Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

CuFe-P from a Prussian Blue Analogue as an Electrocatalyst for Efficient Full Water Splitting

*Xianjun Xing, Yuqiang Song, Wen Jiang, Xianwen Zhang**

Hefei University of Technology, Hefei 230000, China

** Corresponding author E-mail: xianwen.zhang@hfut.edu.cn*

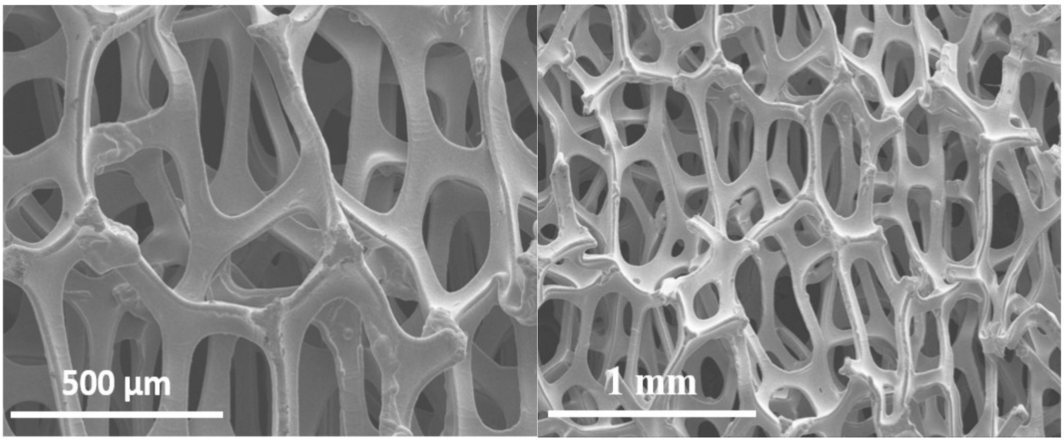

Figure S1. SEM images of NF.

