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Supporting information

In Situ Generated Highly Active Copper Oxide Catalyst for Oxygen Evolution Reaction at Low Overpotential in Alkaline Solutions

Xiang Liu, Shengsheng Cui, Manman Qian, Zijun Sun, Pingwu Du*

Key Laboratory of Materials for Energy Conversion, Chinese Academy of Sciences, Department of Materials Science and Engineering, *i*ChEM (Collaborative Innovation Center of Chemistry for Energy Materials), University of Science and Technology of China (USTC), 96 Jinzhai Road, Hefei, Anhui Province, 230026, P. R. China

*To whom correspondence should be addressed

E-mail: dupingwu@ustc.edu.cn

Tel/Fax: 86-551-63606207

Experimental section

Materials. copper(II) ethylenediamine (**Cu-EA**, 1.0 M water solution), $Cu(ClO_4)_2 \cdot 6H_2O$ (99.0%), NaCl (99.5%), NaOH (96.0%), and potassium hydroxide (KOH, 85.0%) were purchased from Aldrich or Acros. All chemicals were used without further purification unless otherwise noted. The electrolyte solutions were prepared with Millipore water (resistivity: 18 MΩ·cm).

Synthesis of copper(II) 1,3-propanediamine (Cu-PA) complex and copper(II) 1,4-butanediamine (Cu-BA) complex. The synthesis was performed using a modified method from a previous report.[1] To a stirring solution of $Cu(ClO_4)_2.6H_2O$ (0.741g, 2 mmol) in 15 mL methanol solution, 1,3-propanediamine (0.296g, 4 mmol) or 1,4-butanediamine (0.352g, 4 mmol) ligand in 10 mL methanol was added dropwise. Then, the mixture was stirred for 2 hours at room temperature. The blue solid precipitate of **Cu-PA** (**Cu-BA**) complex was filtered, washed by methanol three times, and dried under vacuum.

Electrochemical methods. All electrochemical measurements were performed with a CHI720E potentiostat (Shanghai Chenhua Instrument Co., Ltd.) at room temperature. The fluorine doped tin oxide (FTO) or glassy carbon (GC) electrode was used as the working electrode. The Ag/AgCl electrode (3 M KCl, 0.21 V vs NHE) was used as the reference electrode and Pt wire was used as the counter electrode. Bulk electrolysis experiments were performed under variable current densities without stirring.

Faradaic efficiency. The oxygen production experiment was performed in a gas-tight electrochemical cell fixed with a fluorescence-based oxygen sensor (Ocean Optics) for quantitative detecting O_2 in 1.0 M KOH. Before the test, air was excluded by bubbling with high purity N_2 for 20 minutes under vigorous stirring. The data was recorded at 2s intervals by the O_2 sensor on the FOXY probe and then converted into the partial pressure of O_2 in the headspace. The Faradaic efficiency was obtained by comparing the real oxygen production obtained from the recorded partial pressure of O_2 to the theoretical oxygen amount.[2-4]

Scanning electron microscopy (SEM). The surface morphologies of the electrodeposited copper-based materials were studied by a SIRION200 Schottky field emission scanning electron microscope (SFE-SEM). All the deposited materials were washed by deionized water at least three times and sprayed Au or Pt to increase conductivity before the experiments.

X-ray photoelectron spectroscopy (XPS) and powder X-ray diffraction (XRD, D/max-TTR III). An ESCALAB 250 X-ray photoelectron spectroscopy (XPS) instrument was used to measure the elemental compositions and the valence states of elements of the copper-based catalysts. Powder XRD diffraction patterns were measured by X-ray diffraction spectroscopy fitted with a graphite monochromator in the diffracted beam, using Cu Kα radiation (λ = 1.54178 Å), operating at 40 kV and 200 mA. The scanning rate was 5° min^{-1} from 10° to 80° in 2θ.

