

Rapid synthesis of ultralong Fe(OH)₃:Cu(OH)₂ core-shell nanowires self-supported on copper foam as a highly efficient 3D electrode for water oxidation

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Experimental Section

Materials. All chemicals and solvents were of analytical grade and used as received without further purification. Copper foam (100 mm × 100 mm) was purchased from Suzhou Jia Shi De Metal Foam Co., Ltd. Platinum foil was bought from Tianjin AIDA Hengsheng Science-Technology Development Co., Ltd. Sodium hypophosphite (NaH_2PO_2 , AR, 99.0%) was purchased from Aladdin Ltd. (Shanghai, China). NaOH, HCl, ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and all solvents were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, 98.0%) were obtained from Xilong Chemical Co., Ltd.

Synthesis of $\text{Cu}(\text{OH})_2/\text{CF}$ and $\text{Fe}(\text{OH})_3:\text{Cu}(\text{OH})_2/\text{CF}$. The $\text{Cu}(\text{OH})_2$ NW/CF was prepared according to previously reported method with some modifications.^[1,2] In a typical procedure, two respective aqueous solution (7.5 mL) containing NaOH (1.6 g) and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (456 mg) were mixed and sonicated for about 10 min. After that, 3 mL of the above solution was taken out and diluted to 6 mL in a plastic vital. Then, a piece of copper foam (1cm x 2 cm), which had been ultrasonically cleaned several times in 3% HCl and deionized water, was immediately immersed into the above solution. A few minutes later, a faint blue color appeared on the copper foam surface, and the initial solution became increasingly blue. In 28 min, a deep blue film was uniformly covered on the copper foam surface. Then, the copper foam was taken out of the solution, rinsed with water and ethanol, and dried in vacuum oven. For the $\text{Fe}(\text{OH})_3:\text{Cu}(\text{OH})_2/\text{CF}$ film, in a typical procedure, the as-prepared $\text{Cu}(\text{OH})_2/\text{CF}$ were placed into a 30 mL aqueous solution containing 10 mM iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and kept at room temperature for several time. After this, the sample was taken out, washed several times by deionized water and dried in vacuum oven.^[3]

Materials Characterizations. Powder X-ray diffraction patterns (PXRD) were carried out using a Bruker AXSD8 X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) samples were deoxygenated under Ar for 1 h and investigated on a PHI 5300 ESCA system. An Al $K\alpha$ X-ray source with a power of 250 W was used. The charge effect was calibrated using the binding energy of C1s (285.0 eV). Samples for transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and energy-dispersion X-ray (EDX) spectroscopy measurements were analyzed by using a transmission electron microscope (JEM 2100F) with an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images and corresponding energy-dispersion X-ray spectroscopy measurements were conducted on a Hitachi S-4800 field emission scanning electron microscope. For all TEM, HRTEM and corresponding EDX measurements, the samples were firstly dispersed in ethanol and sonicated for at least 30 min, then dropped on an ultrathin carbon film copper mesh and allowed to dry in air at room temperature prior to these measurements. Raman spectroscopy was carried out on an inVia-Reflex confocal laser micro-Raman spectrometer from 1500 cm^{-1} to 200 cm^{-1} using Ar^+ laser excitation with a wavelength of 532 nm.

Electrochemical measurements. Electrochemical measurements were performed on a computer-controlled CHI660E electrochemical workstation and conducted in a typical three-

electrode setup in one compartment cell with as-synthesized 3D Cu-based nanomaterials (loading density $\sim 2.8 \text{ mg cm}^{-2}$) as working electrode, Pt foil as counter electrode and a commercial Ag/AgCl (3.5M KCl) as reference electrode. The experiments were conducted in an electrolyte solution of 1.0 M KOH and all the potentials reported in our work were calibrated with respect to reversible hydrogen electrode (RHE): $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.2046 + 0.059 \text{ pH}$ unless stated otherwise. The theoretical potential for water oxidation was 1.23 V vs. RHE. The LSV measurements were conducted in 20 mL O_2 bubbled 1.0 M KOH at a scan rate of 5 mV s^{-1} . The geometrical surface area of the CF electrode used for electrocatalysis is 1 cm^2 and the current density was calculated using the geometrical surface area of 1 cm^2 . For 100% iR correction, the ionic resistance from the solution was determined by the EIS technique.^[4,5]

Calculation methods

The value of ECSA (cm^2) was estimated from the electrochemical double-layer capacitance (C_{dl}) of the catalytic surface and was calculated as:²

$$\text{ECSA} = C_{dl} / C_s \quad (1)$$

where C_s is the specific capacitance of the sample or the capacitance of an atomically smooth planar surface of the material per unit area under identical electrolyte conditions. The values of RF were calculated by taking the estimated ECSA and dividing by the geometric area of the electrode S:

$$\text{RF} = \text{ECSA} / S \quad (2)$$

The specific current density, j_s , was calculated by dividing the current density per geometric area at a given overpotential, j_g by the RF of the surface as shown as:

$$j_s = j_g / \text{RF} \quad (3)$$

[1]. W. X. Zhang, X. G. Wen and S. H. Yang, *Inorg. Chem.*, 2003, **42**, 5005–5014.

