Supporting Information

EXPERIMENTAL

Synthesis of NiCoFe PBA Polyhedrons

The uniform NiCoFe PBA polyhedrons with a size of ~200 nm were synthesized by a simple precipitation method [78]. In a typical procedure, 0.3 mmol of nickel nitrate, 0.3 mmol of Cobalt acetate and 0.9 mmol of sodium citrate were dissolved in 20 mL of deionized (DI) water to form solution A. At the same time, 0.4 mmol of potassium ferricyanide (III) was dissolved in 20 mL of DI water to form solution B. Then, solutions A and B were mixed under magnetic stirring for 3 min. The obtained mixed solution was aged for 20 h at room temperature. After collected by centrifugation and washed with water and ethanol, the precipitates were dried at 60 ℃ overnight.

Synthesis of NiCo PBA Nanocubes

The uniform NiCo PBA cubes with a size of 500 nm were synthesized by a simple precipitation method. In a typical procedure, 0.6 mmol of nickel nitrate and 0.9 mmol of sodium citrate were dissolved in 20 mL of deionized (DI) water to form solution A. At the same time, 0.4 mmol of potassium hexacyanocobaltate (III) was dissolved in 20 mL of DI water to form solution B. Then, solutions A and B were mixed under magnetic stirring for 3 min. The obtained mixed solution was aged for 20 h at room temperature. After collected by centrifugation and washed with water and ethanol, the precipitates were dried at 60 ℃ overnight.

Synthesis of NiFe PBA Nanocubes

The uniform NiFe PBA cubes with a size of 200 nm were synthesized by a simple precipitation method. In a typical procedure, 0.6 mmol of nickel nitrate and 0.9 mmol of sodium citrate were dissolved in 20 mL of deionized (DI) water to form solution A. At the same time, 0.4 mmol of potassium ferricyanide (III) was dissolved in 20 mL of DI water to form solution B. Then, solutions A and B were mixed under magnetic stirring for 3 min. The obtained mixed solution was aged for 20 h at room temperature. After collected by centrifugation and washed with water and ethanol, the precipitates were dried at 60 ℃ overnight.

Synthesis of CoCo PBA nanocubes

The uniform CoCo PBA cubes with a size of 200 nm were synthesized by a simple precipitation method. In a typical procedure, 0.6 mmol of cobalt acetate and 0.9 mmol of sodium citrate were dissolved in 20 mL of deionized (DI) water to form solution A. At the same time, 0.4 mmol of potassium hexacyanocobaltate (III) was dissolved in 20 mL of DI water to form solution B. Then, solutions A and B were mixed under magnetic stirring for 3 min. The obtained mixed solution was aged for 20 h at room temperature. After collected by centrifugation and washed with water and ethanol, the precipitates were dried at 60 ℃ overnight.

Synthesis of NiCoFe Phosphide Polyhedrons

To convert the as-prepared NiCoFe PBA polyhedrons into Ni-Co-Fe phosphide, $NaH_2PO_4 \cdot 2H_2O$ was used as the phosphorus source. The obtained NiCoFe PBA and $NaH_2PO_4 \cdot 2H_2O$ were placed at two separate positions in a quartz boat with $NaH_2PO_4 \cdot 2H_2O$ at the upstream side. The mass ratio of NiCoFe PBAs to $NaH_2PO_4 \cdot 2H_2O$ was 1:10 Subsequently, the samples were heated to 320 °C at a heating rate of 2 °C min^{-1} and kept at 320 °C for 2 h in argon flow. The phosphide polyhedrons were obtained after cooling to ambient temperature. For comparison, NiCo phosphides, NiFe phosphides and Co phosphides (denoted as NiCo-P, NiFe–P and Co-P) were also prepared using the NiCo PBA, NiFe PBA and CoCo PBA through the same phosphating process.

MATERIALS CHARACTERIZATION

Morphologies of the products were tested by using a JEM-2100 TEM. EDS spectroscopy was obtained with the TEM equipped with EDXA. Element distribution on the nanoparticles was gotten by using a Tecnai-G2-F30 S-TWIN, which was equipped with a high-angle-annular-dark-field (HAADF) detector. Element in the near-surface layers was demonstrated with X-ray photoelectron spectroscopy (XPS), which was performed with an ESCALAB 250Xi system. An X' Pert PROM MPD (Panalytical) system with a Cu Ka X-ray source (λ = 1.5406) was used to achieve the powder X-ray diffraction (PXRD) spectrum.

Electrochemical Characterization RDE Tests

The HER and OER activity were evaluated in a three-electrode configuration using a rotating disk electrode (RDE) on an Autolab potentiostat/galvanostat (PGSTAT-302N) workstation at room temperature. A glassy carbon disk electrode (GCE) with a diameter of 5 mm was used as the working electrode. The catalyst was prepared by dispersing 4 mg of catalysts in the mixed solution of deionized water (0.8 mL), isopropanol (0.2 mL) and Nafion solution (10 μL, Sigma-Aldrich, 5 wt. %) followed by ultrasonication for 30 min. 15 μL of the catalyst suspension was pipetted onto the GCE surface using a micropipette and then dried at ambient temperature. The catalyst loading amount on the GCE is 0.306 mg cm^{-2}. A graphite rod and a pure platinum foil with an area of 1.0 cm^2 were used as counter electrodes for HER and OER respectively. Hg/HgO electrode was used as the reference electrode. All the potentials in this paper are given with respect to the reversible hydrogen electrode (RHE). The potential was converted to RHE scale by using the equation

$$E_{RHE} = E_{Hg/HgO} + 0.098 + 0.0591 \times pH \qquad (1)$$

where the E_{RHE} is the potential referred to RHE, $E_{Hg/HgO}$ are the measured potential. Linear sweep voltammetry (LSV) was recorded in 1 M KOH (pH = 14) at scan rates of 5 mV s^{-1} for HER and 10 mV s^{-1} for OER to obtain the polarization curves.

