Supporting information

Self-Supported Three-dimensional Cu/Cu$_2$O-CuO/rGO Nanowire Arrays Electrode for Efficient Hydrogen Evolution Reaction

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1. Experimental

1.1. Catalyst preparation

**Synthesis of Cu/Cu-MOF/GO.** All chemicals used in this study were of analytical grade and used without further purification. Graphene oxide (GO) was synthesized following the Hummers’ method with a slight modification. Before growing the Cu-MOF on the surface of Cu foam, the commercially purchased Cu foams were cut into circular shapes with a diameter of 1.0×1.2 cm$^2$, which were cleaned by acetone and 6 M HCl by ultrasonication in sequence to remove the organic molecules and the oxide layer, followed by washing with water and ethanol respectively and then dried at room temperature. To grow Cu-MOF on the surface of Cu foam, the Cu foam was first treated with a mixture of 4.0 ml of 10M NaOH aqueous solution, 2.0 ml of 1M ($\text{NH}_4$)$_2\text{S}_2\text{O}_8$ aqueous solution, and 9.0 ml of deionized water for 15 min at room temperature to form the copper hydroxide. Subsequently, the Cu/Cu-MOF/GO was prepared by immersing the obtained copper hydroxide substrate in a saturated ligand solution (3.6 ml of water, 9.3 ml of ethanol mixture, 0.1 g of 1,4-benzenedicarboxylic acid ($\text{H}_2\text{BDC}$)) with 4.0 mg GO at room temperature for 30 min. After that, the resulted substrate was collected from the solution and washed with water and ethanol, and then dried under air. For comparison, Cu/Cu-MOF was also prepared in a similar way with the absence of GO.

**Synthesis of Cu/Cu$_2$O-CuO/rGO.** The Cu/Cu$_2$O-CuO/rGO was obtained by annealing the as-prepared Cu/Cu-MOF/GO in a tubic furnace under Ar atmosphere at different temperatures varying from of 400 °C to 600 °C for 5h. The products are denoted as Cu/Cu$_2$O-CuO/rGO-X, where the X represents the calcination temperature. For comparison, Cu/Cu$_2$O-CuO was also prepared in a similar way without GO.

1.2. Characterization.** X-ray diffraction (XRD) patterns were collected on a Model D8 Avance X-ray diffractometer (Bruker, Germany) with Cu K$\alpha$ radiation. The morphology of the samples was characterized by a field emission scanning electronmicroscopy (SEM) (JSM-6700F). For thermogravimetry analysis (TGA,
Setsys, Setaram) analyses, the calcination process was performed under Ar atmosphere under 800°C with ramping rate of 5 °C/min. The transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were obtained in a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. The powder particles were supported on a carbon film coated on a 3 mm diameter fine-mesh copper grid. The sample suspension in ethanol was sonicated and a drop was dripped on the support film. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum 2000 XPS system (PHI, USA) with a monochromatic Al Kα source and a charge neutralizer. All the binding energy was referenced to C 1s peak observed in the XPS spectrum of pure porous carbon. BET surface area was carried out on an ASAP2020M apparatus (Micromeritics Instrument Corp., USA). Raman spectroscopy was performed using an invia-Reflex Micro-Raman Spectroscopy system (Renishaw Co.) with 532 nm and 633nm line of an Ar ion laser at room temperature.

1.3 Electrochemical tests. All the electrochemical measurements were carried out in a conventional three-electrode cell using a CHI660E electrochemical work station (Shanghai Chenhua Instrument Co., China) at room temperature. The Cu/Cu₂O-CuO/rGO was used directly as the working electrode, with carbon rods and Hg/HgO electrode (with saturated KCl solution) as the counter electrode and reference electrode respectively. The reaction was performed in 1.0 M KOH aqueous. A scan rate of 5 mV s⁻¹ was used for all electrochemical measurements. All potentials were referenced to reversible hydrogen electrode (RHE) by following calculations: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.2415 \text{V} + 0.059 \times \text{pH}$. 
Figure captions

**Fig. S1** The XRD of Cu/Cu-MOF/GO, Cu/Cu(OH)$_2$ and Cu foam.

**Fig. S2** The SEM images of (a) Cu/Cu(OH)$_2$; (b) Cu/Cu-MOF/GO; (c-d) Cu/Cu$_2$O-CuO/rGO-400.

**Fig. S3** The thermogravimetric analysis (TGA) of Cu/Cu-MOF/GO.

**Fig. S4** The XRD pattern of Cu/Cu$_2$O-CuO/rGO-400 and Cu foam.

**Fig. S5** (a) XPS spectra of Cu 2p, (b) the Auger Cu LMM spectra in Cu/Cu$_2$O-CuO/rGO-400.

**Fig. S6** (a) TEM and (b) HRTEM of the Cu/Cu$_2$O-CuO-400.

**Fig. S7** HRTEM of the Cu/Cu$_2$O-CuO/rGO-400.

**Fig. S8** The Raman of the Cu/rGO.

**Fig. S9** The corresponding Tafel plots of the Cu/Cu-MOF/GO, Cu/Cu$_2$O-CuO-400 and Cu/Cu$_2$O-CuO/rGO-400.

**Fig. S10** The XPS spectra of Cu/Cu$_2$O-CuO/rGO-400 before and after the chronoamperometry (i-t) measurement (a) Cu 2p; (b) O 1s.

**Fig. S11** The XRD pattern of Cu/Cu$_2$O-CuO/rGO-400 before and after the chronoamperometry (i-t) measurement.

**Fig. S12** The XRD pattern of Cu/Cu$_2$O-CuO/rGO-X calcination at different temperature.

**Fig. S13** SEM images of Cu/Cu$_2$O-CuO/rGO-X calcinating at different temperature (a) 500 °C and (b) 600 °C.

**Fig. S14** The HER activity of Cu/Cu$_2$O-CuO/rGO-X with different temperature.

**Fig. S15** Estimation of $C_d$ through plotting current density as a function of scan rate of the Cu/Cu$_2$O-CuO/rGO-X.
Captions for Table

Table S1 Electrocatalytic performances of various nanostructured catalysts in hydrogen evolution reaction reported in the literatures.
Fig. S1 The XRD of Cu/Cu-MOF/GO, Cu/Cu(OH)$_2$ and Cu foam.
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<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solution</th>
<th>Current density (mA cm⁻²)</th>
<th>Overpotential (mV vs. RHE)</th>
<th>Ref.</th>
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<tr>
<td>Cu/Cu₂O-CuO/rGO-400</td>
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<td>G-coated Cu NWs</td>
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<td>Current Density</td>
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References


