

# Supporting Information

## Normal-Pulse-Voltage-Assisted in Situ Fabrication of Graphene-Wrapped MOF-Derived CuO Nanoflowers for Water Oxidation

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## Experimental section

**Chemical and Materials.** Copper foam (CF, thickness  $\sim 1.6$  mm), trimesic acid ( $H_3BTC$ ,  $> 99\%$ ), ammonium fluoride ( $NH_4F$ ,  $> 98\%$ ), potassium hydroxide ( $KOH$ ,  $> 98\%$ ), dehydrated alcohol (EtOH), acetate (HAc,  $> 99\%$ ), N, N-Dimethylformamide (DMF,  $> 98\%$ ) were purchased from Aladdin. All the chemical reagents were used received without further purification. All the solutions were prepared using deionized water ( $18.2 M\Omega$ ).

**Preparation of CuO NP@G/CF.** High quality graphene were prepared by chemical vapor deposition (CVD) method. The CF was cut into a size of  $1.0\text{ cm}^2$  and soaked in 10% HAc for 10 min to remove CuO on the surface, and washed 4 times with deionized water, and then blown dry with  $N_2$ . The pretreated CF was placed in a tube furnace with the temperature rising at the rate of  $40\text{ }^\circ\text{C min}^{-1}$  from room temperature to  $300\text{ }^\circ\text{C}$  in a low pressure system. And then the sample was oxidized for 15.0 minutes at  $300\text{ }^\circ\text{C}$ . The substrate was heated to  $1040\text{ }^\circ\text{C}$  at a heating rate of  $78.5\text{ }^\circ\text{C min}^{-1}$  in a hydrogen atmosphere with a flow rate of 10 sccm and annealed at this temperature for 3.0 h. At the end of annealing, the hydrogen flow was increased to 40 sccm, and methane ( $1.5\text{ sccm}$ ) was introduced into as carbon source for feeding the graphene growing. Finally, the graphene was harvested after 3.0 h which featured surface-covered, monolayer, uniform and continuous.

The PMMA was spin-coated on Cu foam covered graphene (G/CF), dried at  $170\text{ }^\circ\text{C}$  for 3.0 min, and soaked in 2.0 M  $FeCl_3$  for 1.0 min to make a small interspace between graphene and Cu foam. Finally, the product washed with deionized water for 3 times. Then, HKUST-1/CF was synthesized through a typical electrochemical method, and some simple modifications were carried out as follows. The preparation of HKUST-1 was conducted in a two-electrode system with as-prepared G/CF as the anode and graphite rod as cathode. The ligand solution was obtained by dissolving  $H_3BTC$  (5.0 mmol) and  $NH_4F$  (10.0 mmol) in 300.0 mL  $H_2O$ , 100.0 mL EtOH and 100.0 mL DMF. The applied potential was to 15.0 V, and the growth time with 90.0 s were used to prepare the appropriate amount of HKUST-1, and the graphene-wrapped HKUST-1 composite on CF (HKUST-1@G/CF) was obtained. Finally, the HKUST-1@G/CF was immersed into 100.0 mL solution which contained 2.0 M  $KOH$  for 20.0 min to convert HKUST-1 to CuO nanoparticles (CuO NPs). Then, the PMMA on the graphene was removed by annealing at  $300\text{ }^\circ\text{C}$  for 2.0 h in Ar atmosphere to form a structure of graphene-wrapped CuO nanoparticles on CF (CuO NP@G/CF).

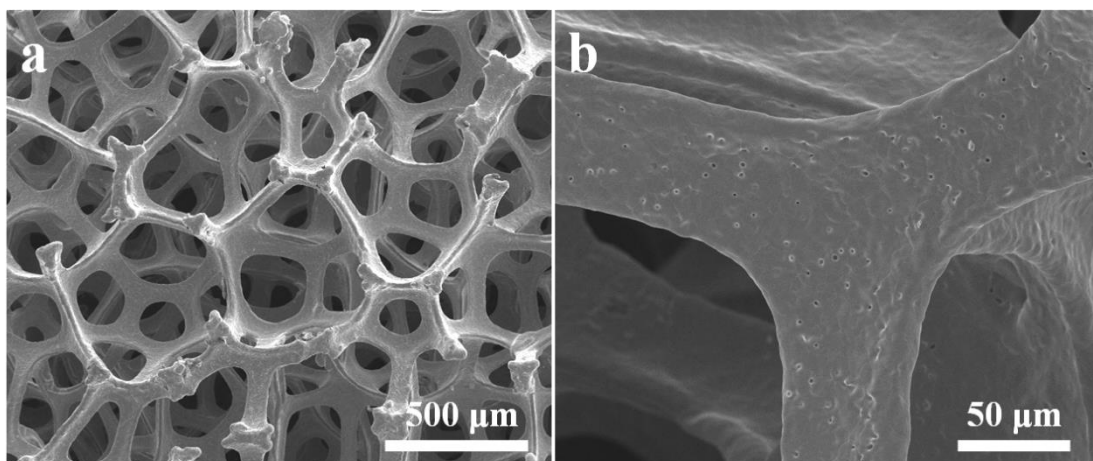
**preparation of CuO NF@G/CF.** In 1.0 M  $KOH$ , CuO NF@G/CF were synthesised in a three-electrode system by using CuO NP@G/CF, Pt wire, and saturated Ag/AgCl electrodes as working electrode, counter electrode, and reference electrode, respectively, according NPV

method. The pulse range was 1.10-1.70 V vs. RHE, with a pulse of 0.05 s at per interval of 0.001 V and a pulse period of 0.10 s. This process was repeated for 7 times, and soaked in 1.0 M KOH for 24.0 h to obtain CuO NF@G/CF.