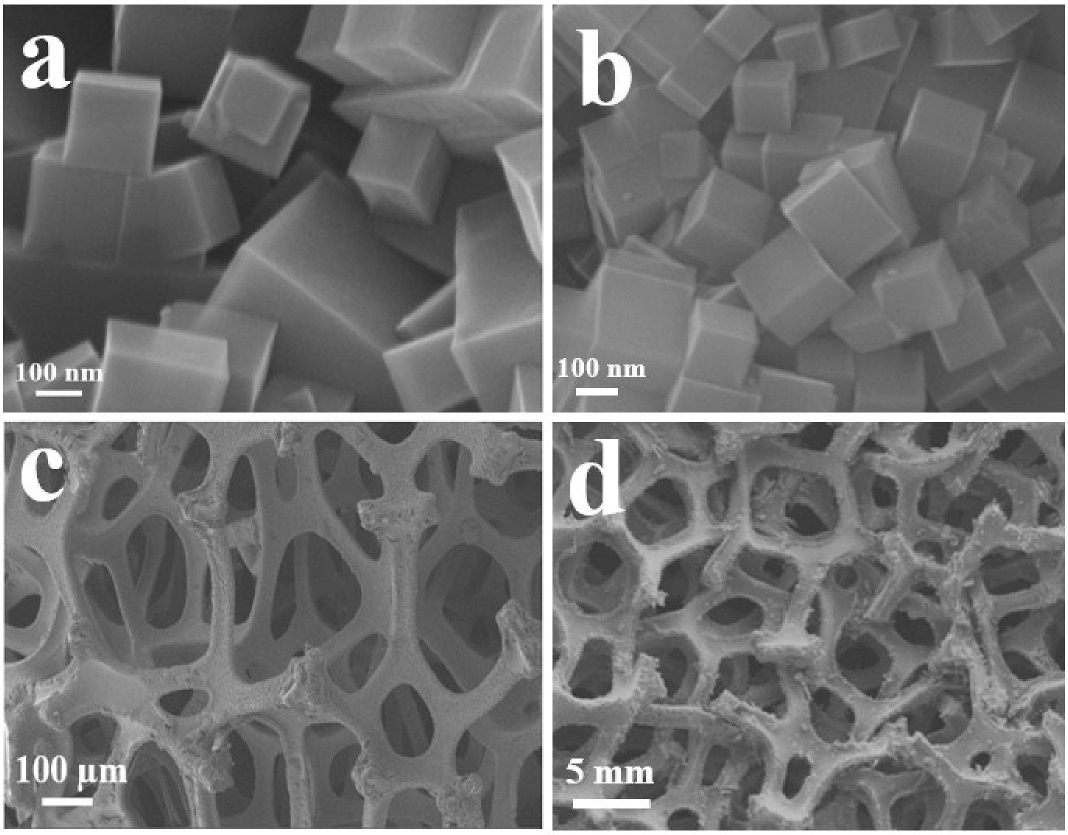

Figure S2. SEM images of CuFe PBA/NF.

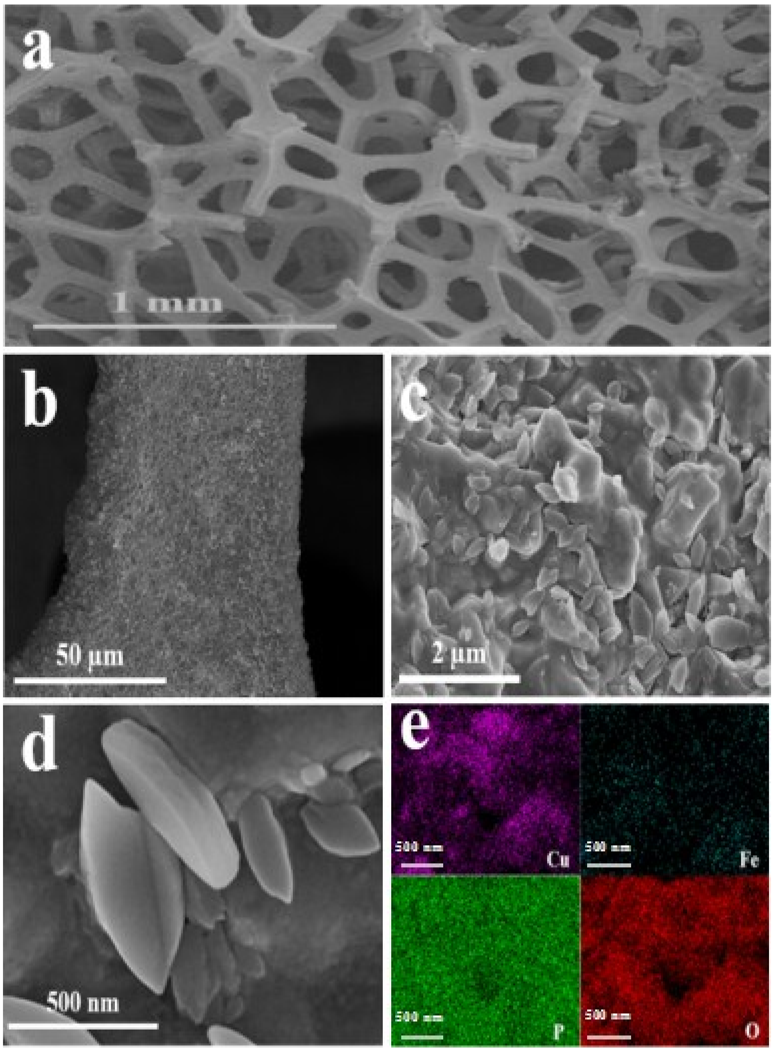

Figure S3. SEM images and EDS elemental mapping images of CuFe-P/NF.