Roughness Factor (RF). The glassy carbon electrode (GC, with diameter of 3 mm) was used to electrodeposit CuO materials from 0.1 M KOH solution containing 3.0 mM **Cu-EA** or **Cu-PA** precursors. CVs of these two CuO catalysts deposited from different precursors at various scan rates are obtained in 1.0 M KOH. The RF was calculated using the function $RF=C_{dl}/(C_s*S_{geo})$. In this equation, C_{dl} is the electrochemical double layer capacitance, which was determined by the above-mentioned measuring the CVs at various scan rates in the non-Faradaic region. C_s is specific electrochemical double layer capacitance of an atomically smooth surface, which could be typically 40 μF/cm^2. S_{geo} is the surface area of the glassy carbon disk electrode (0.071 cm^2).[5]

References

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4 X. Liu, H. Zheng, Z. Sun, A. Han, P. Du, *ACS Cata.* 2015, ***5***, 1530-1538.

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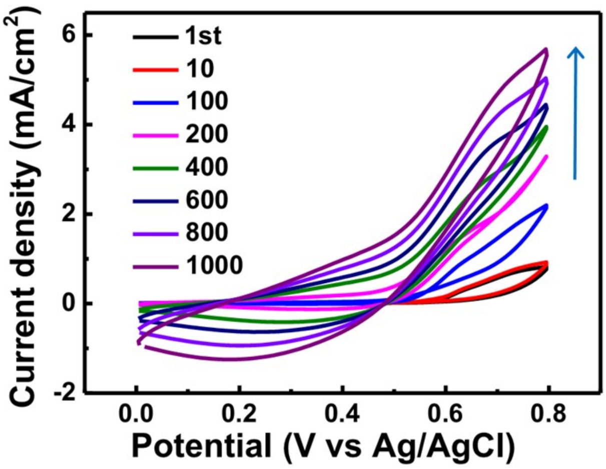

Figure S1. CVs (1000 scan cycles) of 3.0 mM **Cu-EA** in 0.1 M KOH solution using FTO as the working electrode with a scan rate of 100 mV/s at room temperature.

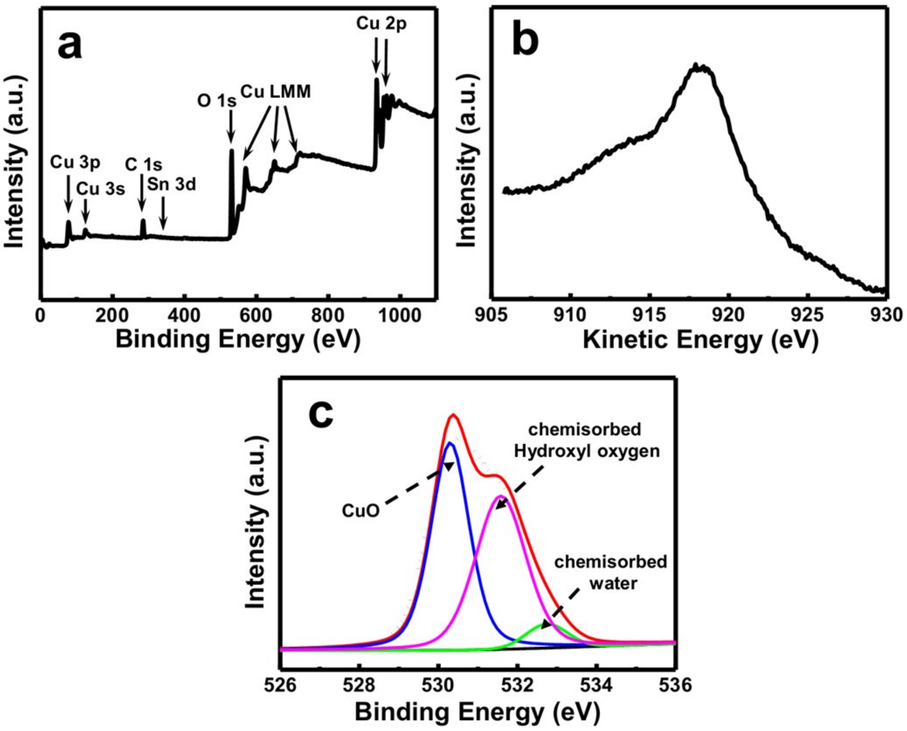

Figure S2. (a) The XPS Survey spectrum; (b) high resolution Cu LMM; and (c) high resolution O 1s of the CuO catalyst electrodeposited from **Cu-EA**.