[2]. C. -C. Hou, W. -F. Fu and Y. Chen, *Chemsuschem*, 2016, **9**, 2069–2073.

[3]. Y. Yan, B. Y. Xia, X. M. Ge, Z. L. Liu, A. Fisher and X. Wang, *Chem. Eur. J.*, 2015, **21**, 18062–18067.

[4]. M. B. Stevens, L. J. Enman, A. S. Batchellor, M. R. Cosby, A. E. Vise, C. D. M. Tang and S. W. Boettcher, *Chem. Mater.*, 2016, DOI: 10.1021/acs.chemmater.6b02796.

[5]. M. Gao, W. Sheng, Z. Huang, Q. Fang, S. Gu, J. Jiang and Y. Yan, *J. Am. Chem. Soc.*, 2014, **136**, 7077–7084.

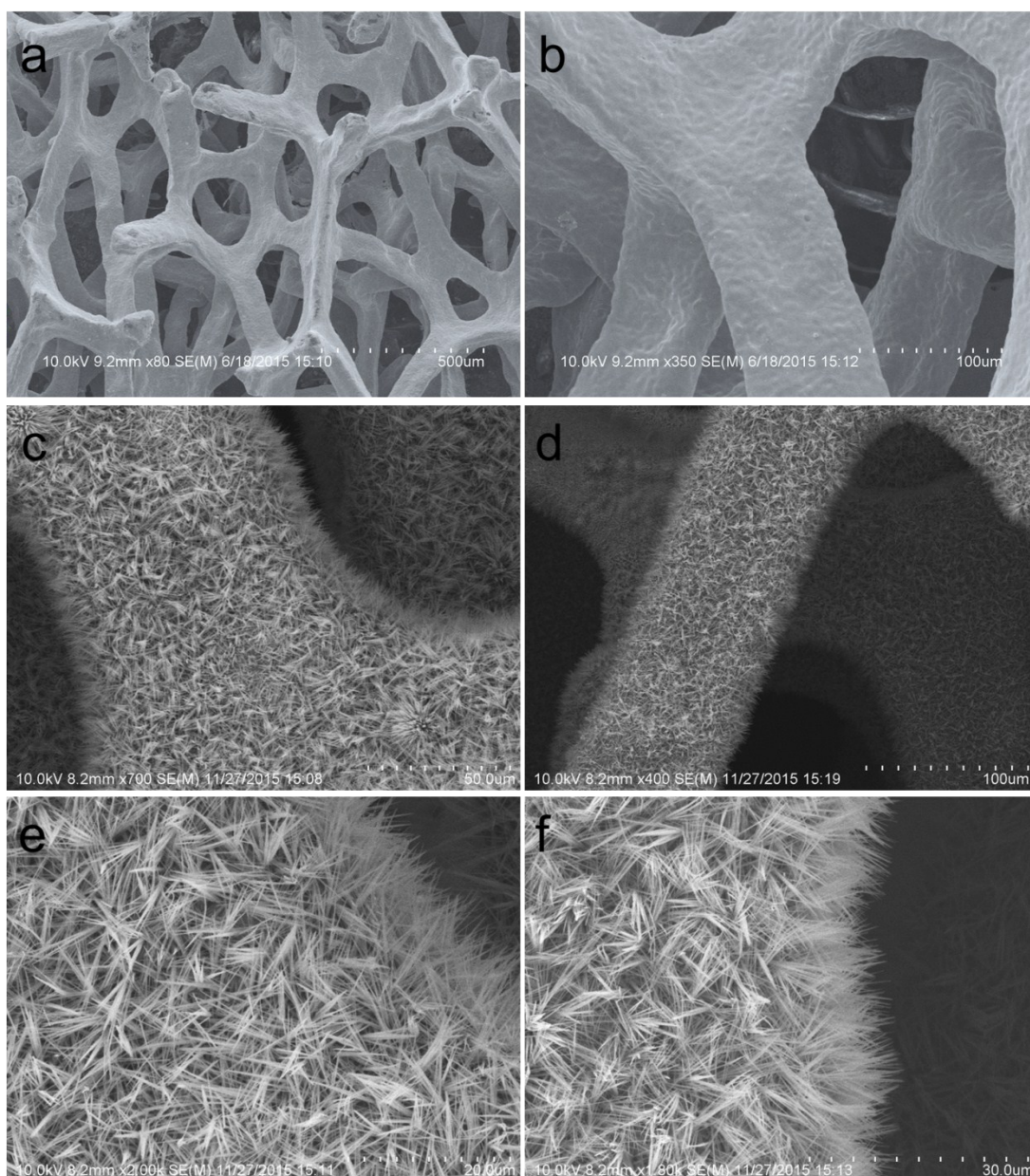


Fig. S1 (a, b) SEM images of pristine copper foam. (c–f) SEM images of Cu(OH)₂/CF.