Practical Carbon Paper Electrode Tests

The catalysts were loaded onto carbon paper and tested using the same three-electrode configuration described above, using the carbon paper electrode (CPE) as the working electrode. A piece of carbon paper was cut into a 1 cm × 2 cm size. The catalyst ink was prepared by mixing 3 mg catalyst and 1 mg carbon black (Cabot, Vulcan XC-72) in a 1.0 mL pretreated solution (a mixture of 0.8 mL deionized water, 0.2 mL isopropanol and 10 μL Nafion solution) followed by ultrasonication for 10 min to obtain a homogeneous ink mixture. Then, the mixture was drop-casted onto the dried CPE (active area: 1 cm^2) achieving the loading of 3 mg cm^{-2} catalyst. Linear sweep voltammetry (LSV) was recorded in 1 M KOH (pH = 14) at scan rates of 5 mV s^{-1} for HER and 10 mV s^{-1} for OER to obtain the polarization curves.

Electrochemical Stability Tests

The stability of the catalyst was tested through two methods. One is to perform constant overpotentials on the working electrode and the responding current densities were recorded. The other one is to successively perform linear sweep voltammetry (LSV) on the working electrodes. The polarization curves were then recorded to detect the degradation of the catalyst.

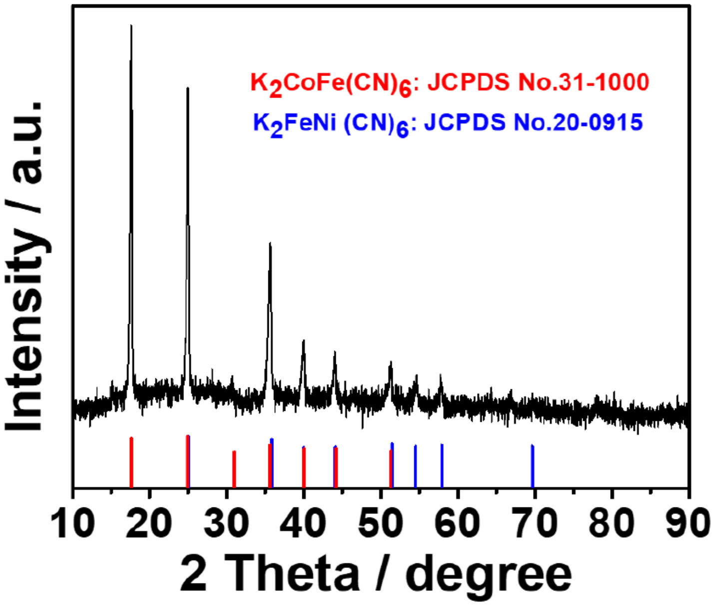


Figure S1: Powder X-ray diffraction (XRD) profiles of as-prepared NiCoFe PBA.

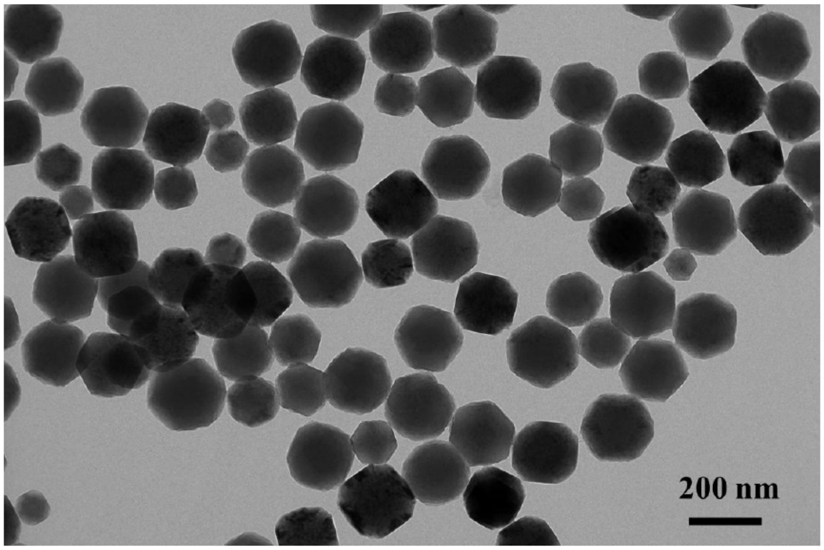
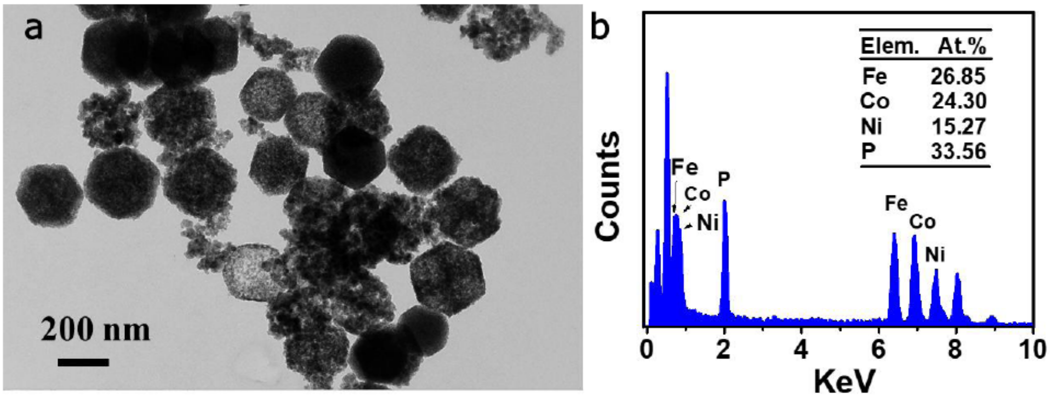


Figure S2: TEM image of the NiCoFe PBA nanostructure.