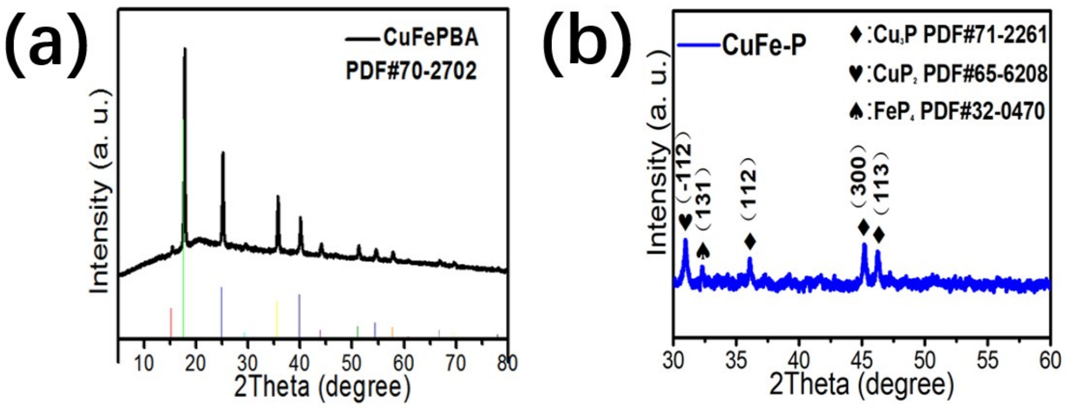

Figure S4. XRD pattern of CuFe PBA and XRD pattern of CuFe-P scraped from the NF.

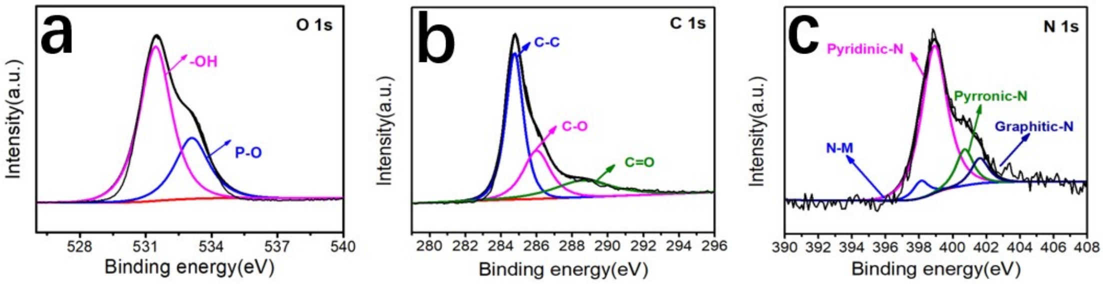

Figure S5. High resolution XPS spectra of O1s(a), C1s(b) and N1s(c) for CuFe-P.

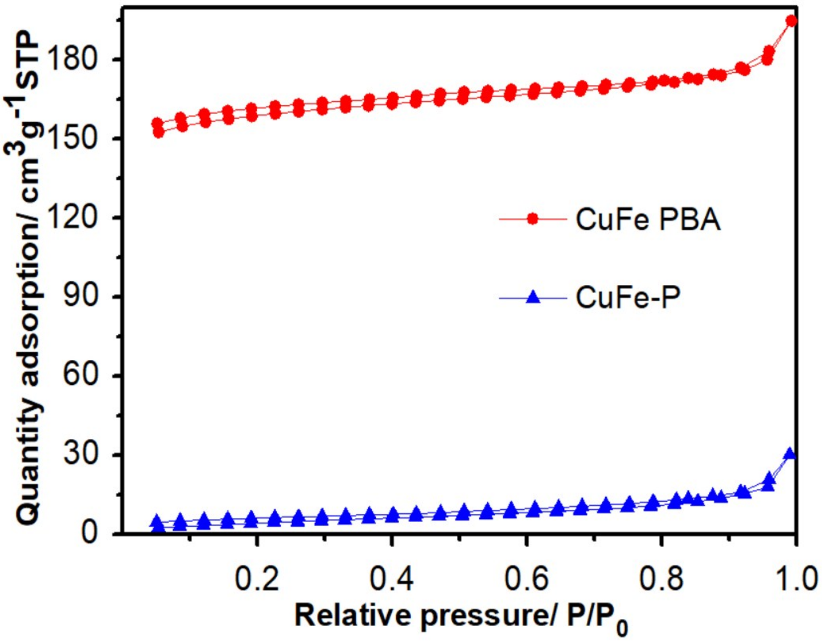

Figure S6. N_2 sorption isotherms of CuFe PBA and CuFe-P.