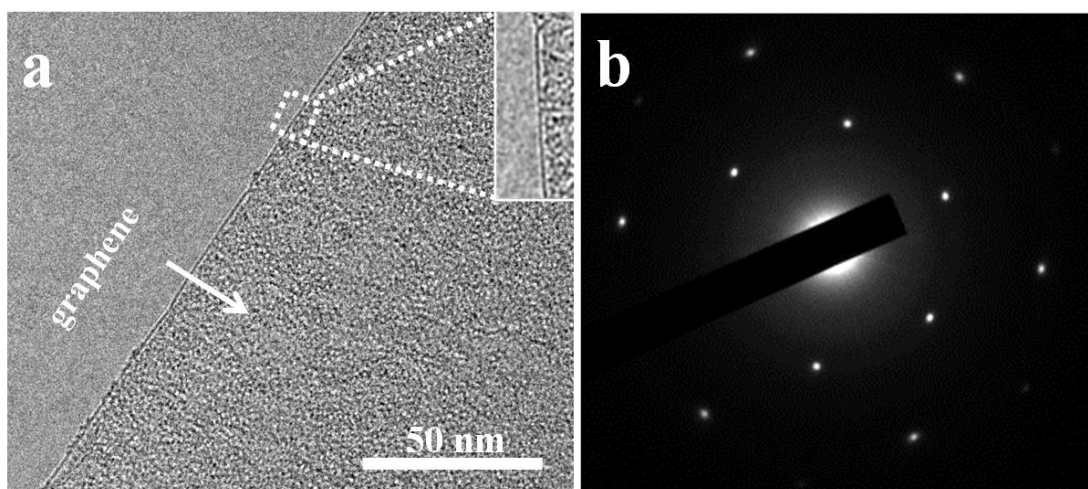
**Characterizations.** The scanning electron microscopy (SEM, Nova Nano SEM-200, 10 kV) and transmission electron microscopy (TEM, JEOL JEM-1200EX, 200 kV) was used to detect the morphology and size of the samples. The crystalline structure was carried out by powder X-ray diffraction (PXRD) using Bruker D8 Advance (Cu-K $\alpha$ ,  $\lambda = 0.15418$  nm). The X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi) measurements were taken using an Al K $\alpha$  X-ray source, and the binding energies were calibrated with reference to the C 1s peak at 284.4 eV.

**Electrochemical measurements.** All electrochemical measurements were conducted in a standard three-electrode system in which the as-prepared samples were used as working electrode, a Pt wire as auxiliary electrode, and Ag/AgCl electrode as reference. 1.0 M KOH solution (pH = 13.8) was used as electrolyte. Polarization curves were used to evaluate OER activity and were obtained by linear sweep voltammetry (LSV) with a scan rate of 2 mV s<sup>-1</sup>. IR compensation correction had not been applied in any data and all the potentials were converted to the reversible hydrogen electrode (RHE), in which  $E$  (vs. RHE) =  $E$  (vs. Ag/AgCl) + 0.197 + 0.059 pH. The electrochemical double-layer capacitance ( $C_{dl}$ ) of the electrocatalysts were obtained by measuring the CV at different scan rate (10, 20, 40, 60, 80, 100 mV s<sup>-1</sup>) in the non-Faradaic window, which is taken here as 1.22-1.32 V vs. RHE. The electrochemically active surface area (ECSA) was determined by  $C_{dl}$  and can be obtained by the function:  $ECSA$  (cm<sup>2</sup>) =  $C_{dl}/C_s$ , where  $C_s$  is the specific electrochemical double-layer capacitance and typically taken to be 0.04 mF cm<sup>-2</sup>.

We used a fluorescence-based oxygen sensor (Ocean Optics) to detect the oxygen evolution amount in an electrochemical cell with good air tightness and calculated the corresponding Faraday efficiency. First, remove O<sub>2</sub> from the electrochemical cell by bubbling in 1 M KOH solution with high purity N<sub>2</sub> for 20 minutes. CuO NF@G/CF, Pt net and saturated Ag/AgCl were used as working electrode, counter electrode and reference electrode respectively. In addition, the position of the reference electrode is a few millimeters away from the working electrode. The O<sub>2</sub> sensor on the FOXY probe recorded the partial pressure converted to O<sub>2</sub> in the headspace of electrochemical cell every 1 s. The partial pressure of O<sub>2</sub> was recorded for 30 minutes to check the stability without applying an electric potential, and then bulk electrolysis was performed at 1.20 V without iR drop compensation.