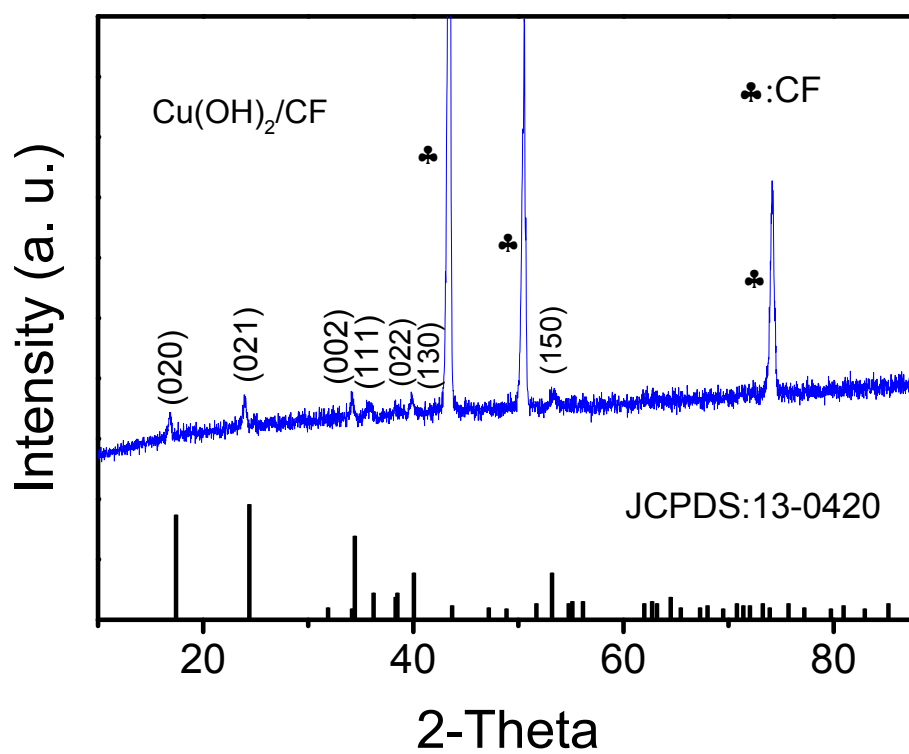


Fig. S2 XRD pattern of $\text{Cu(OH)}_2/\text{CF}$.

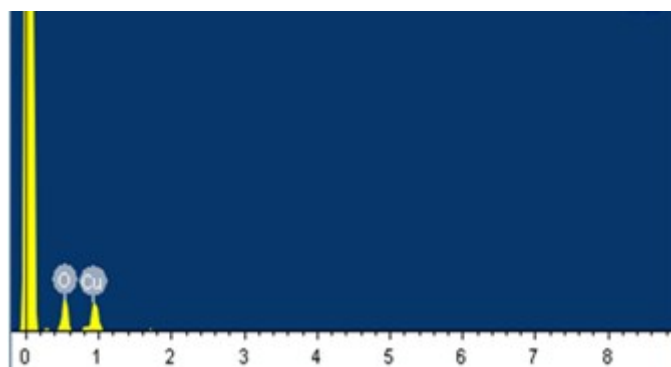


Fig. S3 EDX analysis of the as-prepared Cu(OH)_2 NWAs/CF film.