Elem.	At.%
Fe	26.85
Co	24.30
Ni	15.27
P	33.56

Figure S3: (**a**) TEM image and (**b**) TEM-EDS spectra of NiCoFe-P.

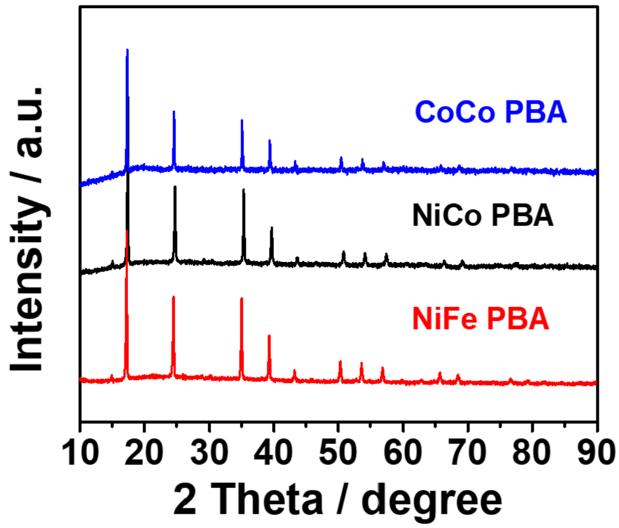


Figure S4: Powder X-ray diffraction (XRD) profiles of as-prepared CoCo PBA, NiCo PBA and NiFe PBA.

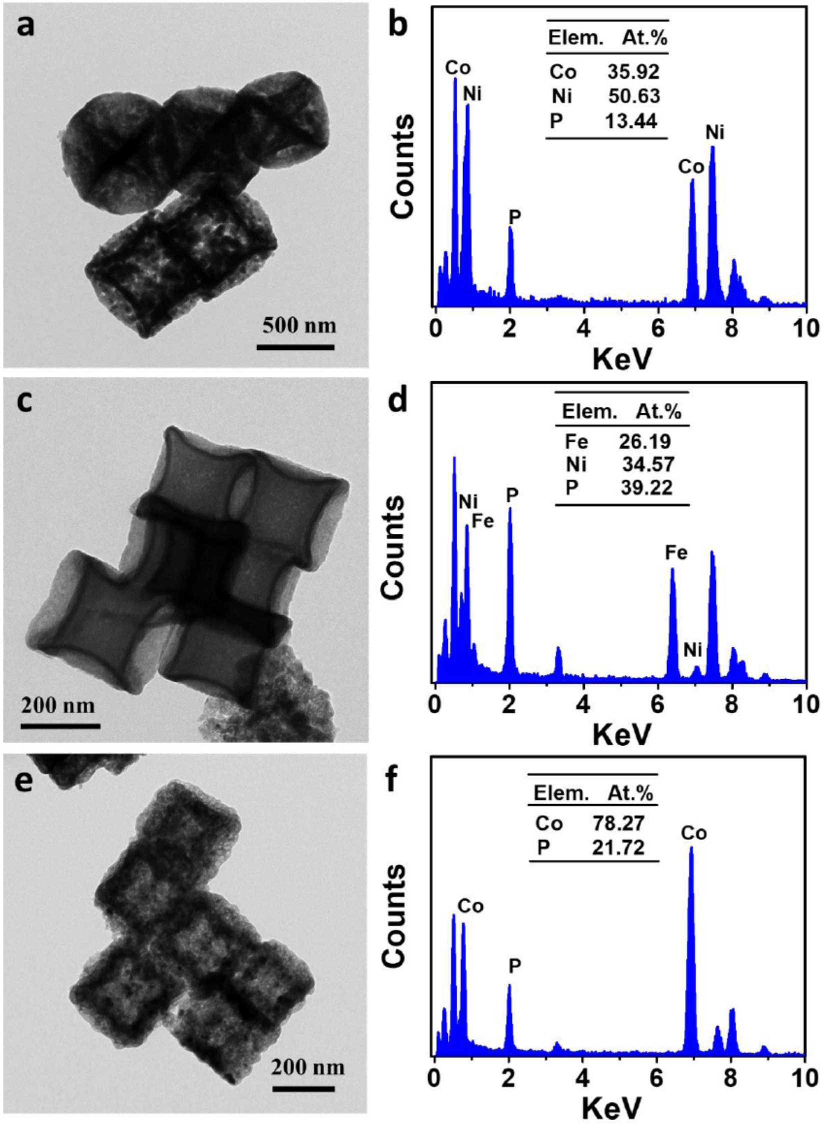


Figure S5: (**a**)(**c**)(**e**) TEM images and (**b**)(**d**)(**f**) TEM-EDS spectra of the NiCo-P, NiFe-P and Co-P.