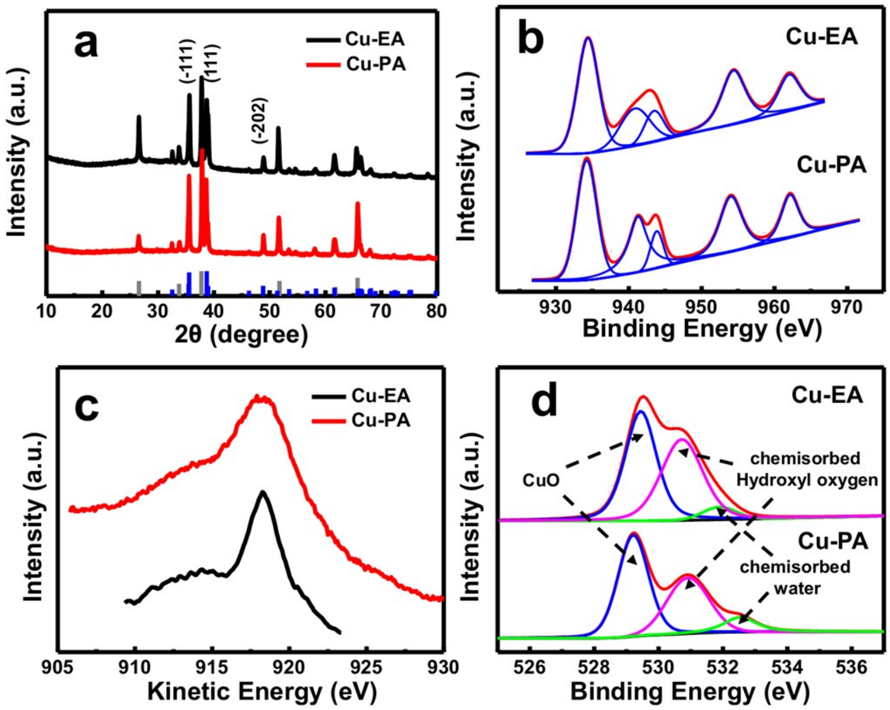

Figure S3. (a) XRD diffraction patterns; (b) high resolution Cu 2p XPS spectra; (c) Cu LMM XPS spectra; and (d) high resolution O 1s XPS spectra of the electrodeposited CuO materials from **Cu-EA** and **Cu-PA** precursors.