**Fig. S1** SEM images of the CF.



**Fig. S2** (a) TEM image of the graphene. (b) SEAD pattern of a single graphene layer.

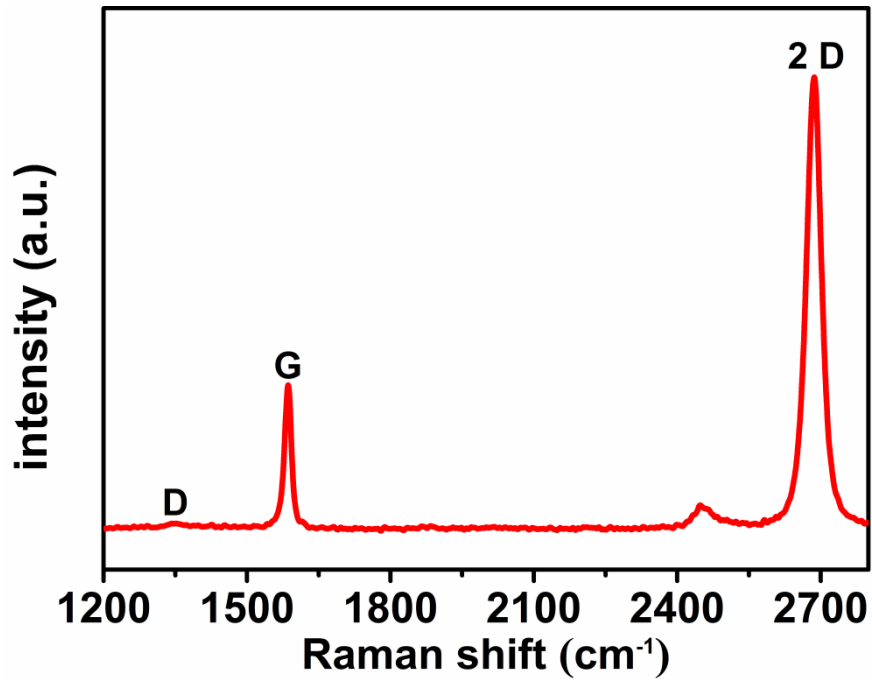


Fig. S3 Raman spectrum of the as-made G/CF.

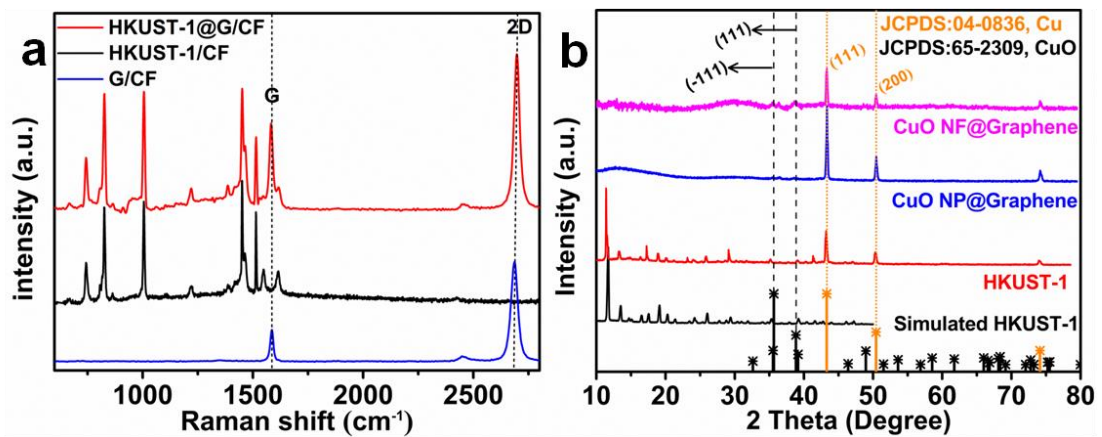


Fig. S4 (a) Raman spectra of HKUST-1@G/CF, HKUST-1/CF and G/CF; (b) XRD patterns of

HKUST-1/CF, CuO NP@G/CF and CuO NF@G/CF.