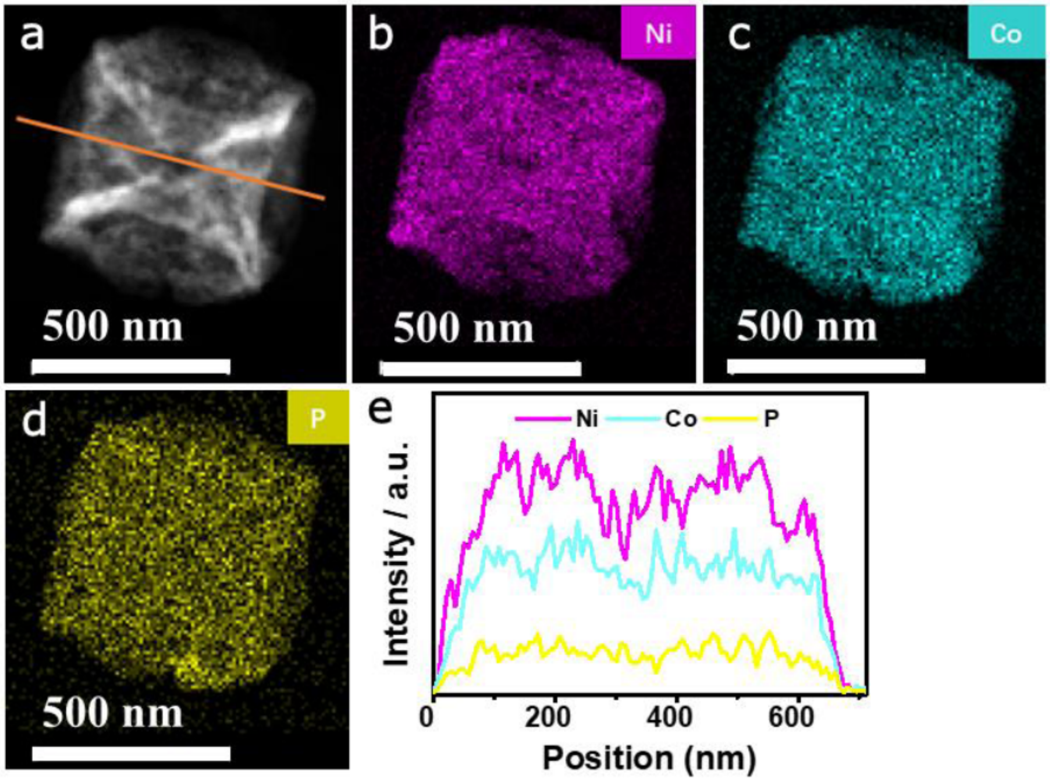


Figure S6: (**a**) Scanning TEM (STEM) image of NiCo-P and the corresponding elemental mapping of (**b**) Nickel, (**c**) Cobalt, and (**d**) Phosphorus. (**e**) Line-scanning profile of the nanostructure of NiCo-P.

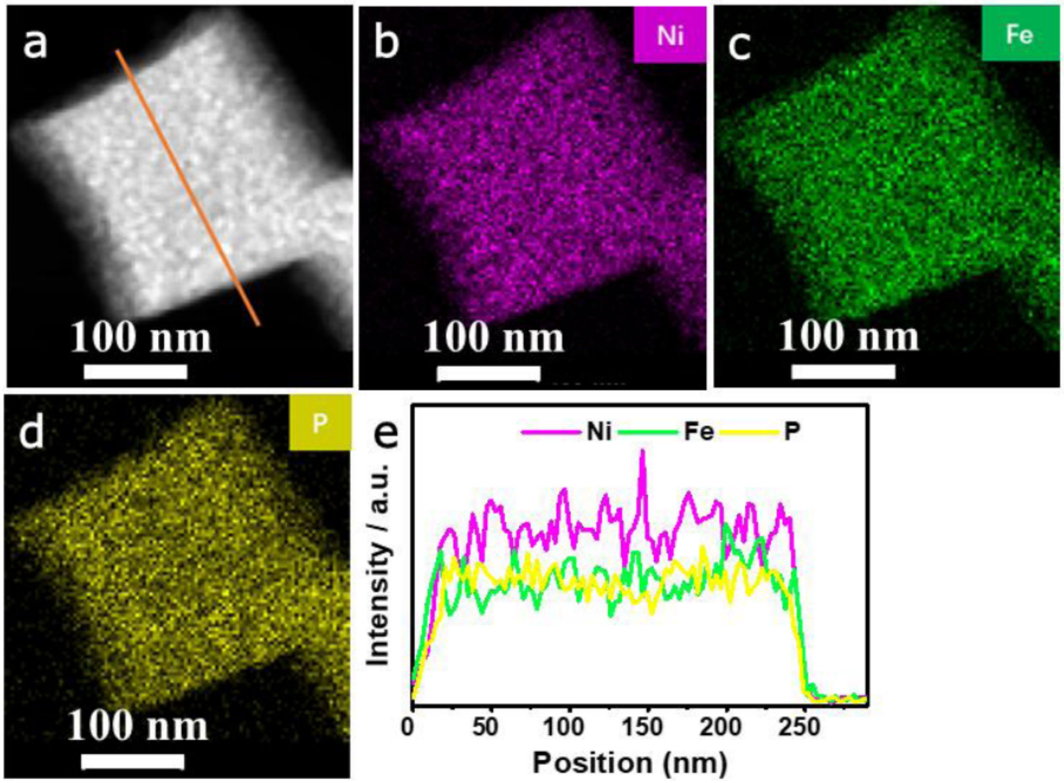


Figure S7: (**a**) Scanning TEM (STEM) image of NiFe-P and the corresponding elemental mapping of (**b**) Nickel, (**c**) Iron, and (**d**) Phosphorus. (**e**) Line-scanning profile of nanostructure of NiFe-P.

