Supporting Information

A General MOF-intermediated synthesis of hollow CoFe-based trimetallic phosphides composed of ultrathin nanosheets for boosting water oxidation electrocatalysis

Cheng Wang [a], Hongyuan Shang [a], Yuan Wang [a], Jie Li [a], Siyu Guo *[a], Jun Guo [b], Yukou Du*[a]

[a] *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, 199 Renai Road, Suzhou 215123, P.R. China.*

[b] *Testing and Analysis Center, Soochow University, Suzhou, 215123, P.R. China.*

** Corresponding authors: Tel: 86-512-65880089, Fax: 86-512-65880089;*

E-mail: syguo@suda.edu.cn; duyk@suda.edu.cn (Y. Du)

Experimental section

Synthesis of CoFe hydroxide

In a typical synthesis, $Co(NO_3)_2{\cdot}6H_2O$ (1.092 g) and $Fe(NO_3)_3{\cdot}9H_2O$ (0.048 g) were dissolved in methanol solution (15 mL) to form solution A, and 2-methyl imidazole (0.616 g) was dissolved in methanol (15 mL) to form solution B. Subsequently, solution B was dropped into solution A under sonication, and sustained sonication for 10 minutes. The mixed solution was then transformed into a Teflon-lined stainless-steel autoclave and maintained at 120 °C for 4 h. After being cooled to room temperature, the CoFe were collected by centrifugation and washing 3 times with methanol.

Synthesis of CoFeM (M = Bi, Ni, Mn, Cu, Ce, Zn)

$Co(NO_3)_2 \cdot 6H_2O$ (1.092 g), $Fe(NO_3)_3 \cdot 9H_2O$ (0.024 g) and $Bi(NO_3)_3 \cdot 5H_2O$ (0.028 g) were dissolved in methanol solution (15 mL) to form solution A, and 2-methyl imidazole (0.616 g) was dissolved in methanol (15 mL) to form solution B. Subsequently, solution B was dropped into solution A under sonication, and sustained sonication for 10 minutes. The mixed solution was then transformed into a Teflon-lined stainless-steel autoclave and maintained at 120 °C for 4 h. After being cooled to room temperature, the CoFeBi were collected by centrifugation and washing 3 times with methanol. For the synthesis of other CoFe-based hydroxides, all the conditions are same to those of CoFeBi except by using $Ni(NO_3)_2 \cdot 6H_2O$ ($Mn(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$) as another metal precursor under sonication conditions.

Syntheses of CoFeM phosphides

To obtain CoFe-based trimetallic phosphides, 10 mg of the as-prepared CoFe-based hydroxides and excessive NaH_2PO_2 were placed in two separate positions in a tube furnace with NaH_2PO_2 at the upstream side. Then, the precursor were heated up to 350 ^{o}C with a heating rate of 2 °C min^{-1} and kept at this temperature for 2 h under flowing Ar. The final products were collected as CoFeM phosphides.

Characterizations

The chemical compositions of the all samples were determined by SEM-energy-dispersive-X-ray spectroscopy (SEM-EDX). Low-magnification transmission electron microscopy (TEM) was performed on a HITACHI HT7700 at 120 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and

HRTEM was recorded on a FEI TecnaiG2F2 FEI Talos F200X S/TEM with a field-emission gun at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on SSI S-Probe XPS Spectrometer. Powder X-ray diffraction (PXRD) patterns were collected on X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu Kα X-ray source ($\lambda = 1.540598$ Å).

Electrochemical tests

All electrochemical measurements were performed on CHI660 workstation (Chenhua, Shanghai) by using the three-electrode system. The system consisted of a graphite rod counter electrode, Ag/AgCl reference electrode, and a glassy carbon electrode (GCE) as working electrode. To prepare the catalyst ink, 6 mg catalysts were added into a mixture solution including 1.6 mL of isopropanol, 0.4 mL of H_2O and 20 μL Nafion. After 30 min sonication, 20 μL catalyst ink was deposited on glassy carbon electrode (diameter 5 mm, area: 0.196 cm^2) as a working electrode. The polarization curves were performed in 1 M KOH solution. The Tafel slopes were derived from polarization curves. Prolonged CP tests were conducted at the current density of 10 mA cm^{-2}. Electrochemical water splitting was tested by using a two-electrode system.