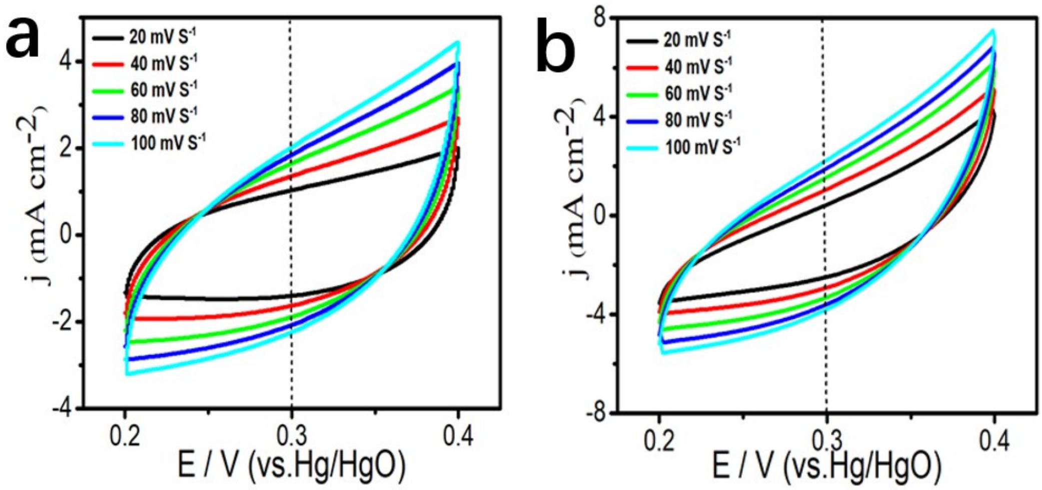

Figure S7. CVs of (a) CuFe/NF and (b) CuFe-P/NF in the non-faradic capacitance current range from 20 to 100 mV s^{-1}.

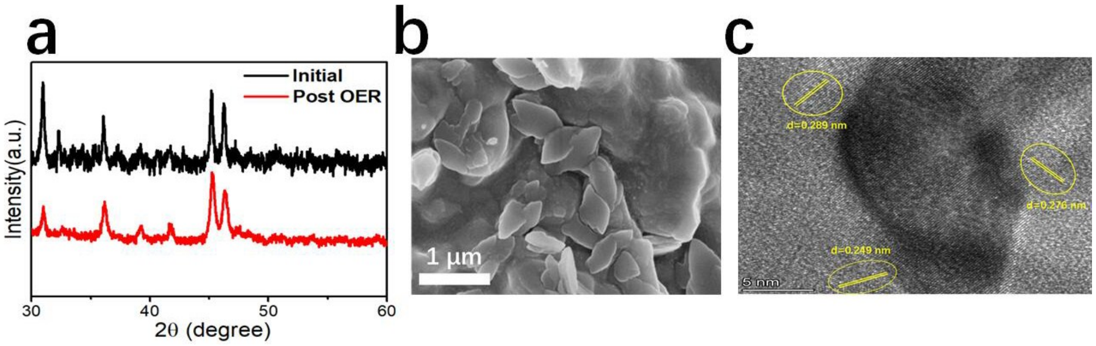

Figure S8. (a) XRD patterns of CuFe-P before and after OER test. SEM (b) and HRTEM (c) images of CuFe-P after OER test.

