copper based materials were probed with an ESCALAB 250 X-ray photoelectron spectroscopy (XPS) instrument. The survey scan, high resolution O 1s, Cu 2p, and Cu LMM spectra were obtained. All the spectra were referenced to the C 1s peak (285.0 eV).

X-ray diffraction spectroscopy (XRD, D/max-TTR III). XRD profiles were measured by X-ray diffraction spectroscopy fitted with a graphite monochromator in the diffracted beam, using Cu Kα radiation ($\lambda = 1.54178$ Å), operating at 40 kV and 200 mA. The scanning rate was 5° min^{-1} from 10° to 80° in 2θ.

Reference.

[1] a) P. Du, K. Knowles, R. Eisenberg, *J Am Chem Soc* **2008**, *130*, 12576-12577; b) Z. Yan, X. Yu, A. Han, P. Xu, P. Du, *J Phys Chem C* **2014**, *118*, 22896-22903.

Table S1. Comparison of electrochemical properties for HER based on copper complexes.

catalyst	onset potential (mV)	η (mV vs 1.0 mA/cm^2)	Refs.
Na[Cu(opba)]^a	~380	~480	[18] *RSC. Adv.* 2014, ***4***, 53674-53680.
Cu[L]^b	~480	~580	[19] *Int. J. Hydrogen Energy* 2014, ***39***, 13972-13978
[(bztpen)Cu](BF$_4$)$_2$^{c}	~240	~340	[20] *Angew. Chem. Int . Ed.* 2014, ***53***, 13803-13807.
Cu(TPA)^d	~200	~440	[24] *ACS Catal.* 2015, ***5***, 1530-1538.
Cu-EA	~70	~150	This work

^{a,b}: data for this part from CV scan at 100 mV/s using GC (diameter: 1 mm) as working electrode at pH 7.0. ^{c}: data for this part from CV scan at 50 mV/s using GC (diameter: 1 mm) as working electrode at pH 2.5. ^{d}: data for this part from Tafel curve in 0.1 M KBi buffer at pH 9.2.

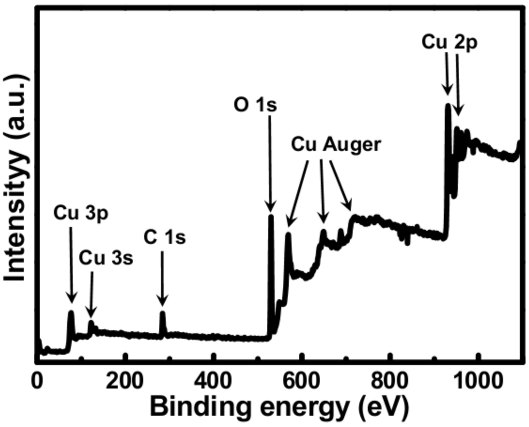

Figure S1. XPS survey spectrum of the electrodeposited copper materials after washing with Millipore water for five times.