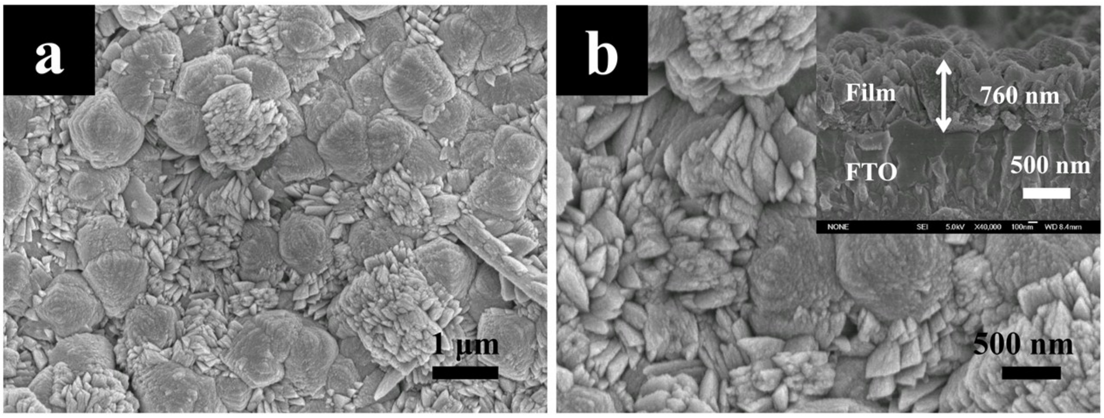

Figure S4. SEM images electrodeposited CuO material obtained from Cu-PA at different scale bars. Inset: the cross-sectional SEM image of the catalyst thin film on FTO plate.

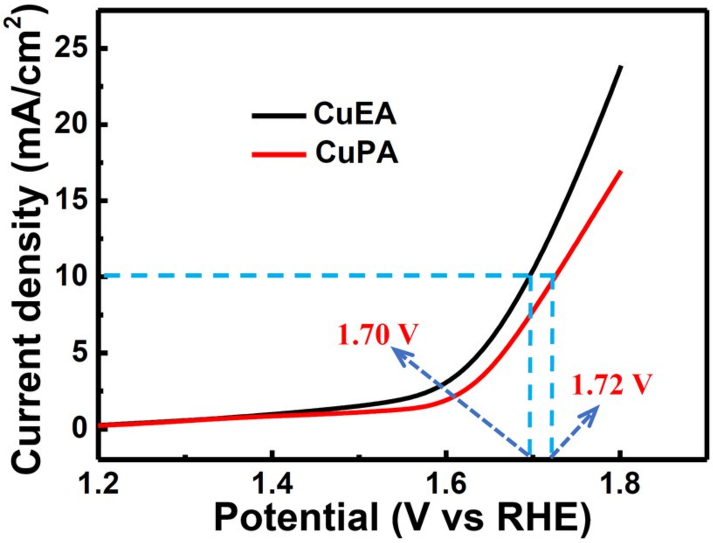

Figure S5. Polarization curves for the CuO materials electrodeposited from **Cu-EA** (black) and **Cu-PA** (red) without iR compensation in 1.0 M KOH solution.