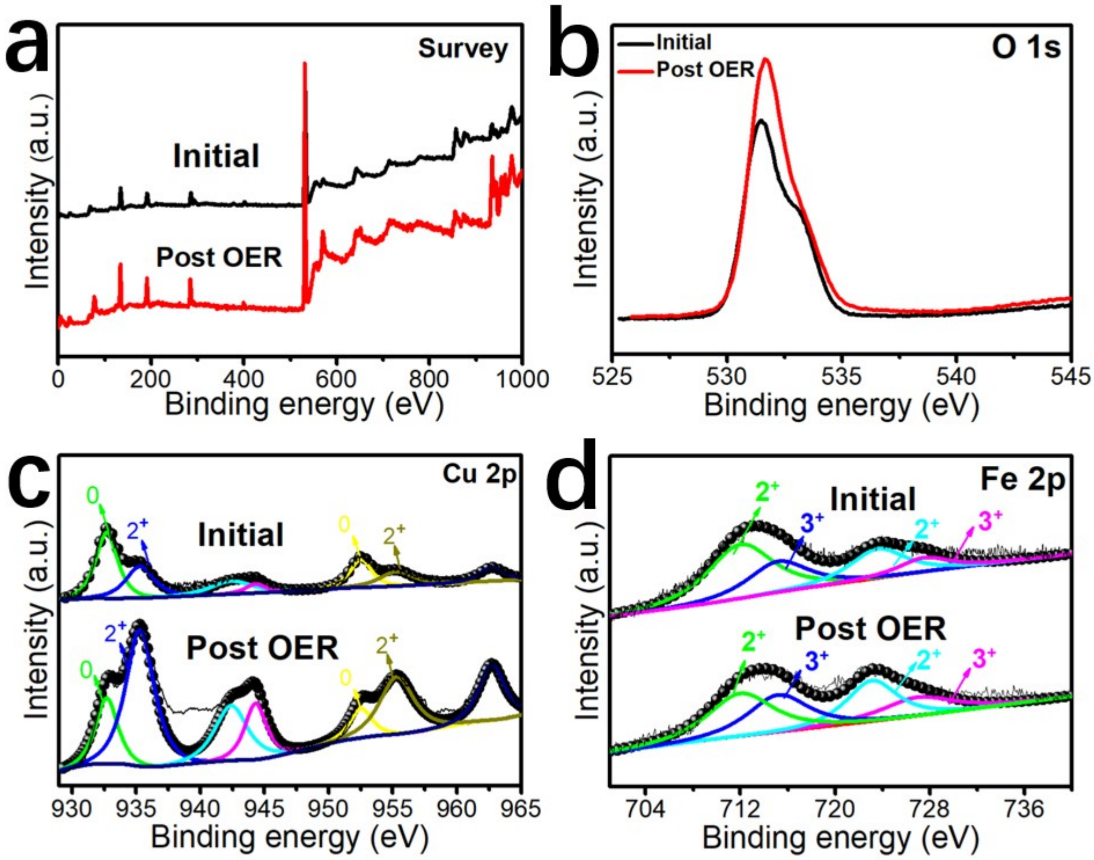

Figure S9. (a) XPS survey, (b) O 1s, (c) Cu 2p and (d) Fe 2p of CuFe-P/NF spectrum before and after OER test.