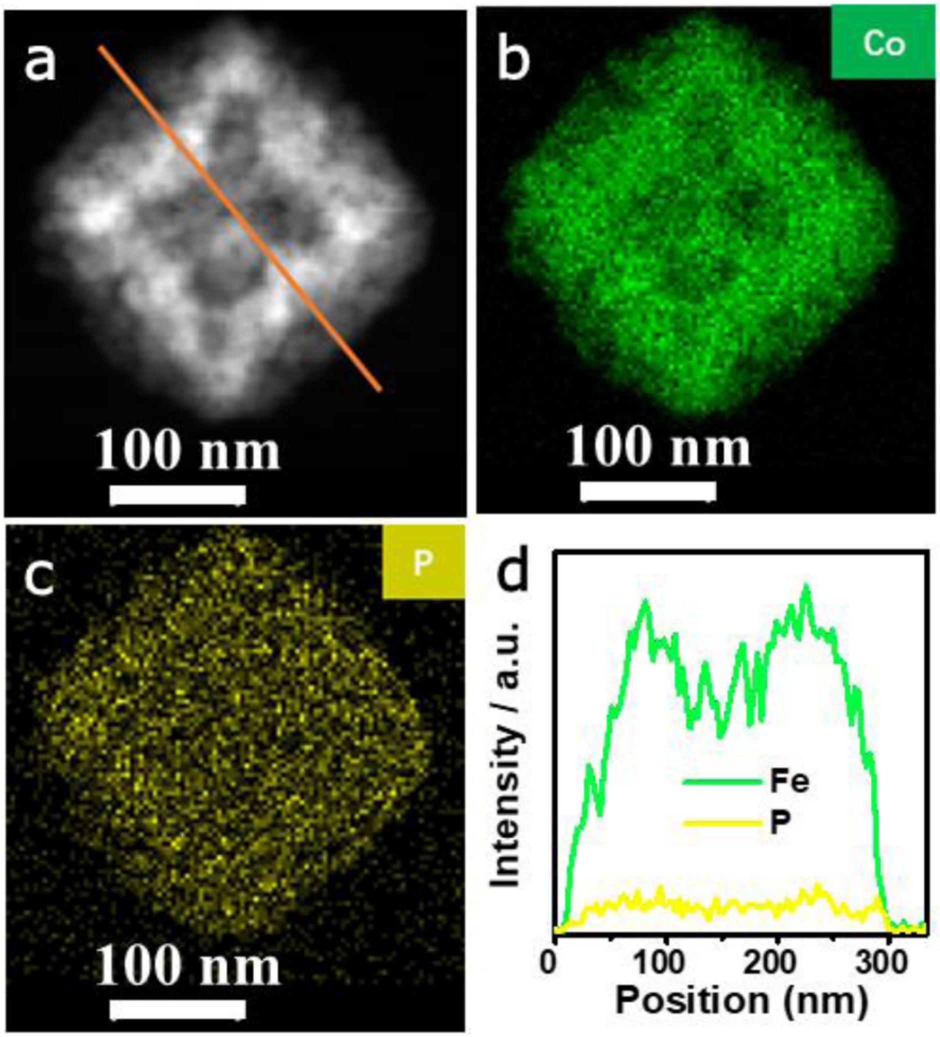


Figure S8: (a) Scanning TEM (STEM) image of CoP and the corresponding elemental mapping of (b) Cobalt and (c) Phosphorus. (d) Line-scanning profile of nanostructure of CoP.

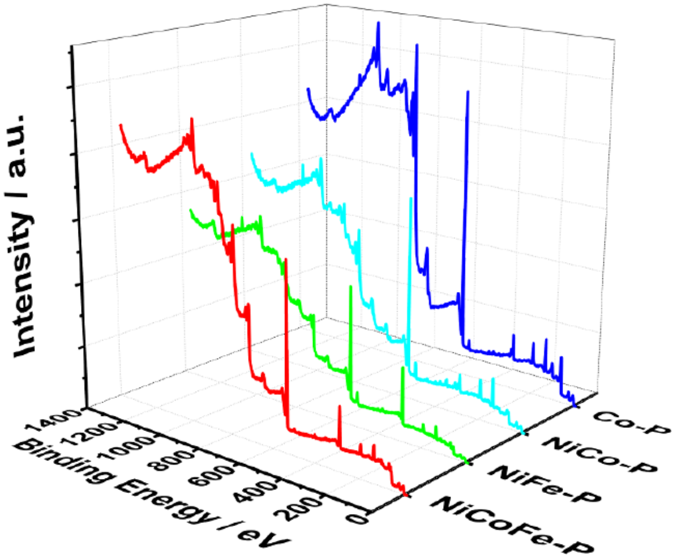


Figure S9: XPS survey spectra of NiCoFe-P, NiCo-P, NiFe-P and Co-P.

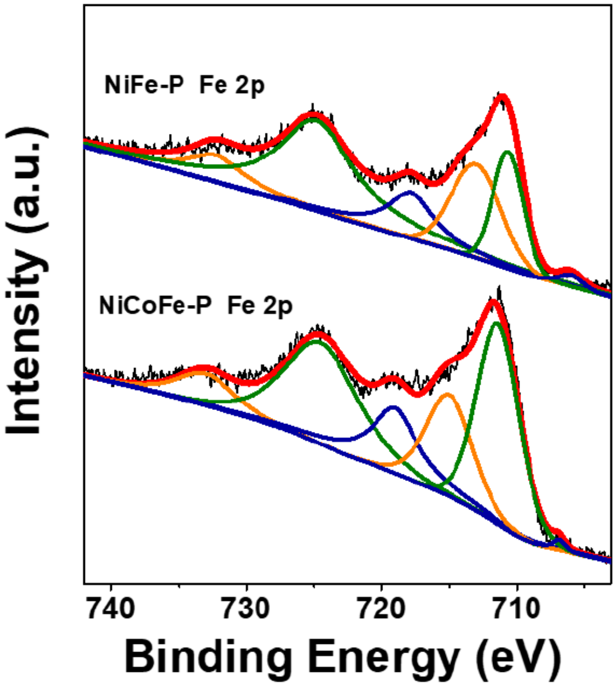


Figure S10: High-resolution XPS spectra of Fe 2p of NiFe-P and NiCoFe–P.