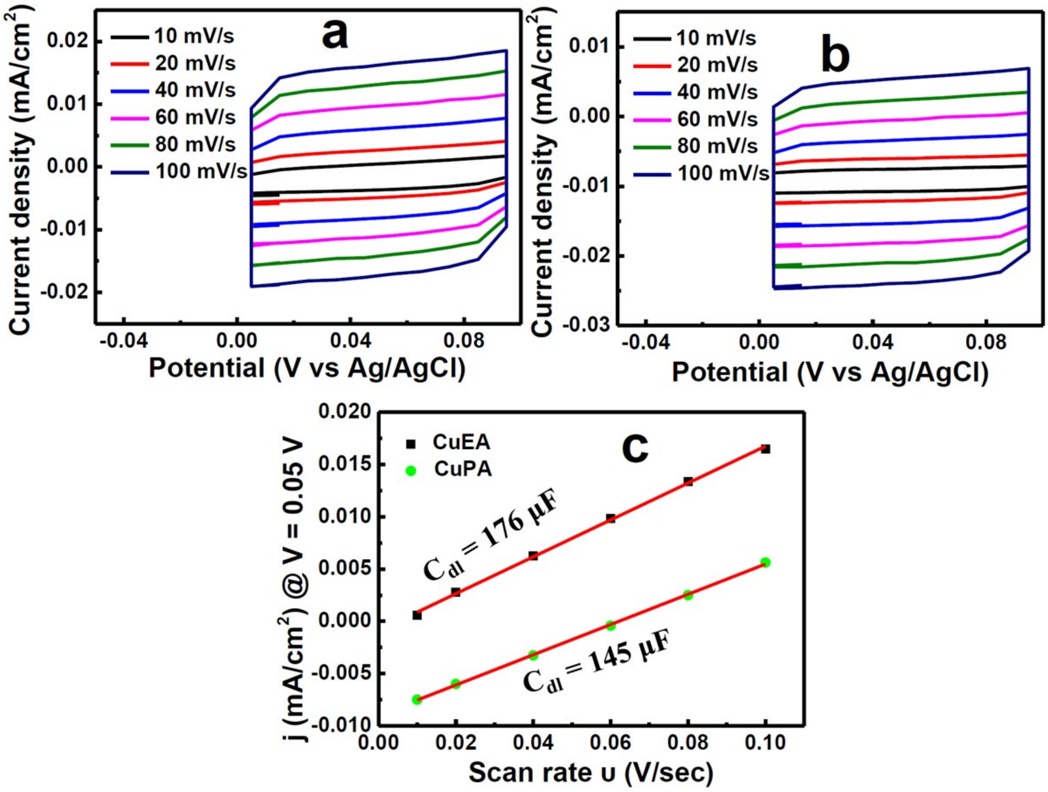

Figure S6. (a-b) CVs of CuO materials deposited from **Cu-EA** (a) and **Cu-PA** (b) in the range of 0 to +0.1 V vs. Ag/AgCl at various scan rates in 1.0 M KOH solution. (c) The cathodic current measured at 0.05 V vs. Ag/AgCl as a function of scan rate for CuO materials from (a) and (b).

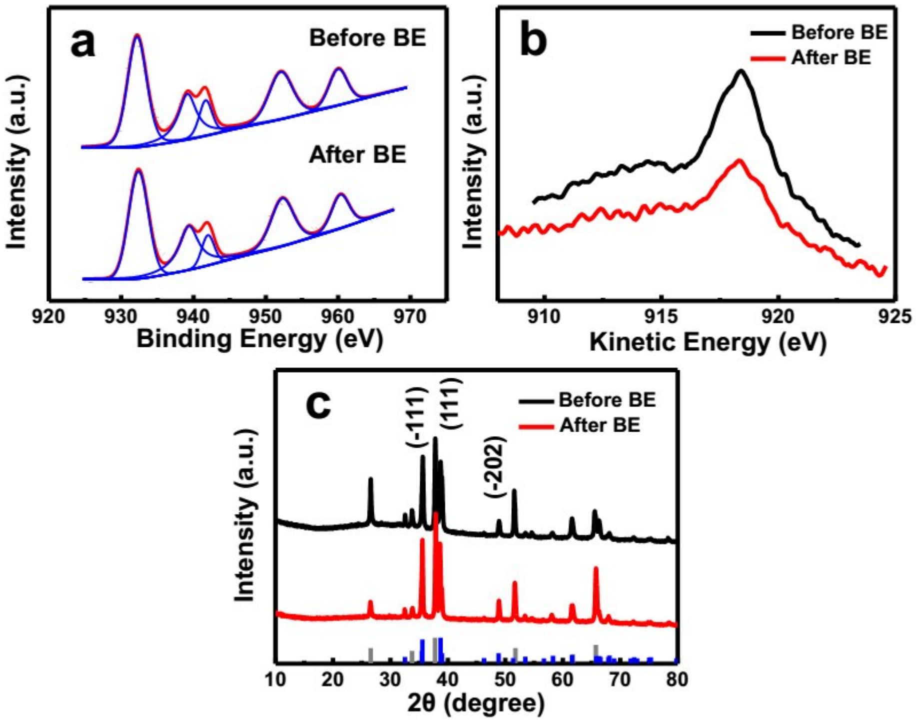

Figure S7. (a) high resolution Cu 2p; (b) Cu LMM; (c) XRD diffraction patterns of the electrodeposited CuO material from **Cu-EA** before and after bulk electrolysis for 10 hours.