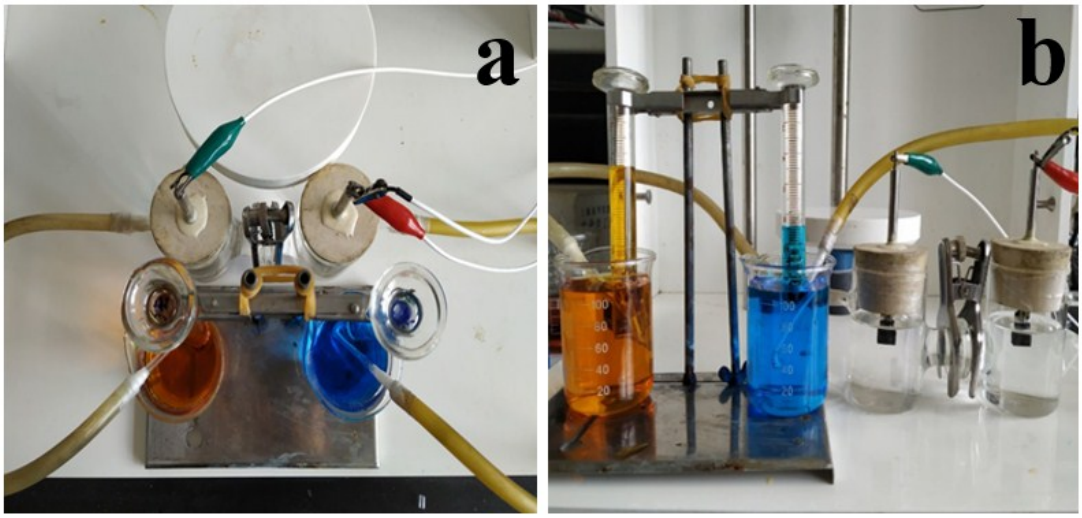

Figure S10. Gas collection device of water splitting in 1.0 M KOH aqueous solution.

Video S1：The dynamic process of water splitting.

Table S1. Comparison of OER activity for some reported electrocatalysts.

Catalyst	η at 10 mA cm^{-2} (mV)	η at 100 mA cm^{-2} (mV)	Substrate	Reference
CuFe-P	230	301	NF	This work
$CoFe_2O_4$/C NRAs	240	290	NF	Adv. Mater. 2017, 29, 1604437
Co-Fe-P	244	N.A.	NF	ACS Appl. Mater. Interfaces 2017, 9, 362-370
NiCoP	242	330	CC	ACS Catal. 2017,7, 4131-4137
$Ni_{1.5}Fe_{0.5}P$	264	293	CFP	Nano Energy 2017, 34, 472-480
$W_{0.5}Co_{0.4}Fe_{0.1}$	250	310	NF	Angew. Chem. Int. Ed. 2017, 56, 4502-4506
CoMnCH	N.A.	349	NF	J. Am. Chem. Soc. 2017, 139, 8320-8328

Table S2. Comparison of the overall water splitting activity for some reported bifunctional electrocatalysts.

Catalyst	OER η at 10 mA cm^{-2} (mV)	HER η at 10 mA cm^{-2} (mV)	Cell voltage (10 mA cm^{-2} for overall water splitting) (mV)	Substrate	Reference
CuFe-P	230	153	1.61	NF	This work
Co-P films	345	94	1.64	Cu foil	Angew. Chem. Int. Ed. 2015, 54, 6251-6254
$NiCo_2S_4$	260	210	1.63	NF	Adv. Funct. Mater. 2016, 26, 4661-4672
FeCoOOH	211	126	1.62	NF	Chem. Eur. J. 2018, 24, 4724-4728
$FeNi_3N$	202	75	1.62	NF	Chem. Mater. 28 (2016) 6934-6941.
CoFe	220	110	1.64	NF	Small 2018, 14, 1702568
S-$NiFe_2O_4$	267	138	1.65	NF	Nano Energy 2017, 40, 264-273

Experimental Section

Materials and reagent:

Cupric (II) nitrate trihydrate ($Cu(NO_3)_2·3H_2O$), sodium citrate dehydrate, potassium hexacyanoferrate（Ⅲ）($K_3[Fe(CN)_6]$) and sodium hypophosphite ($NaH_2PO_2·H_2O$) were obtained from Sinopharm Group Chemical Reagent. Potassium hydroxide (KOH), absolute ethanol and acetone were purchased from Beijing Chemical Works. IrO_2, Pt/C (20 wt %) and Nafion (5 wt %) were purchased from Sigma-Aldrich. All the reagents are analytical grade and used without further treatment. Deionized (DI) water was employed as solvent.