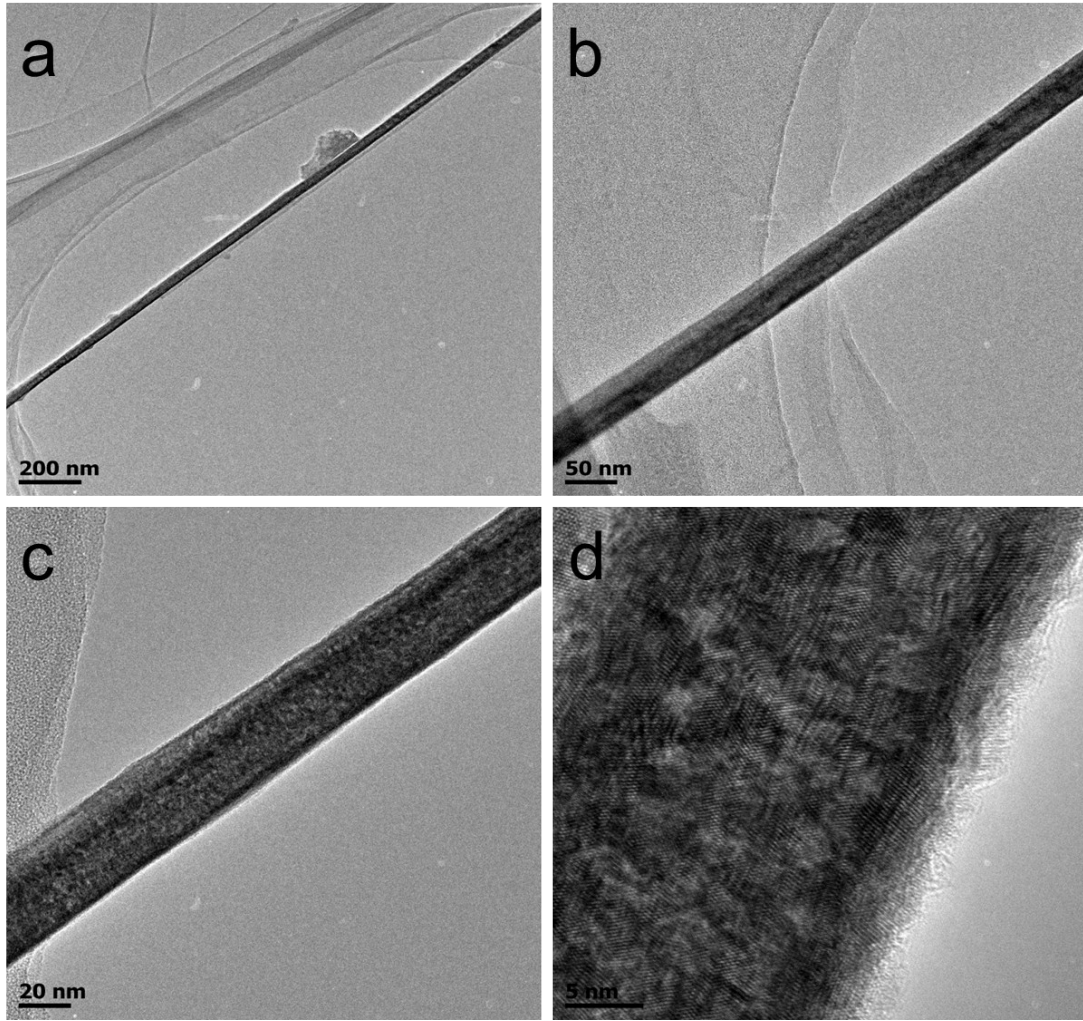


Fig. S4 TEM images of a single $\text{Cu}(\text{OH})_2$ nanowire.

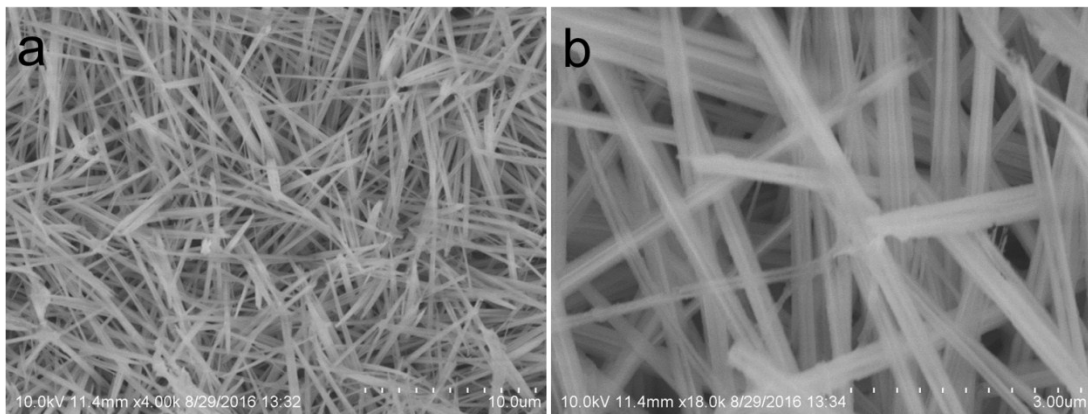


Fig. S5 SEM images of $\text{Fe}(\text{OH})_3:\text{Cu}(\text{OH})_2/\text{CF}$.