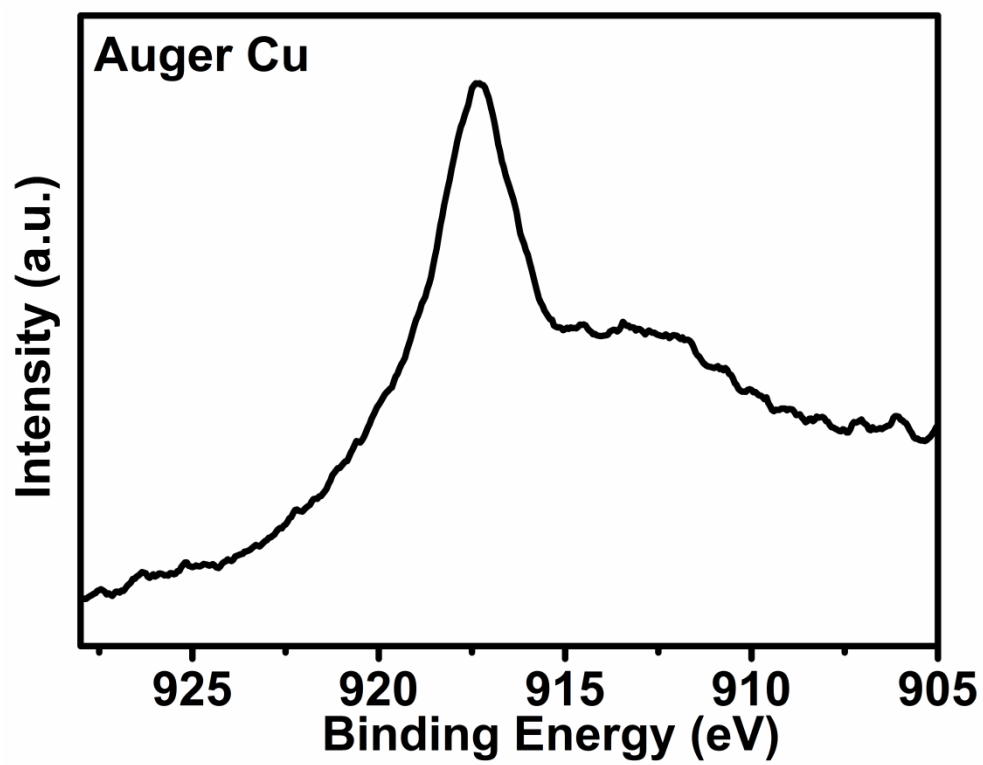
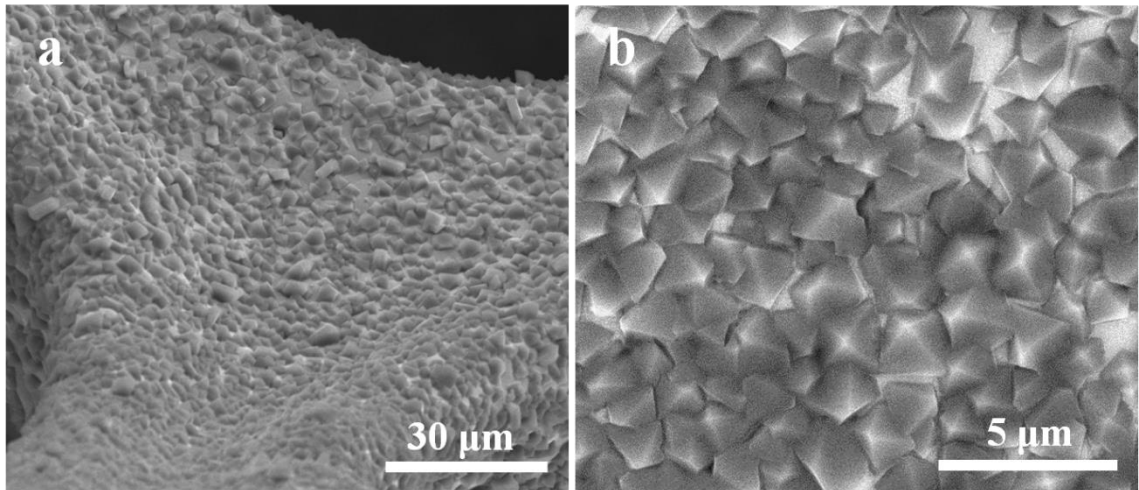
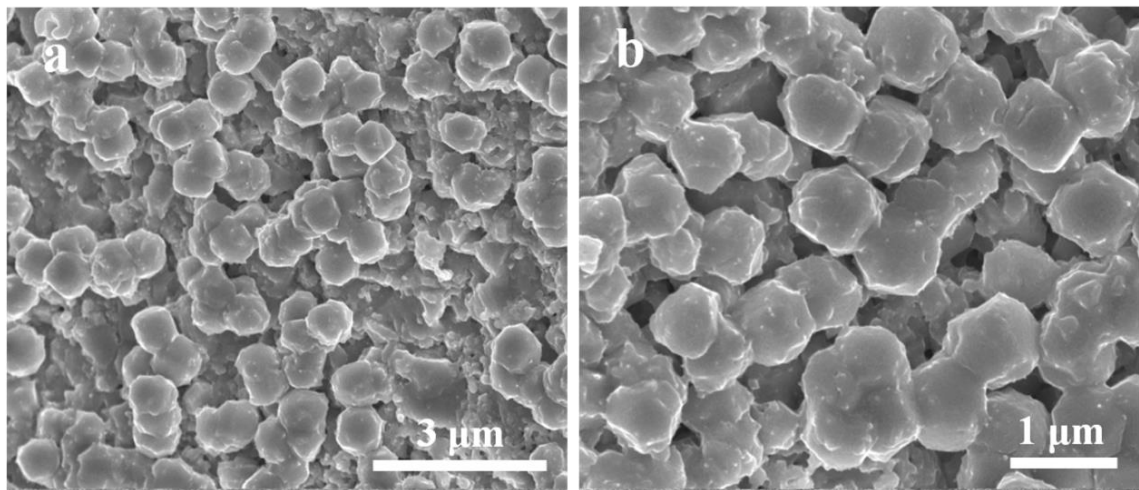