Preparation of Cu-Fe PBA on NF (CuFe/NF):

A piece of NF (3 cm × 3 cm) was first carefully sonicated in ethanol and acetone for 10 min to clean the surface. In a typical synthetic procedure, $Cu(NO_3)_2·3H_2O$ (0.6 mmol) and sodium citrate dihydrate (0.9 mmol) were dissolved in 30 mL DI water to form a clean solution. Then, a 30 mL solution containing 0.4 mmol $K_3[Fe(CN)_6]$ was poured into the solution and shaken vigorously for 3 min. Afterward, the pre-treated NF was immersed into the solution for 24 h without interruption. Finally, the obtained CuFe/NF was washed with ethanol and dried at 60 °C，the yield of CuFe/NF is 45%. The isolated Cu-Fe PBA was synthesized in the absence of NF under the similar method.

Preparation of CuFe-P/NF:

The CuFe-P/NF electrode was fabricated through a facile phosphorization treatment.

Briefly, $NaH_2PO_2 \cdot H_2O$ (1.0 g) and pre-prepared CuFe/NF were put at the upstream side and center of the tube furnace, respectively. The sample was then calcined at 350 °C for 2 h in an inert atmosphere. Finally, the CuFe-P/NF was obtained after cooling down to room temperature，the yield of CuFe-P/NF is 38%.

Material Characterization:

X-ray diffraction (XRD) patterns were collected on a Rigaku X-ray diffractometer equipped with a Cu *Kα* radiation source. The morphology and structure were characterized by scanning electron microscopy (SEM, Zeiss Ultra Plus) and by transmission electron microscopy (TEM, HITACHIH-8100). X-ray photoelectron spectroscopy (XPS) was carried out on an II X-ray photoelectron spectrometer.

Electrochemical Measurements：

All electrochemical measurements were performed in a conventional three-electrode system at room temperature using a CHI 660E electrochemical analyzer (CHI Instruments, Shanghai, China). A graphite rod and Hg/HgO were used as the counter electrode and the reference electrode, respectively. The as-prepared electrocatalysts with a geometric area of 0.25 cm^2 were directly served as the working electrodes. As for powdery catalysts (IrO_2 and Pt/C), the working electrodes were prepared by dropping electrocatalyst ink onto NF. The 1 M KOH aqueous solution was used as the electrolytes, and all the polarization curves were recorded at a scan rate of 2 mV s^{-1} unless specifically indicated. In HER and OER characterizations, the polarization curves were iR-corrected using the equation: $E_{\text{iR-corrected}} = E - iR$, where E is the original potential, R is the solution resistance, i is the corresponding current, and $E_{iR\text{-corrected}}$ is the *iR*-corrected potential. Electrochemical impedance spectroscopy (EIS) tests were carried out in a frequency ranging from 0.01 Hz to 100 kHz with AC amplitude of 10 mV. Furthermore, the HER and OER potentials were converted to RHE scale according to the equation: E (vs. RHE) = E (vs. Hg/HgO) + 0.059*pH + 0.098 V. The electrochemical double layer capacitance (C_{dl}) was determined with typical cyclic voltammetry (CV) measurements at various scan rates (20, 40, 60, 80 and 100 mV s^{-1}) in 0.2 ~ 0.4 V versus Hg/HgO. The C_{dl} was further used to obtain the electrochemical active surface area (ECSA) values according to the equation: ECSA = C_{dl}/C_s, where C_s is the specific capacitance value of an ideal flat surface with a real surface area of 1 cm^2. In our estimates of ECSA, we take the general value of 60 μF cm^{-2} for C_s. The electrocatalyst CuFe-P/NF was used as both cathode and anode in a two-electrode configuration for overall water splitting. Notably, the generated H_2 and O_2 gases during overall water splitting were quantitatively collected by the water drainage method.