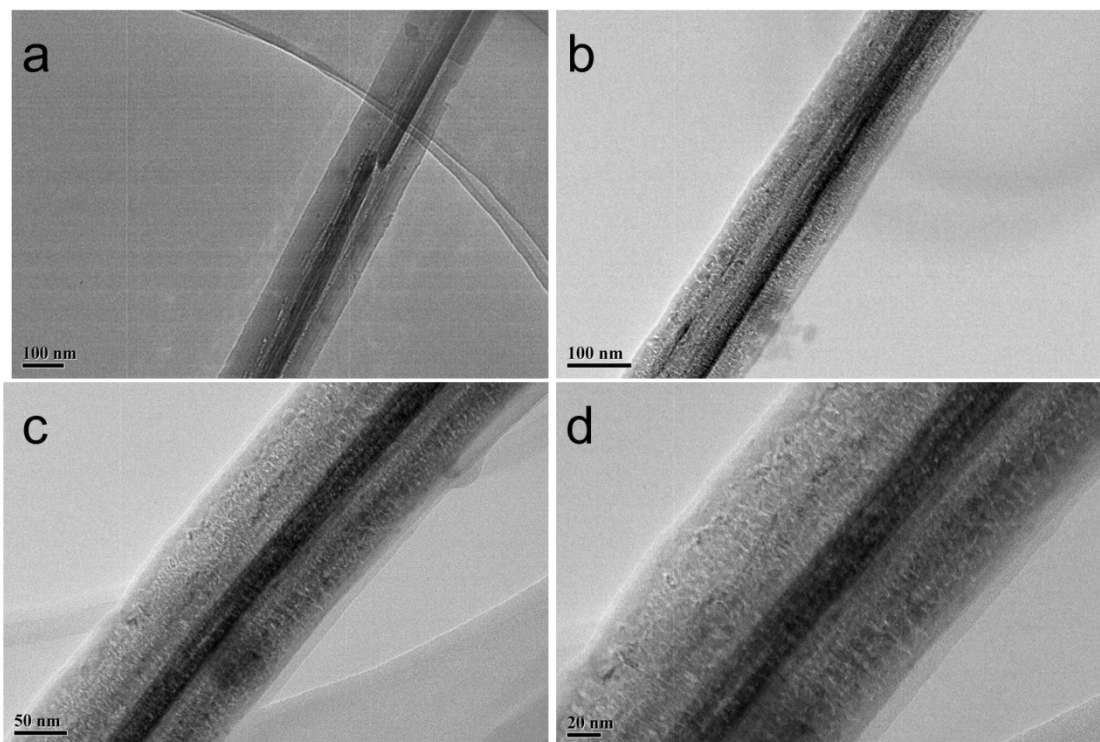


Fig. S6 TEM images of a single Fe(OH)₃:Cu(OH)₂ nanowire.

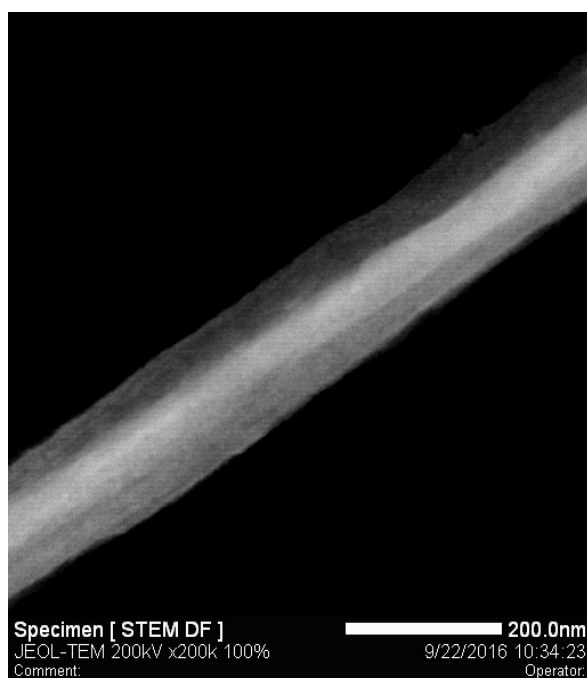


Fig. S7 STEM-DF image of a single Fe(OH)₃:Cu(OH)₂ nanowire.

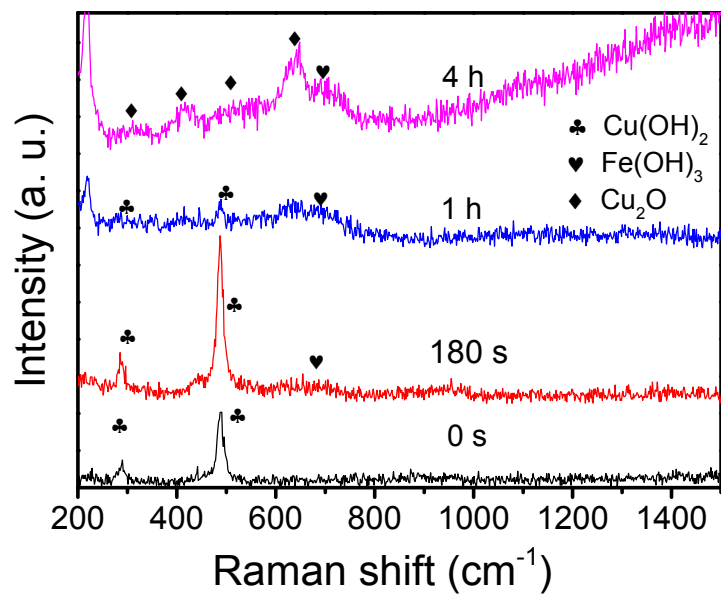


Fig. S8 The Raman spectra of Cu(OH)₂/CF film immersed in 10 mM Fe³⁺ solution for different time.

Table S1. Comparison of some representative Cu, Fe-based OER heterogeneous catalysts in alkaline media^a

Catalysts	η (mV vs. 1 mA cm ⁻²)	η (mV vs. 10 mA cm ⁻²)	η (mV vs. 100 mA cm ⁻²)	References
Cu-Bi	530	–	–	<i>ACS Catal.</i> , 2015, 5, 627.
CuO from Cu-TEOA ^b	780	–	–	<i>Inorg. Chem.</i> , 2015, 54, 3061.
CuO NW	485	580	–	<i>Angew. Chem. Int. Ed.</i> , 2015, 54, 2073.
Cu-Bifunctional	749	–	–	<i>ACS Catal.</i> , 2015, 5, 1530.
Cu(OH) ₂ nanowires	–	430	–	<i>ChemSusChem</i> , 2016, 9, 2069.
Cu ₃ P	–	–	420	<i>ACS Appl. Mater. Interfaces</i> , 2016, 8, 23037.
Cu/(Cu(OH) ₂ -CuO)	–	417	–	<i>Electrochim. Acta</i> , 2015, 163, 102.
Fe ₂ O ₃	–	420	–	<i>Chem. Eur. J.</i> , 2015, 21, 18062.
FeO _x H _y	~350	–	–	<i>J. Phys. Chem. Lett.</i> , 2015, 6, 3737.
Fe(OH) ₃ :Cu(OH) ₂	–	365	407	This work

^aThe current densities given are based on the projected geometric area of the electrode. ^bTEOA=triethanolamine.