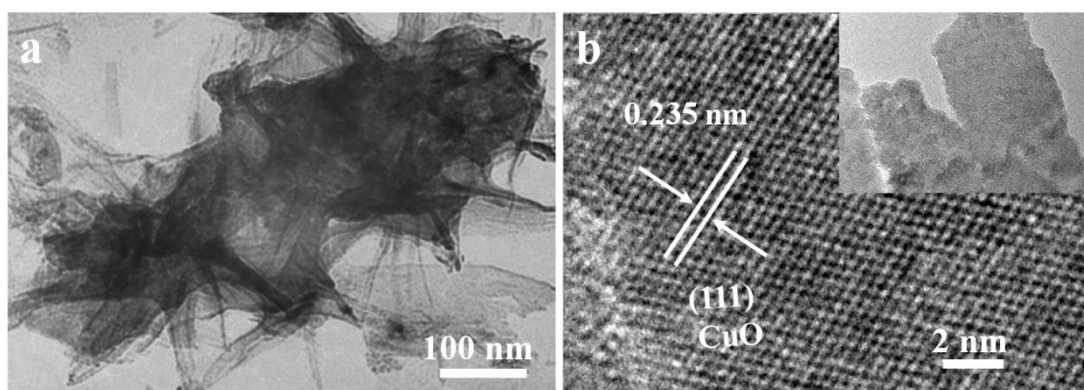
Fig. S5 High-resolution XPS spectrum of Cu LMM.



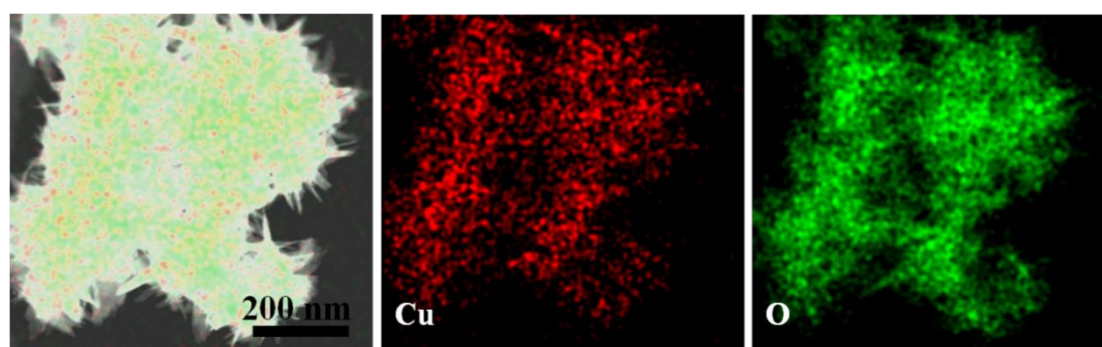
**Fig. S6** SEM images of the HKUST-1/CF.



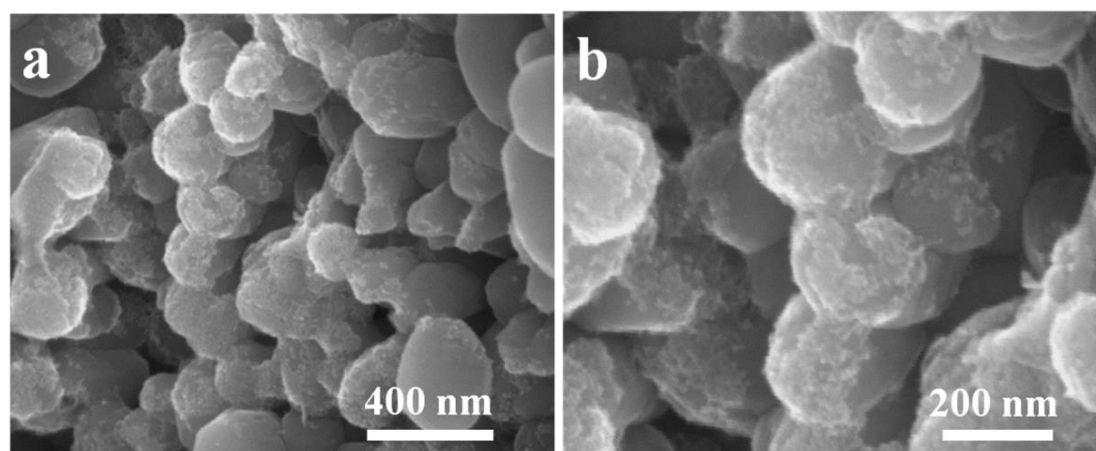
**Fig. S7** SEM images of the CuO NP/CF.