Supporting Figures and Tables

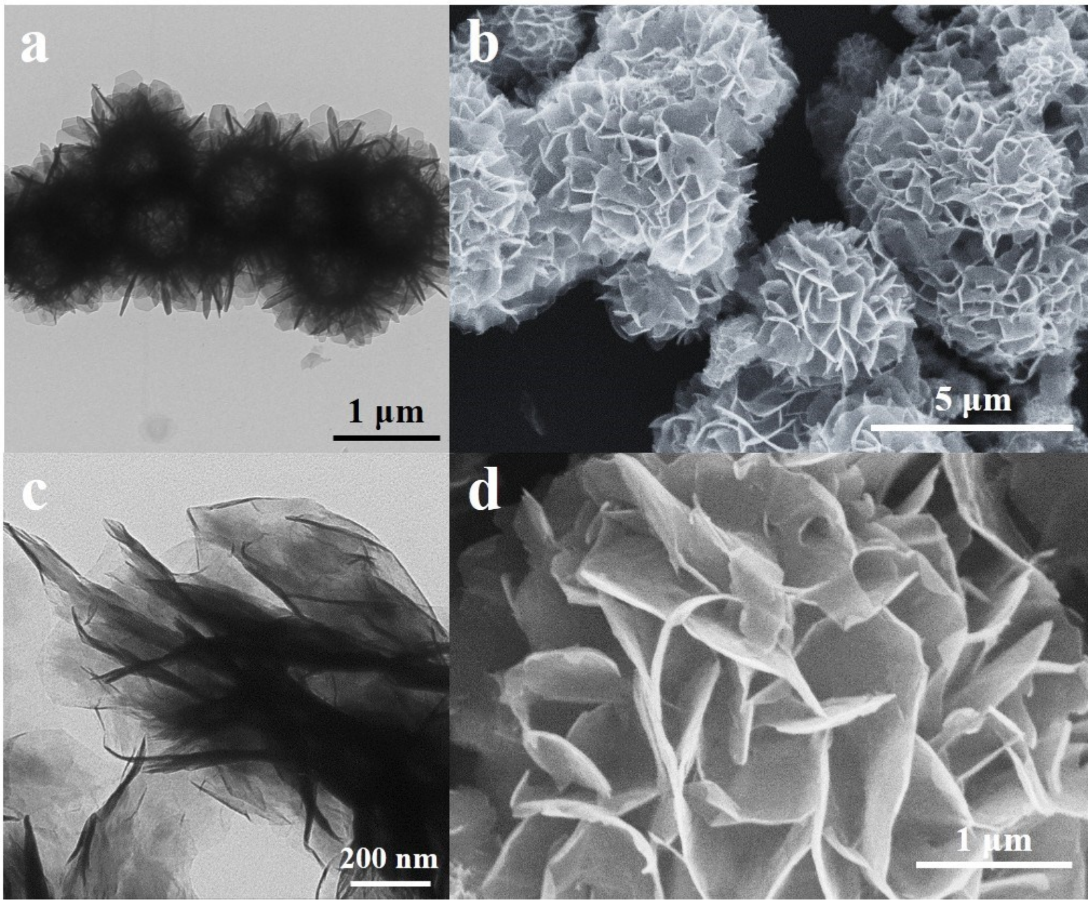

Fig. S1 (a, c) The TEM and (b, d) SEM images of CoFe.