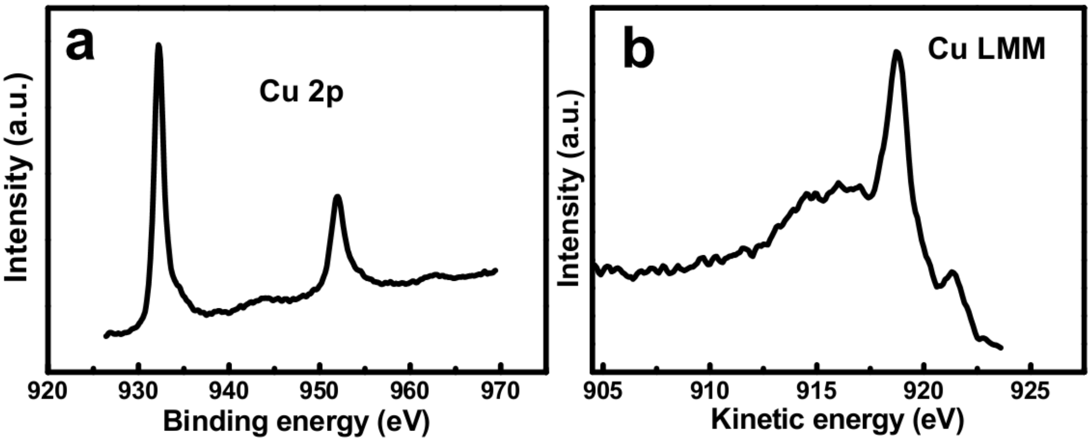

Figure S2. High resolution XPS spectra of (a) Cu 2p, and (b) Cu LMM of the electrodeposited Cu(0) materials.

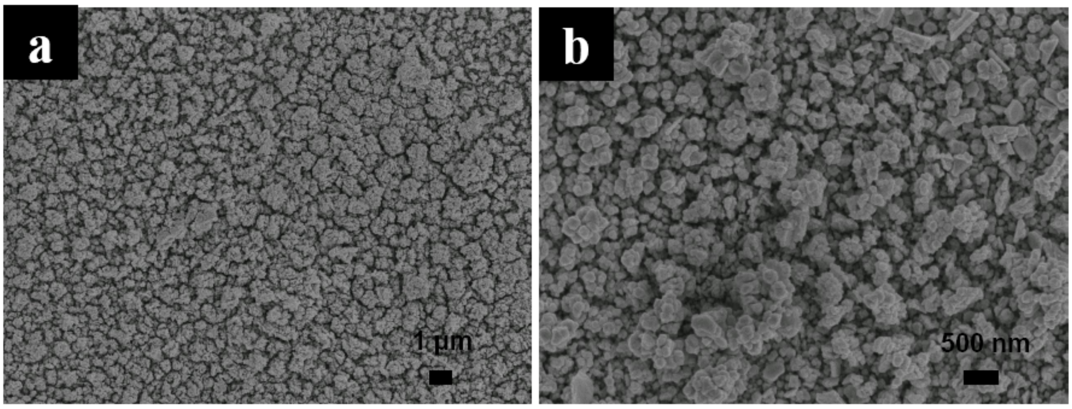

Figure S3. SEM images of the copper catalyst material electrodeposited in a 0.1 M KPi solution (pH 7.0) containing 3.0 mM $CuCl_2$ under an applied potential of -1.2 V for 10 h.

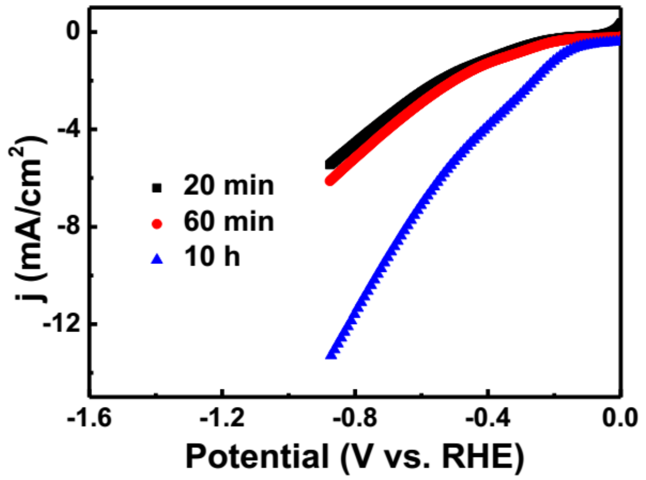

Figure S4. LSV plots of the Cu(0) materials electrodeposited in a 0.1 M KPi solution (pH 7.0) containing 3.0 mM **Cu-EA** for 20 min, 60 min, and 10 hours.