**Fig. S8** (a) TEM images of the CuO NFs; (b) HR-TEM images of the CuO NFs.

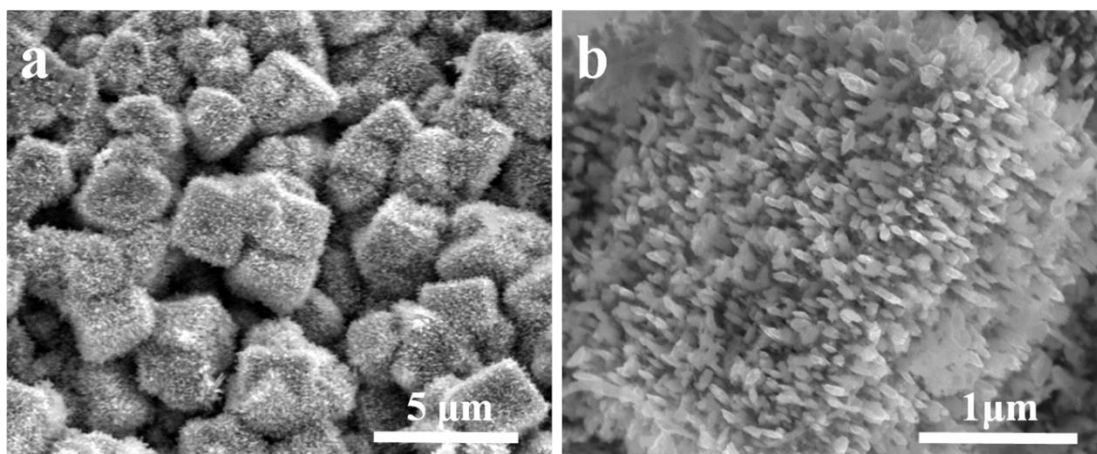


**Fig. S9** Elemental mapping images for CuO NFs.



**Fig. S10** SEM images of the CuO NPs after being soaked 1 M KOH for seven days.





**Fig. S11** SEM images of HKUST-1/CF after NPV.

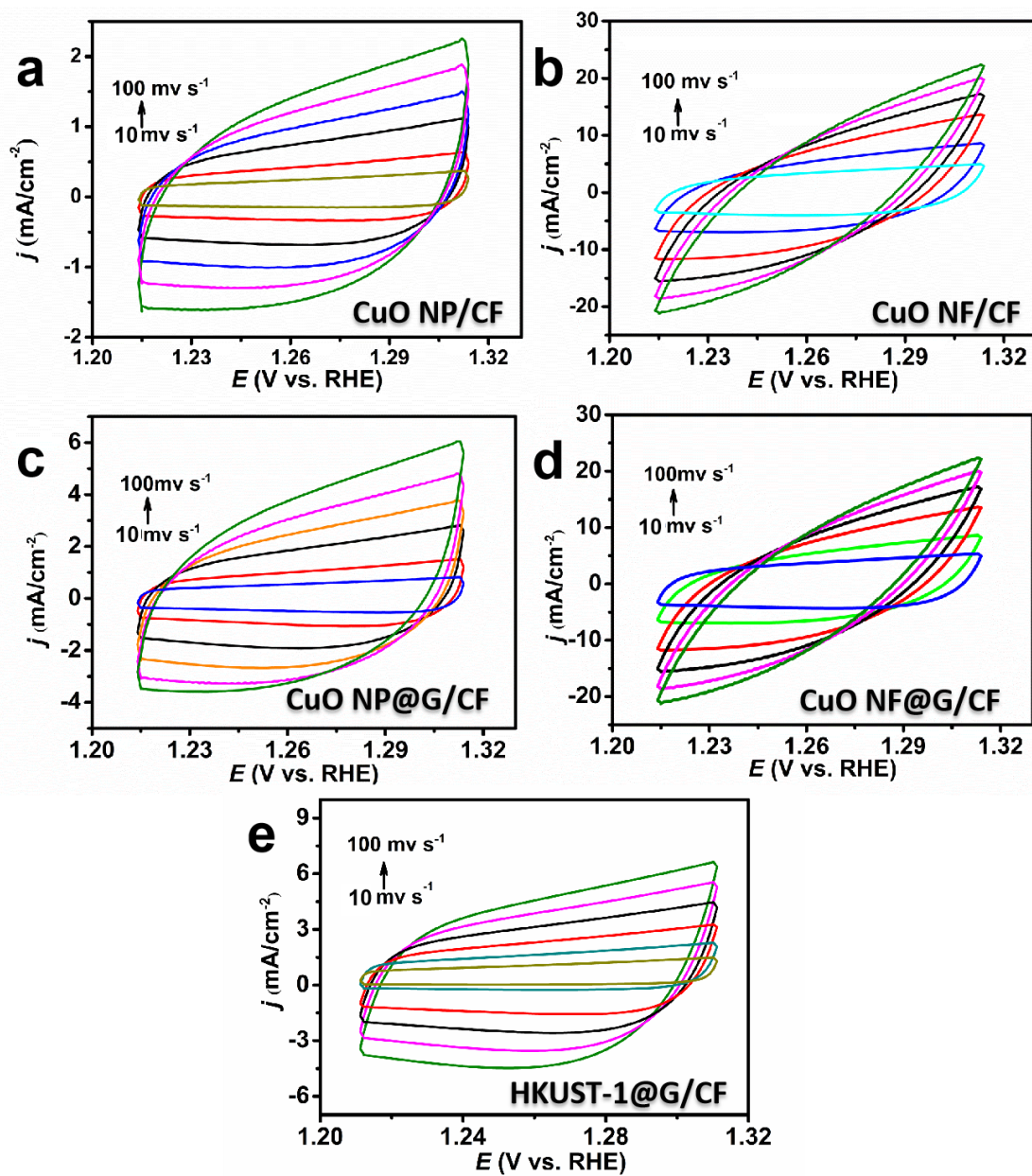