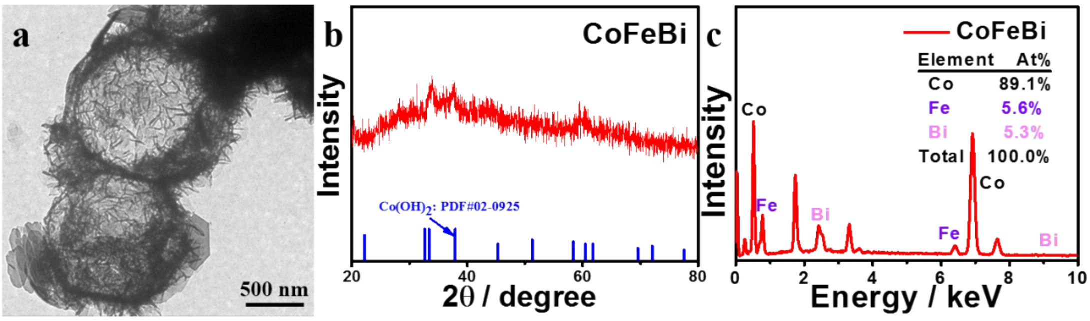

Fig.S2 (a) TEM image, (b) XRD pattern, and (c) SEM-EDS spectrum of the CoFeBi hydroxide.

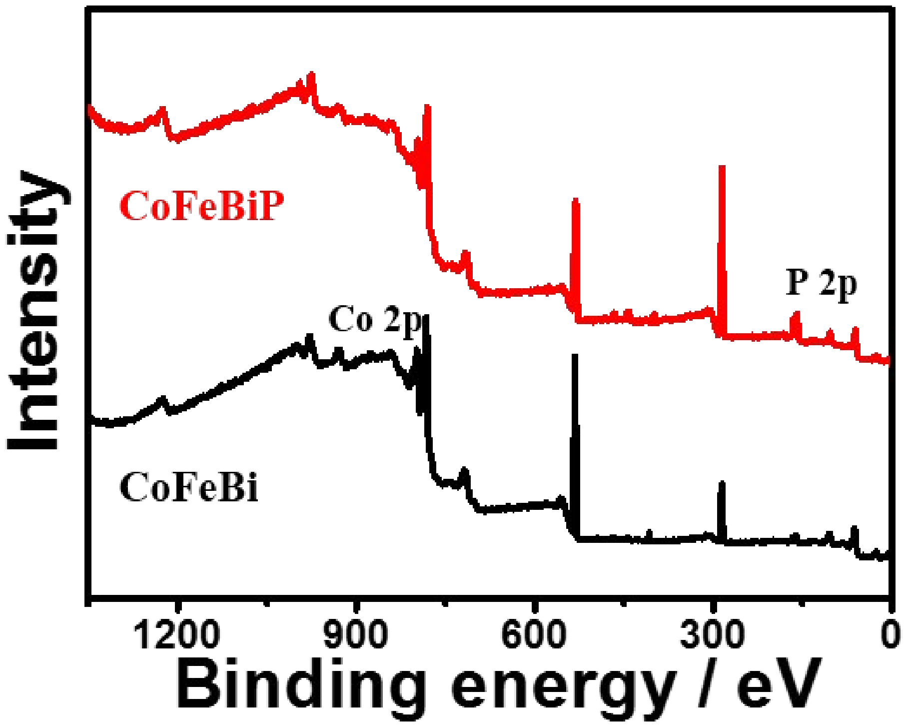

Fig.S3 Survey XPS spectra of the CoFeBiP (red) and CoFeBi hydroxide (black).