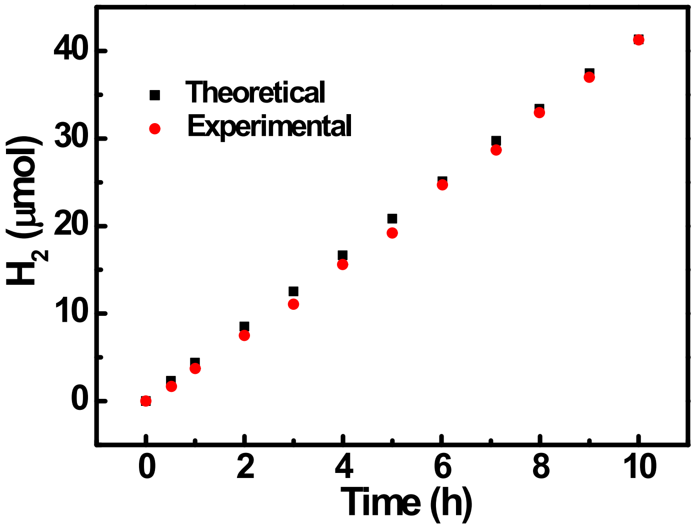

Figure S5. Bulk electrolysis and hydrogen production with a deposited Cu(0) catalyst material on FTO electrode in 0.1 M KPi at pH 7.0 under an applied potential of -70 mV vs. RHE.

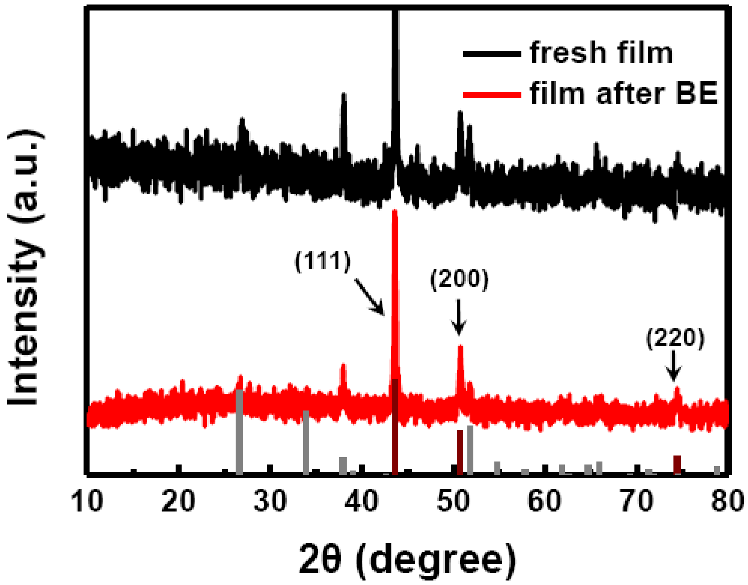

Figure S6. XRD data of the copper catalyst materials deposited from **Cu-EA** before (black) and after (red) a long period of bulk electrolysis (BE) for 10 h. Grey lines: SnO_2 PDF#41-1445; dull red lines: Cu(0) PDF#04-0836.

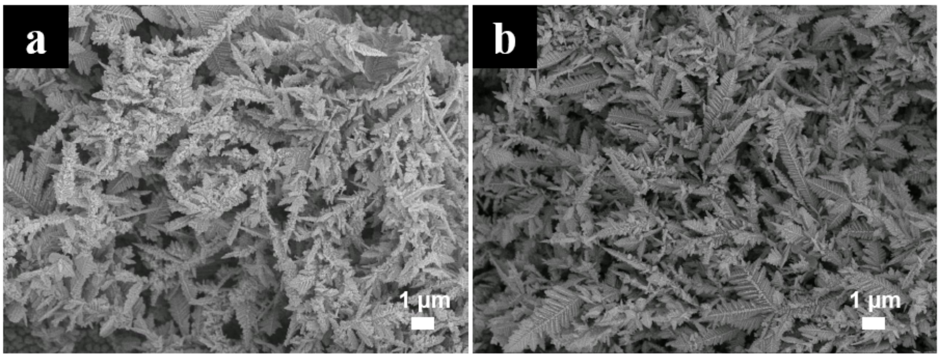

Figure S7. SEM images of the copper catalyst materials deposited from **Cu-EA** before (a) and after (b) a long period of bulk electrolysis for 10 h.