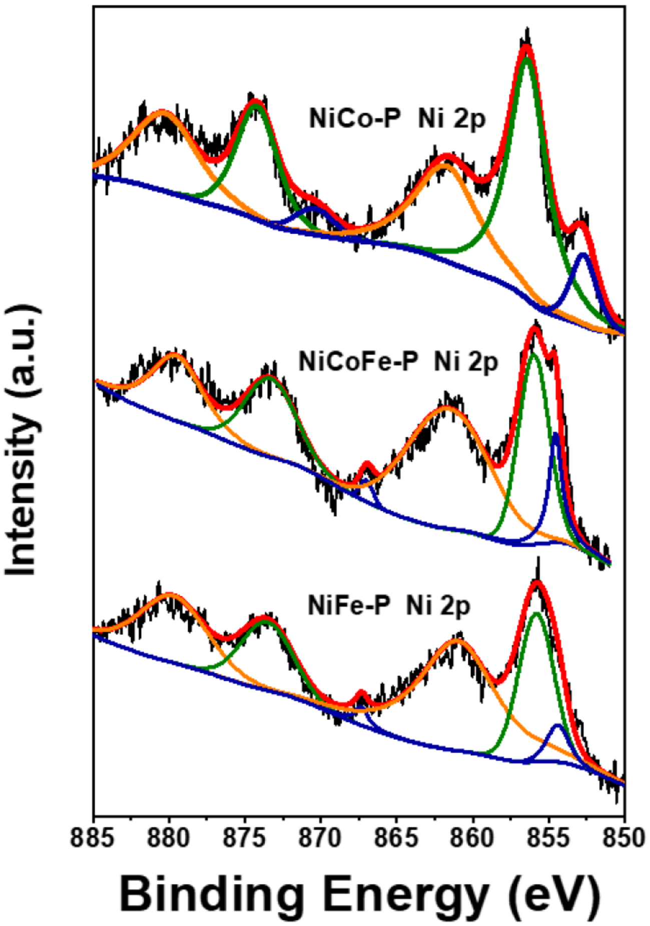


Figure S11: High-resolution XPS spectra of Ni 2p of NiCo-P, NiCoFe–P and NiFe-P.

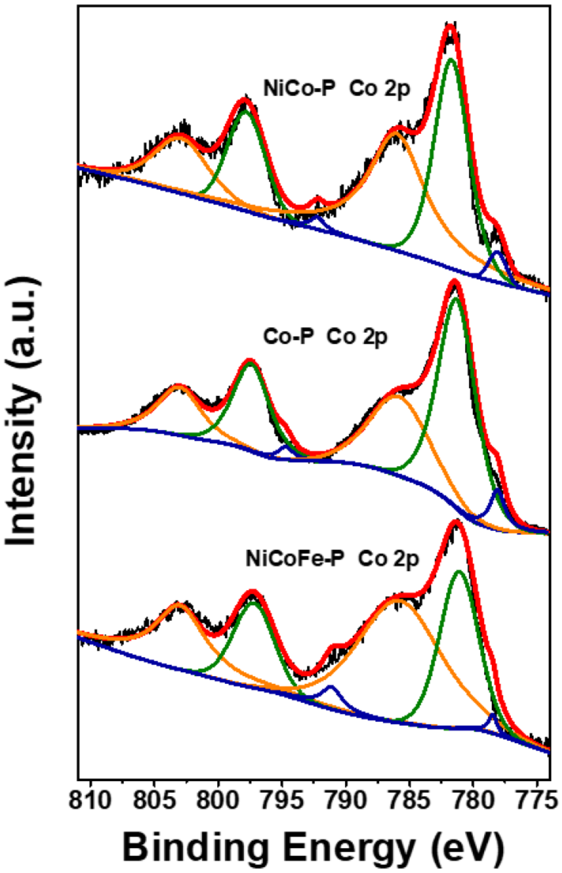


Figure S12: High-resolution XPS spectra of Co 2p of NiCo-P, Co-P and NiCoFe–P.

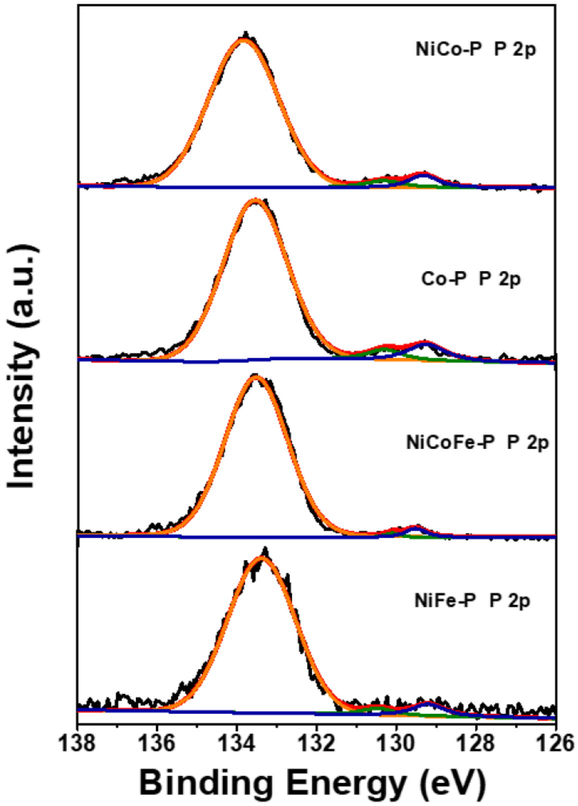


Figure S13: High-resolution XPS spectra of P 2p of NiCo-P, Co-P, NiCoFe–P and NiFe-P.