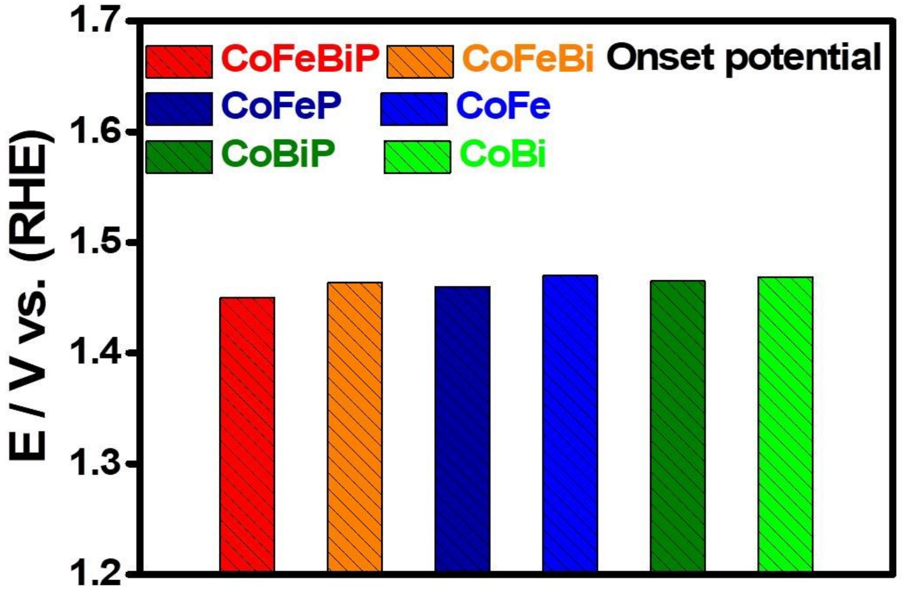

Fig.S4 The onset potentials of different catalysts.

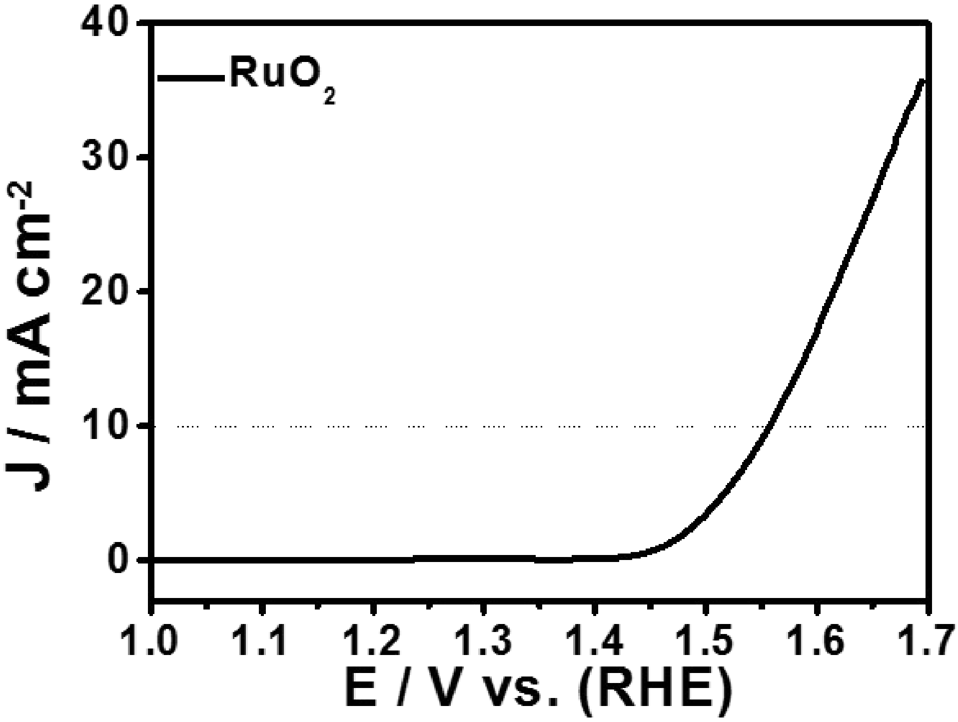

Fig.S5 LSV curves of the RuO_2 in 1 M KOH solution.