Table S2. Measurements of electrochemical impedance spectroscopy (EIS).

The EIS response for each electrode could then be fitted by a simplified Randles equivalent circuit and the geometric values of the electronic elements extracted from this Electrical Equivalent circuit model are listed below:

	$R_s(\Omega \cdot \text{cm}^2)^a$	$R_{ct}(\Omega \cdot \text{cm}^2)^b$
CF	2.10	3.9
$\text{Cu}(\text{OH})_2/\text{CF}$	2.08	5.5
$\text{Fe}(\text{OH})_3:\text{Cu}(\text{OH})_2/\text{CF}$	2.07	39.8

^a R_s is related to the series resistance; ^b R_{ct} denotes the charge transfer resistance.

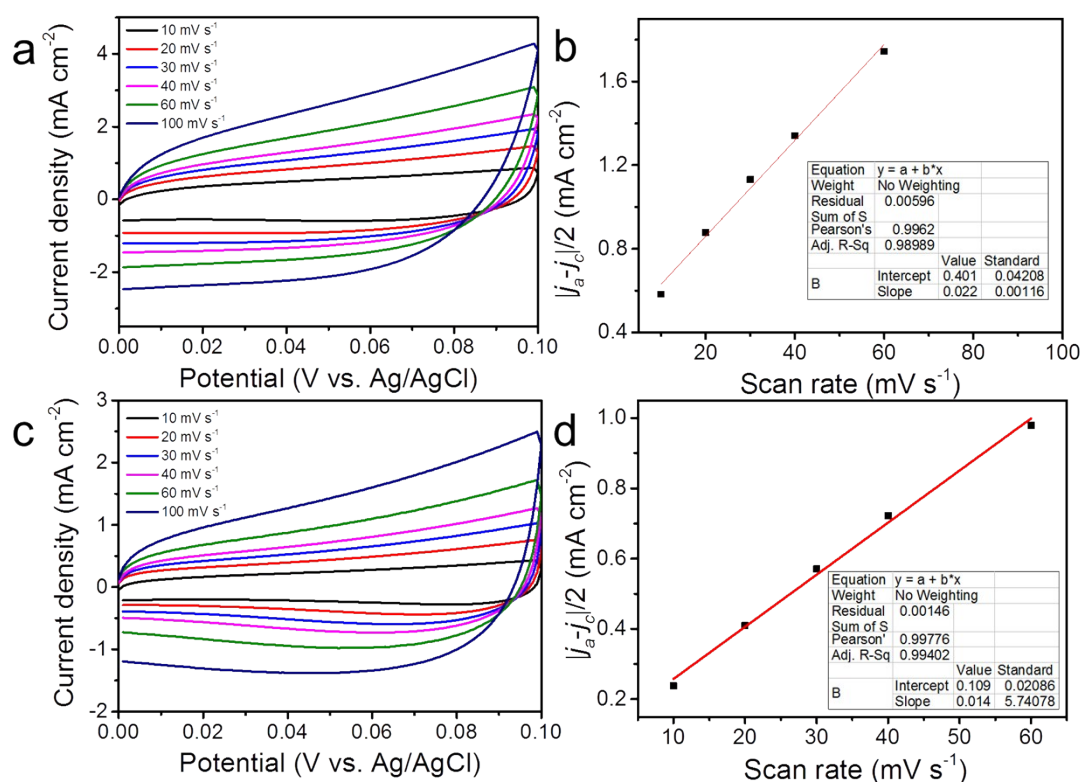


Fig. S9 (a) CVs of $\text{Cu}(\text{OH})_2/\text{CF}$ measured in 1.0 M KOH at scan rates of 10 to 100 mV s^{-1} and (b) Plot showing the extraction of the double-layer capacitance (C_{dl}) for each type of $\text{Cu}(\text{OH})_2/\text{CF}$ electrode at 0.05 V vs. Ag/AgCl. (c) CVs of $\text{Fe}(\text{OH})_3:\text{Cu}(\text{OH})_2/\text{CF}$ measured in 1.0 M KOH at scan rates of 10 to 100 mV s^{-1} and (d) Plot showing the extraction of the double-layer capacitance (C_{dl}) for each type of $\text{Fe}(\text{OH})_3:\text{Cu}(\text{OH})_2/\text{CF}$ electrode at 0.05 V vs. Ag/AgCl.