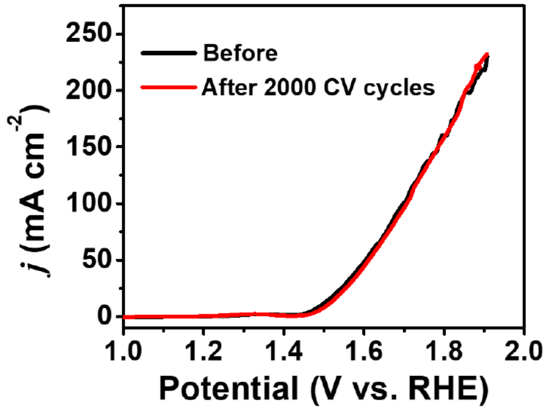


Figure S14: LSV curves of NiCoFe-P obtained before and after a durability test.
Durability test: 2000 negative LSV scans between 1.2 and 1.7 V (vs RHE) at a scan rate of 100 mV s^{-1} in 1 M KOH.

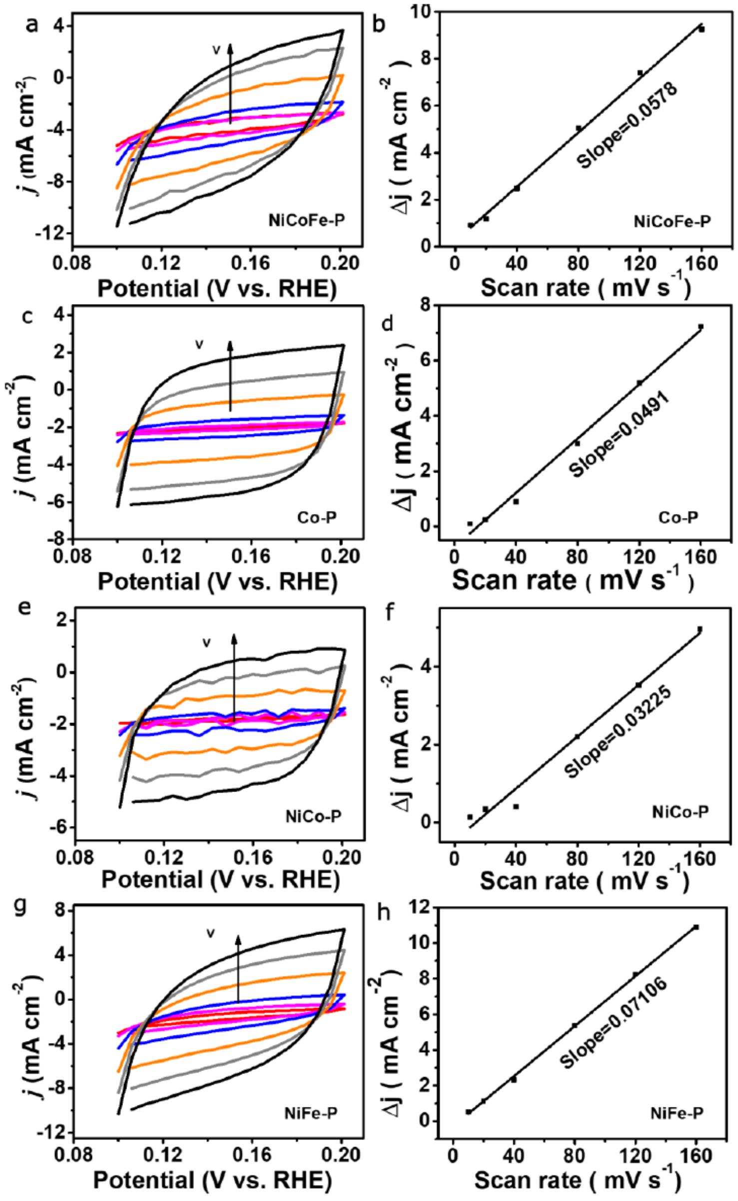


Figure S15: (a, c, e and g) electrochemical active surface area analysis by the CV scans in a non-Faradaic potential range of as-prepared electrodes in 1 M KOH for HER at scan rate of 10 mV s^{-1}, 20 mV s^{-1}, 40 mV s^{-1}, 80 mV s^{-1}, 120 mV s^{-1} and 160 mV s^{-1}. (b, d, f and h) Capacitive current as a function of scan rate.