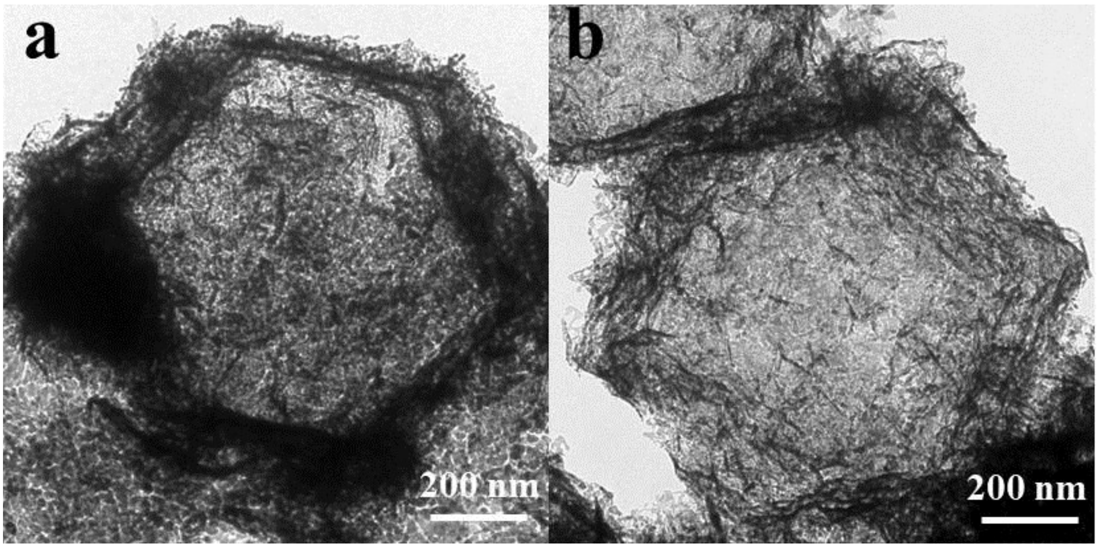

Fig.S6 Representative TEM images of the CoFeNiP hollow microspheres.

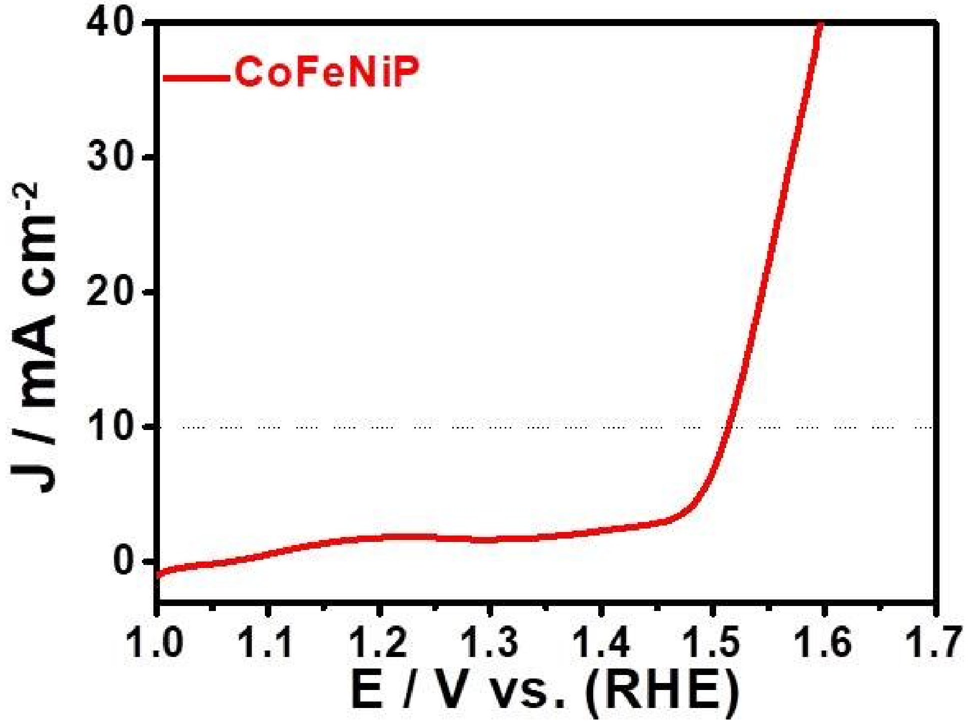

Fig.S7 LSV curves of the CoFeNiP hollow microspheres in 1 M KOH solution.