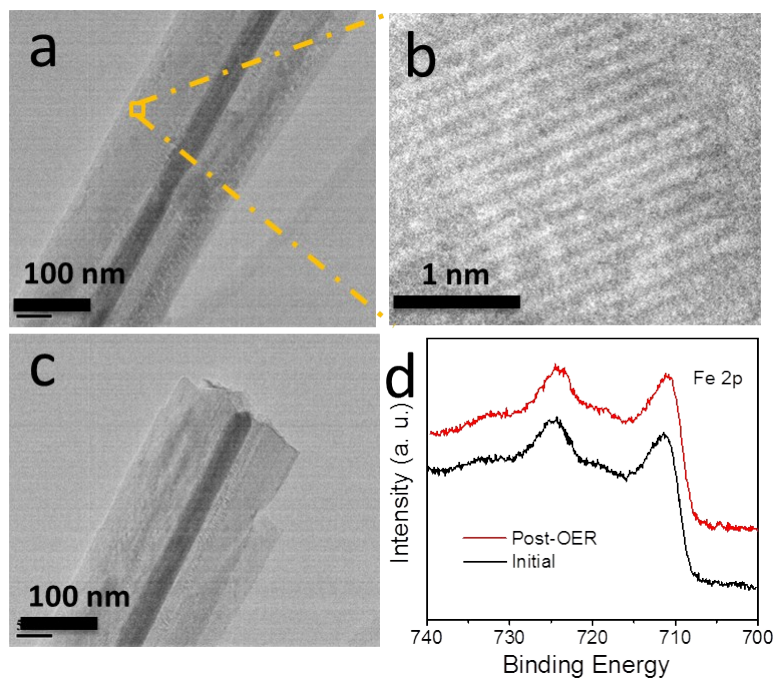


Fig. S10 (a-c) TEM and HRTEM of a single post-OER $\text{Fe}(\text{OH})_3:\text{Cu}(\text{OH})_2$ nanowire. (d) The high-resolution XPS data of Fe 2p of initial and post-OER $\text{Fe}(\text{OH})_3:\text{Cu}(\text{OH})_2$ film.

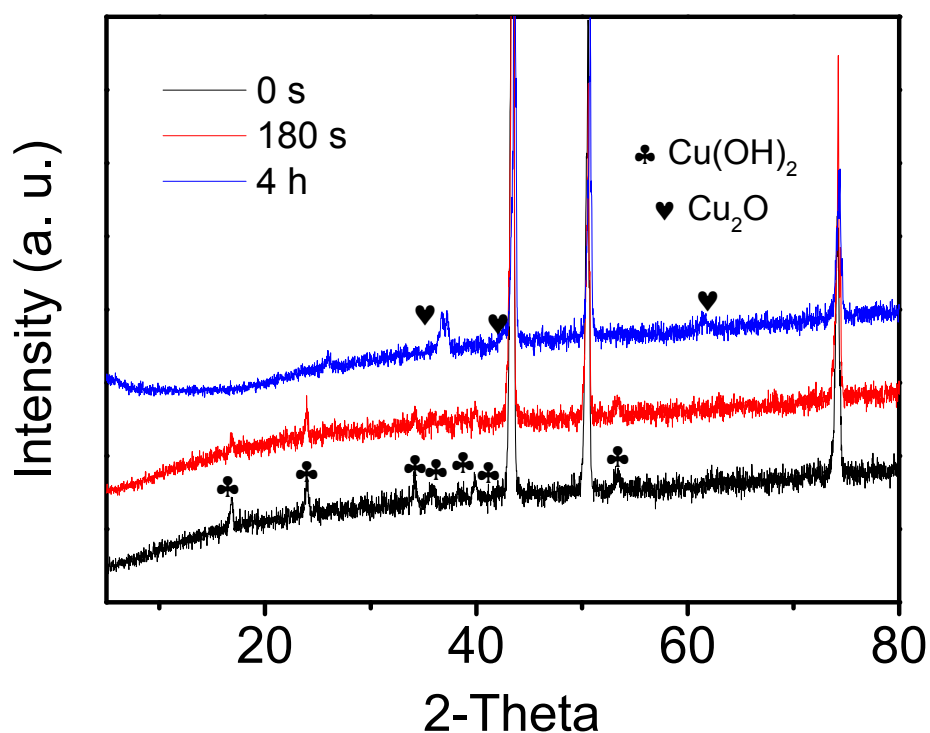


Fig. S11 The XRD patterns of $\text{Cu}(\text{OH})_2/\text{CF}$ film immersed in 10 mM Fe^{3+} solution for different time.

Table S3. The corresponding C_{dl} , ECSA, R_f and the specific current density j_s (at ~ 410 mV) of $\text{Cu}(\text{OH})_2/\text{CF}$ film immersed in 10 mM Fe^{3+} solution for different time.