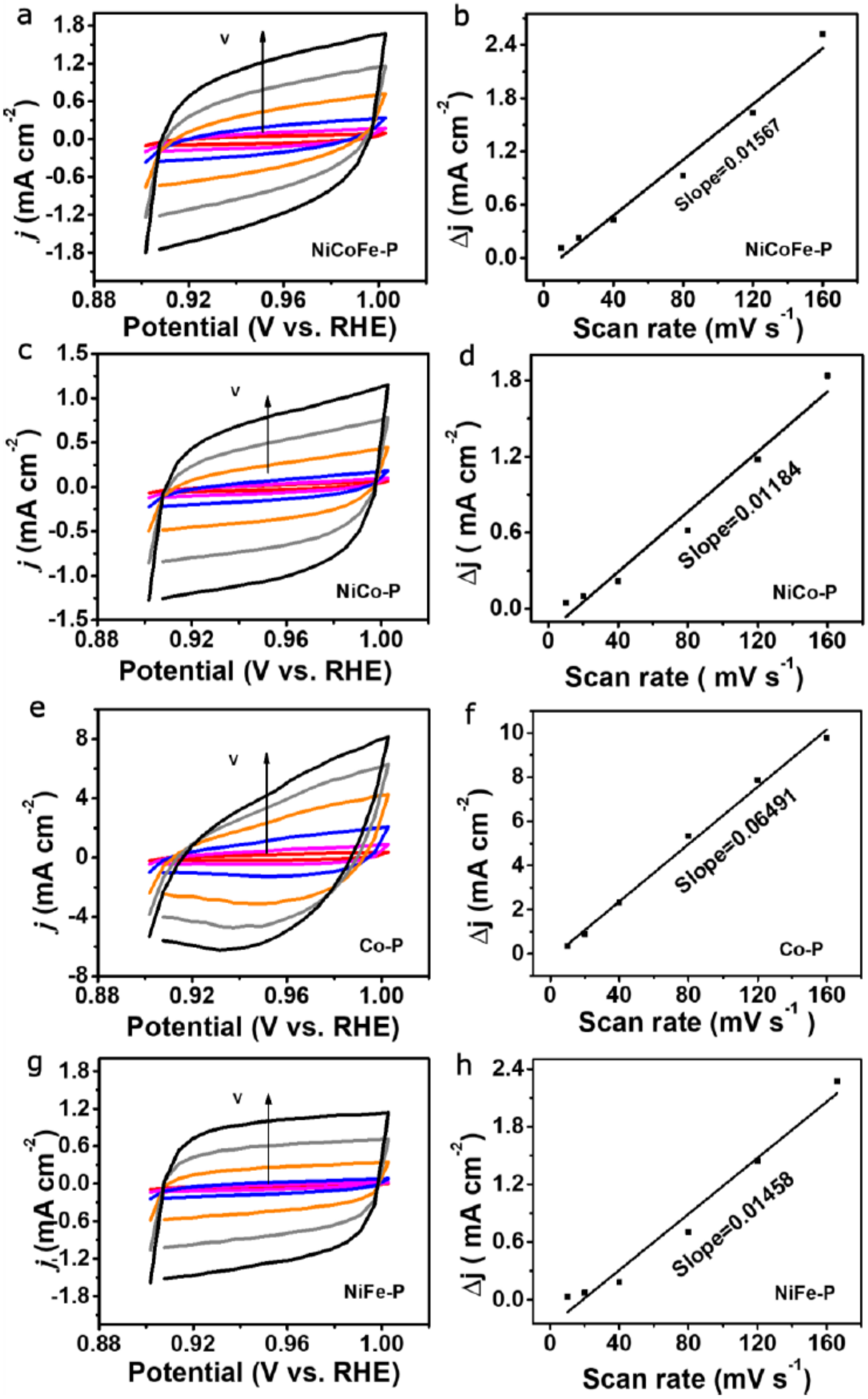


Figure S16: (a, c, e and g) electrochemical active surface area analysis by the CV scans in a non-Faradaic potential range of as-prepared electrodes in 1 M KOH for OER at scan rate of 10 mV s^{-1}, 20 mV s^{-1}, 40 mV s^{-1}, 80 mV s^{-1}, 120 mV s^{-1} and 160 mV s^{-1}. (b, d, f and h) Capacitive current as a function of scan rate.

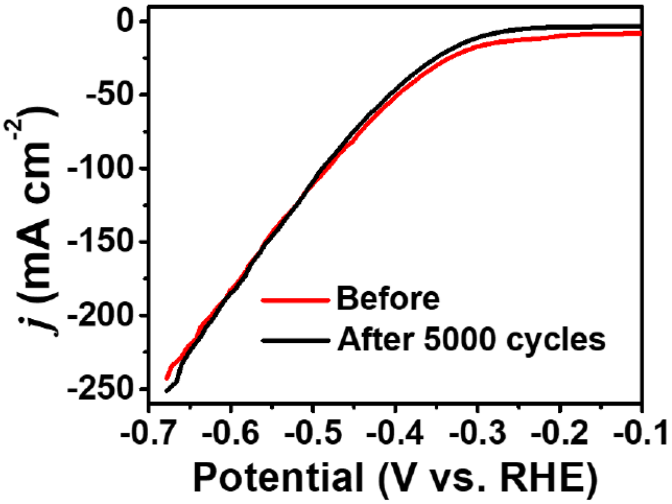


Figure S17: LSV curves of NiCoFe-P/CP obtained before and after a durability test.
Durability test: 5000 negative LSV scans 0.1 and -0.8 V (vs RHE) at a scan rate of 100 mV s^{-1} in 1 M KOH.

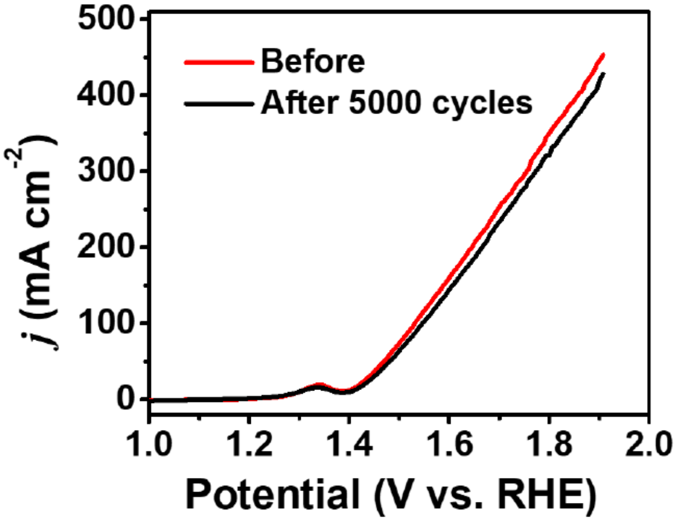


Figure S18: LSV curves of NiCoFe-P/CP obtained before and after a durability test.
Durability test: 5000 positive LSV scans between 1.2 and 1.7 V (vs RHE) at a scan rate of 100 mV s^{-1} in 1 M KOH.