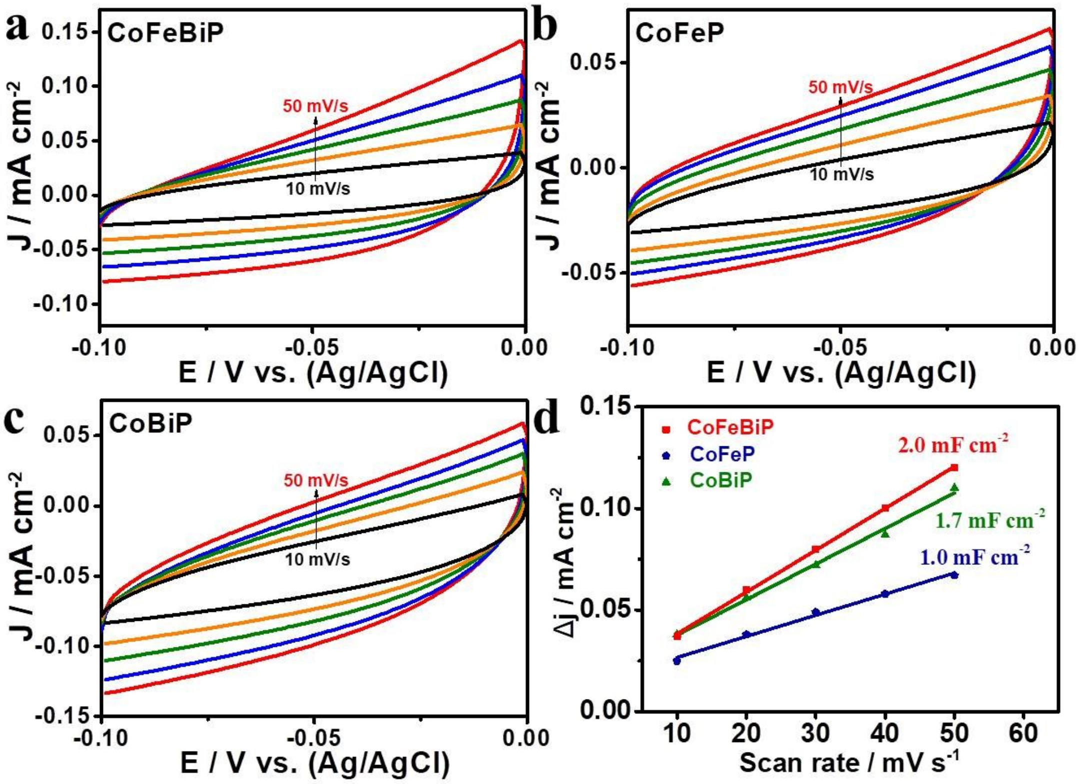

Fig.S8 CV curves of (a) CoFeBiP, (b) CoFeP, and (c) CoBiP. (d) Double layer currents of different catalysts versus scan rate.

Table S1 OER activity comparison of different catalysts in alkaline condition (η: overpotential at the current density of 10 mA cm^{-2}).

Catalyst	**η(mV)**	**Electrolyte**	**Tafel slope (mV/dec)**	**Reference**
CoFeBiP	**273**	1.0 M KOH	**77.3**	**This work**
Co_3O_4-24 h	296	1.0 M KOH	67.7	J. Colloid Interface Sci. 2021, 582, 322-332
Ni_1Co_1-P	343	1.0 M KOH	77	J. Alloys Compd. 2020, 847, 156514
H-Co_9S_8/Fe_3O_4 @SNC	280	1.0 M KOH	87	J. Power Sources 2018, 391, 59-66
N-$NiCoP_x$/NCF	298	1.0 M KOH	60	Chem. Eng. J. 2020, 402, 126257
$CoSe_2$@C-CNT	306	1.0 M KOH	46	J. Colloid Interface Sci. 2019, 533, 503-512
CoP	292	1.0 M KOH	64	Nanomaterials 2018, 8, 89

$CoOx/CoNy@CN_{z,700}$	280	1.0 M KOH	61	Appl. Catal. B: Environ. 2020, 279, 119407
$CoNi/CoNiO_2$	341	1.0 M KOH	/	Adv. Mater. 2018, 30, 1705442
Co/P-N-C-2	300	1.0 M KOH	61	J. Alloys Compd. 2020, 843，156001
Co/FeC@NHC-1	380	1.0 M KOH	70	J. Colloid Interface Sci. 2020, 580, 794-802
FeCo@C	302	1.0 M KOH	75	Int. J. Hydrog. Energy 2020, 45, 26574-26582
Co_3O_4/Fe_2O_3	310	1.0 M KOH	67	Chem. Eng. J. 2019, 355, 336-340