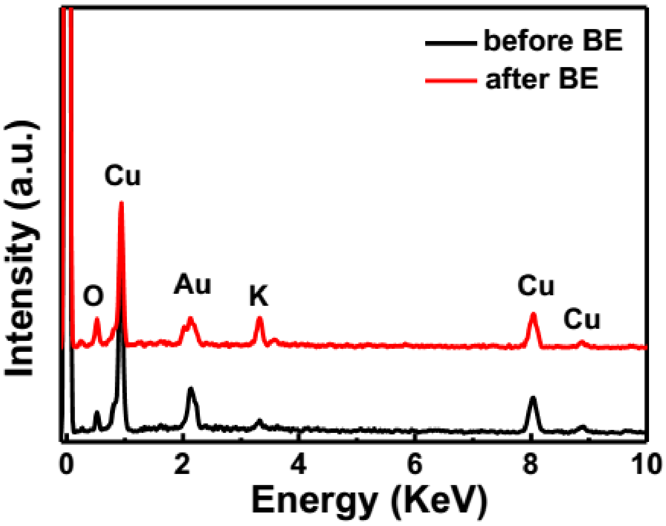

Figure S8. EDX spectra of the copper(0) catalyst materials electrodeposited from **Cu-EA** before (black) and after (red) a long period of bulk electrolysis for 10 h.

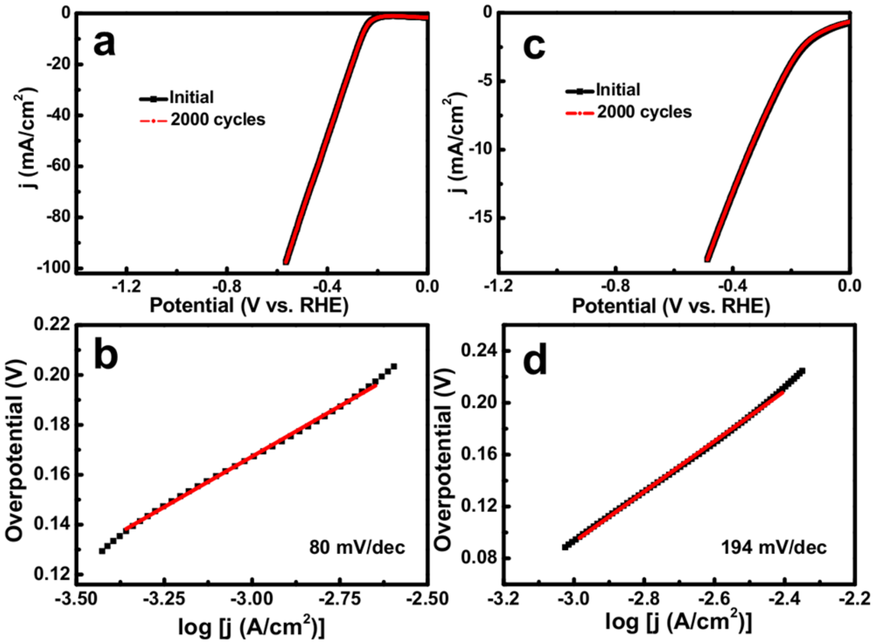

Figure S9. Polarization curves of catalyst materials deposited from **Cu-EA** in (a) 0.5 M H_2SO_4 (pH 0.4) and (c) 1 M KOH (pH 13.6) with a scan rate of 10 mV/s. (b, d) The corresponding Tafel plots of (a, c) with a scan rate of 2 mV/s.