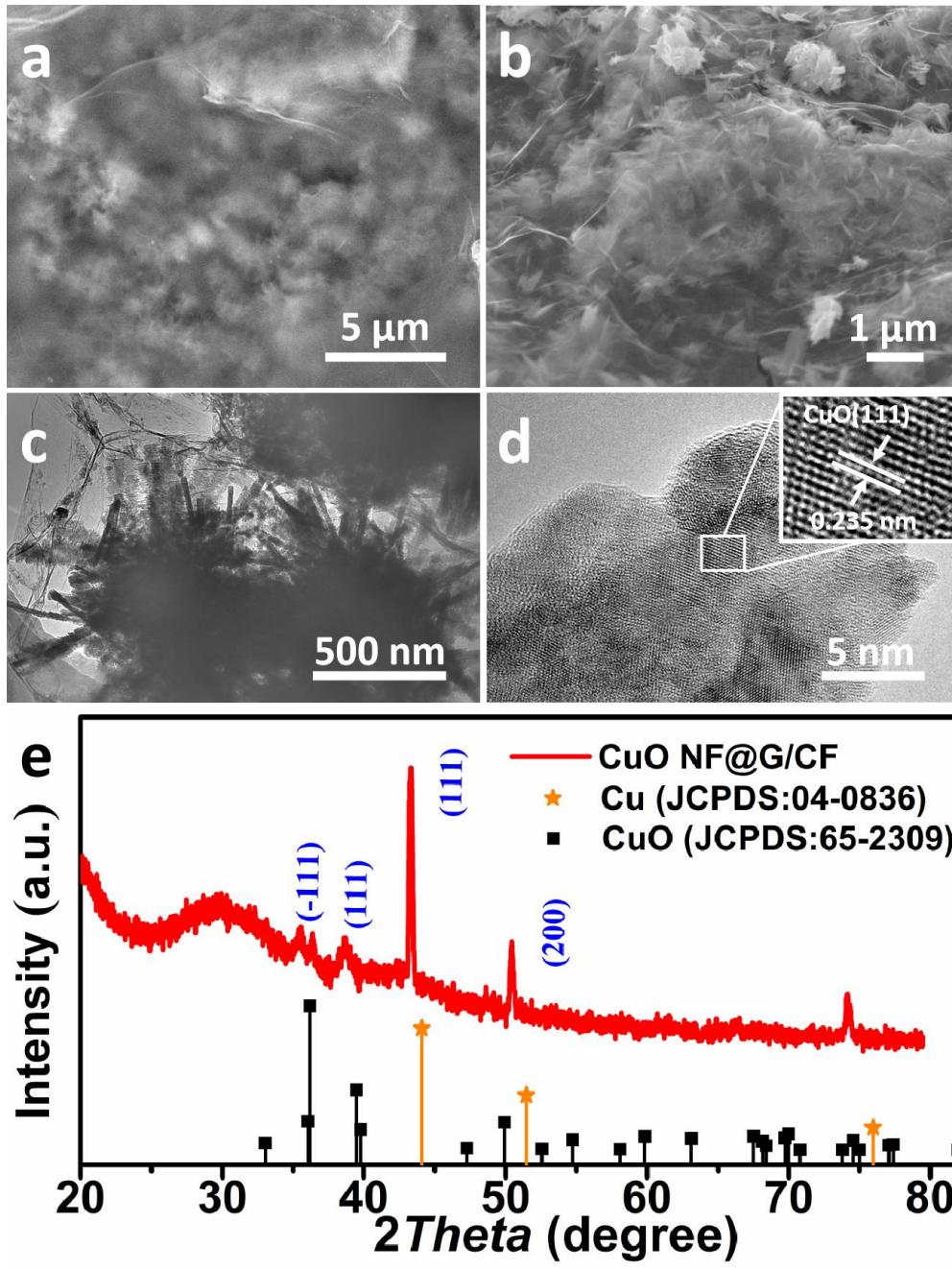


Fig. S12 CV curves of (a) CuO NP/CF; (b) CuO NF/CF; (c) CuO NP@G/CF; (d) CuO NF@G/CF and HKUST-1@G/CF under various scan rates from 10 to 100  $\text{mV s}^{-1}$  in the non-Faradaic potential range

(1.22-1.32 V vs. RHE).