Catalysts	C_{dl} (mF cm ⁻²)	ECSA (cm ²) ^a	R_f ^b	$j_s@ \eta=410$ mV
0 s	23.0	575	575	0.028
5 s	14.29	357	357	0.088
20 s	14.23	356	356	0.161
3 min	14.82	370	370	0.262
5 min	14.44	361	361	0.268
1 h	12.15	304	304	0.212
4 h	10.72	268	268	0.036

^aIn our work, we temporarily use the C_s value of 0.04 mF cm⁻² based on the previous literature (*J. Am. Chem. Soc.* 2013, **135**, 16977–16987). As described in this work, the C_s values of various materials are different and the value of the same material is also different in alkaline and acidic solutions. For example, the values for Ni in 0.5 and 1 M NaOH are 40 and 25 $\mu\text{F cm}^{-2}$, respectively, whilst that of NiMoCd in 0.5 M KOH is 90 $\mu\text{F cm}^{-2}$. Specific capacitances have been measured for a variety of metal electrodes in acidic and alkaline solutions and typical values reported range between $C_s = 0.015\text{--}0.110$ mF cm⁻² in H_2SO_4 and $C_s = 0.022\text{--}0.130$ mF cm⁻² in NaOH and KOH solutions. Therefore, one use general specific capacitances of $C_s = 0.035$ mF cm⁻² in 1 M H_2SO_4 and $C_s = 0.040$ mF cm⁻² in 1 M NaOH based on typical reported values for convenience. In the Supporting Information of this work, Prof. Peters and Prof. Jaramillo mentioned that “NiCo and Ni-Mo-Cd surfaces have also been investigated and have reported specific capacitances of 26 $\mu\text{F cm}^{-2}$ and 90 $\mu\text{F cm}^{-2}$, respectively. The average specific capacitance for these Ni-containing materials is ca. 36.5 $\mu\text{F cm}^{-2}$. If we also include the reported specific capacitances for carbon, Cu, Pt, Co, and Mo in strongly alkaline solutions, then the average specific capacitance increases to ca. 43 $\mu\text{F cm}^{-2}$. Of course, it is unclear how appropriate it is to average these literature values since a simple mean gives artificial weight to those materials studied more thoroughly, but most materials reported showed a specific capacitance between 22 and 40 $\mu\text{F cm}^{-2}$, so we chose 40 $\mu\text{F cm}^{-2}$ as our specific capacitance in 1 M KOH and reported it as a “typical” value for these materials”. Therefore, they all use general specific capacitances of $C_s = 0.035$ mF cm⁻² in 1 M H_2SO_4 and $C_s = 0.040$ mF cm⁻² in 1 M NaOH for different materials like CoO_x , Co-Pi, CoFeO_x , IrO_x , NiO_x , NiCeO_x , NiCoO_x , NiCuO_x , NiFeO_x , NiLaO_x etc.

^bThe geometrical surface area of the CF electrode was 1 cm².

Table S4. Comparison of the OER activities of some representative noble metal and several recently reported active non-noble Ni, Co-based catalysts supported on different substrates.^a

Catalyst	Current density j (mA cm ⁻²)	Overpotential at the corresponding j (mV)	Electrolytes	Tafel slope (mV dec ⁻¹)	substate	reference
Fe(OH) ₃ : Cu(OH) ₂	10 100	365 407	1.0 M KOH	42	Cu foam	This work
Mono-NiTi- MMO	10	~320	1.0 M KOH	52	GC	<i>J. Am. Chem. Soc.</i> , 2016, 138, 6517–6524.
Ni-P@C	10	300	1.0 M KOH	64	RDE	<i>Energy Environ. Sci.</i> , 2016, 9, 1246.
Co ₃ O ₄ -carbon porous nanowire arrays	10	290	0.1 M KOH	70	Cu foil	<i>J. Am. Chem. Soc.</i> 2014, 136, 13925.
Nitrogen-doped crumpled graphene CoO	10	340	1.0 M KOH	71	GC	<i>Energy Environ. Sci.</i> 2014, 7, 609.
Ni _x Co _{3-x} O ₄	10	~370	1 M NaOH	59-64	Ti foil	<i>Adv. Mater.</i> 2010, 22, 1926.
NiO/FeNC sheets	10	~390	0.1 M KOH	76	RDE	<i>Angew. Chem. Int. Ed.</i> 2015, 54, 10530.
α-Ni(OH) ₂	10	331	0.1 M KOH	42	GC	<i>J. Am. Chem. Soc.</i> , 2014, 136, 7077.
NiSe	20	270	1.0 M KOH	64	Ni foam	<i>Angew. Chem. Int. Ed.</i> 2015, 54, 9351.
CoO _x @CN	10	260	1.0 M KOH	—	Ni foam	<i>J. Am. Chem. Soc.</i> 2015,

						<i>137, 2688.</i>
$\text{Co}_3\text{O}_4/\text{NiCo}_2\text{O}_4$	10	340	1.0 M KOH	88	Ni foam	<i>J. Am. Chem. Soc. 2015, 137, 5590.</i>
$\text{LiCo}_{0.8}\text{Fe}_{0.2}\text{O}$	10	340	0.1 M KOH	50	RDE	<i>Adv. Mater. 2015, 27, 7150–7155.</i>
Rutile RuO_2	~ 10	460	0.1 M HClO_4	—	GC	<i>J. Phys. Chem. Lett. 2012, 3, 399.</i>
IrO_2/C	~ 10	370	KOH (pH=13)	—	GC	<i>Nat. Commun. 2013, 4, 2390.</i>

^a To get more details, please see recent review (J. Wang, W. Cui, Q. Liu, Z. Xing, A. M. Asiri and X. Sun, *Adv. Mater.* 2016, **28**, 215-230).