**Fig. S13** (a, b) SEM and (c, d) TEM images of CuO NF@G/CF after OER stability test; (e) PXRD

patterns of CuO NF@G/CF after OER stability test for 10 h.

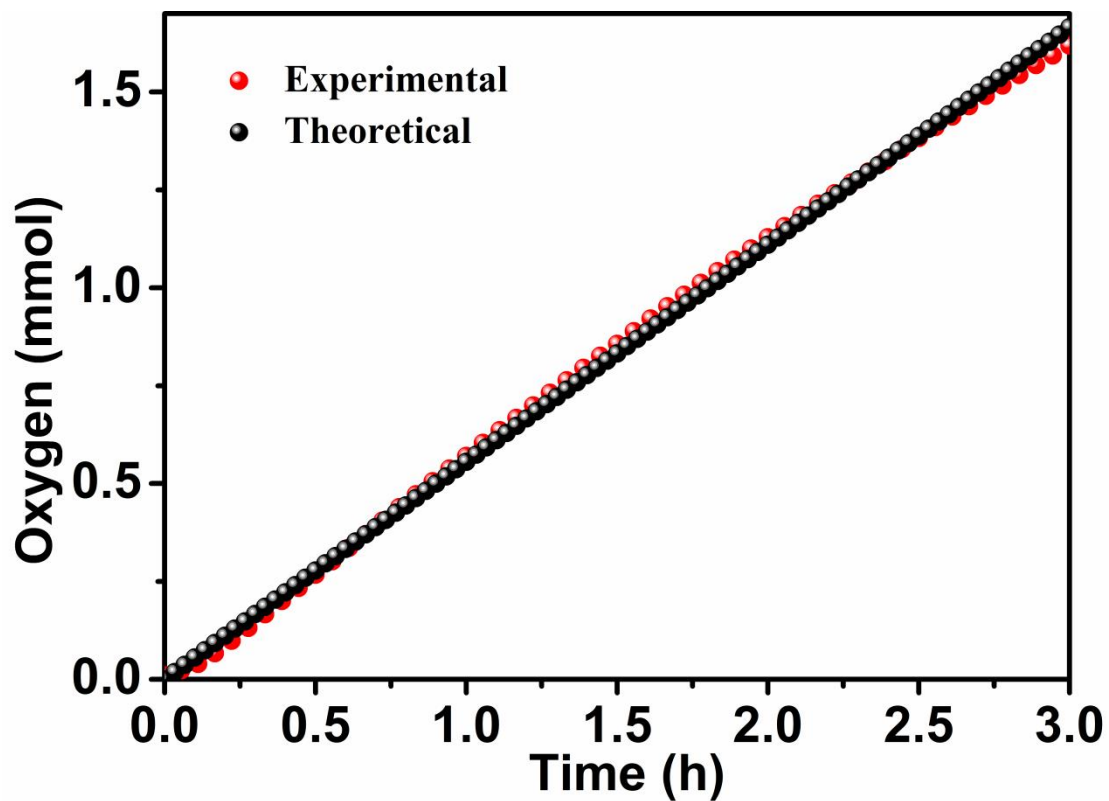


Fig. S14 Theoretical and experimental oxygen evolution from water at 1.55 V using CuO NF@G/CF in 1 M KOH solution.

**Table S1.** Comparison of electrocatalytic water oxidation activities for different electrocatalysts.

Sample	$j$ (mA cm <sup>-2</sup> )	$\eta$ (mV)	Tafel slope (mV dec <sup>-1</sup> )	ECSA (cm <sup>2</sup> )	$C_{dl}$ (mF/cm <sup>2</sup> )
CuO NF@G/CF	10	320	63.1	112.6	4.5
CuO NF/CF	10	347	95.3	80.38	3.22
CuO NP@G/CF	10	373	97.7	57.8	2.31
CuO NP/CF	10	430	103.1	43.55	1.74
HKUST-1@G/CF	10	398	99.6	66	2.64

**Table S2.** Comparison of the OER activity of the recently reported Cu-based OER catalysts.

Catalyst	j(mA cm <sup>-2</sup> )	$\eta$ (mV)	Electrolytes	Tafel slope (mV dec <sup>-1</sup> )	ECSA (cm <sup>2</sup> )	Reference
CuO NF@G/CF	<b>10</b>	<b>320</b>	<b>1.0 M KOH (pH 13.8)</b>	<b>63.1</b>	<b>112.6</b>	<b>This work</b>
CuO <sub>x</sub> -NLs	10	450	carbonate system	44	-	[1]
CuO flowers	10	370	1 M NaOH	41	125	[2]
dendritic Cu/Cu <sub>2</sub> O/CuO	10	290	1.0 M NaOH	64	20.6	[3]
MWCNTs/CuO nanosheets	10	420	1.0 M KOH	53	-	[4]
Cu/(Cu(OH) <sub>2</sub> -CuO) NA/CF	10	417	0.1 M KOH	76	-	[5]
NiFe/Cu <sub>2</sub> O	10	215	1.0 M KOH	42	2450	[6]
Cu@CuO-C	10	340	1.0 M KOH	156	-	[7]

## References

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