Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information for

N-doped Carbon Shelled Bimetallic Phosphates for Efficient Electrochemical Overall Water Splitting

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Experimental Section

Chemicals. Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, AR), iron (III) nitrate monahydrate ($Fe(NO_3)_3{\cdot}9H_2O$, AR), aniline ($C_6H_5NH_2$, AR), and ethanol (C_2H_5OH, AR) were all purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Phytic acid solution ($C_6H_{18}O_{24}P_6$, 70% in H_2O) was purchased from Aladdin. Carbon paper (CP) was purchased from Hesen. The water (H_2O) (18 MΩ/cm) used in all experiments was prepared by passing through an ultra-pure purification system (Aqua Solutions).

Preparation of pre-Fe_xCo_y (pre-Fe, pre-$Fe_{12}Co_1$, pre-Fe_4Co_1 and pre-Fe_3Co_1). In a typical preparation, 400 μL aniline and 0.69 g phytic acid solution were mixed with 8 mL ethanol under ultrasounded for 10 mins, named soultion I. Then 2.69 g $Fe(NO_3)_3{\cdot}9H_2O$ with different amounts of $Co(NO_3)_2{\cdot}6H_2O$ (0 g, 0.97 g, 2.91 g and 3.88 g) were dissolved in 42 mL H_2O, named soultion II. Finally, The soultion I was slowly droped into the soultion II under mechanically stiring for 20 h at room temperature. The obtained suspension products were named as pre-Fe, pre-$Fe_{12}Co_1$, pre-Fe_4Co_1 and pre-Fe_3Co_1, respectively. Finally, the catalysts were washed with water and ethanol for three times and dried in oven at 80 °C for 6 h.

Preparation of $(Fe_xCo_y)P_2O_7$@N-C. The obtained above pre-Fe_xCo_y catalysts were annealed in the tube furance at 700 °C for 1 h with the heating rate of 10 °C under the N_2 protection. After it was cooled down to the room temperature, the obtained catalysts were prepared for the further measurement.

Preparation of $(Fe_4Co_1)P_2O_7$@N-C-Air. For the preparation of $(Fe_4Co_1)P_2O_7$@N-C-Air, the $(Fe_4Co_1)P_2O_7$@N-C was annealed at 600 °C for 1 h with the heating rate of 10 °C under the air atmosphere.

Characterizations. High-resolution TEM (HRTEM), high angle annular dark-field scanning TEM (HAADF-STEM) and corresponding EDX mappings were conducted on an FEI Tecnai F20 transmission electron microscope at an accelerating voltage of 200 kV. Energy dispersive X-ray spectroscopy (EDX) images were conducted on a HITACHI S-4700 cold field emission scanning electron microscope operated at an acceleration voltage of 15 kV. PXRD pattern was collected on X'Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu Kα X-ray source (λ = 1.540598 Å). X-ray photoelectron spectroscopy (XPS) spectra were conducted on a Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer. The Raman spectra were conducted on HORIBA HR800 instrument.

Electrochemical measurements. All the electrochemical measurements were conducted on the electrochemical workstation (CHI660E). In a typical preparation, the electrochemical measurements of HER and OER were conducted in a three-electrode cell with the glass carbon electrode(GC) as the working electrode, the saturated calomel electrode (SCE) as the reference electrode and the graphite rod as the counter electrode, respectively. 4.0 mg catalyst was dispered in 1 mL isopropanol containing 20 L Nafion solution (5 wt %). It was then ultrasounded for 1 h to form a homogeneous ink. The catalyst ink was droped onto the GC electrode with a diameter of 5 mm (the catalyst loading amount of 1mg cm^{-2}) and dried at room temperature. All liner sweep voltammetry (LSV) curves were obtained at the scan rate of 5 mV s^{-1} with 95% *iR* compensation at room temperature in 1 M electrolyte. The Tafel slopes were caculated from the corresponding LSV curves. All currents were normalized to the geometric area of the working electrode. The electrochemical impedance spectra (EIS) experiments were obtained by AC impedance spectroscopy. The chronopotentiometry was measured without *iR* drop compensation.

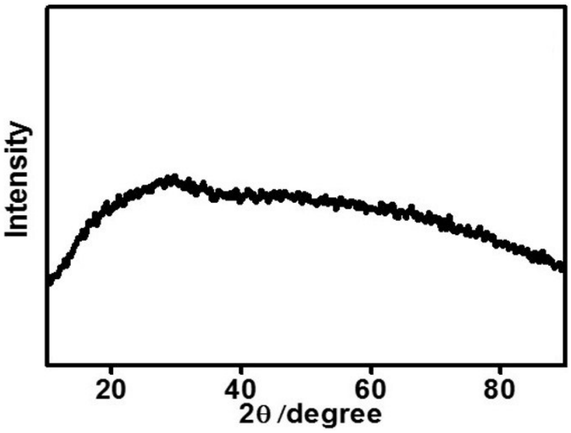


Figure S1. XRD pattern of pre-Fe_4Co_1.

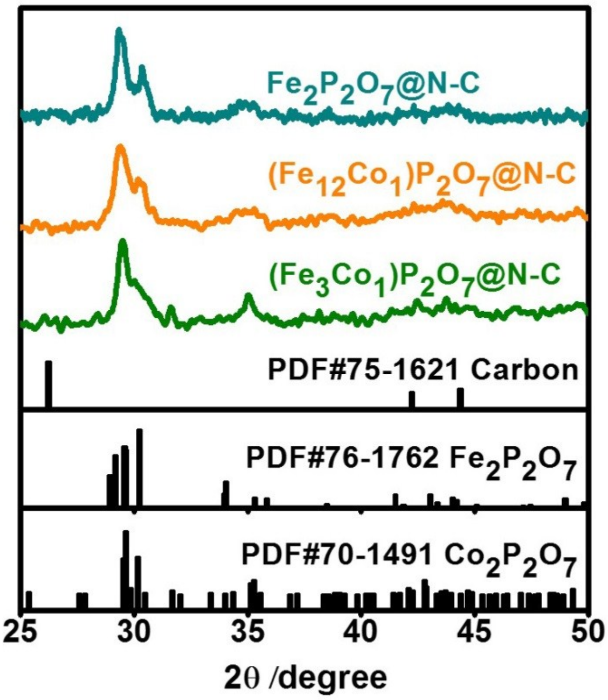


Figure S2. XRD patterns of $Fe_2P_2O_7$@N-C, $(Fe_{12}Co_1)P_2O_7$@N-C and $(Fe_3Co_1)P_2O_7$@N-C.

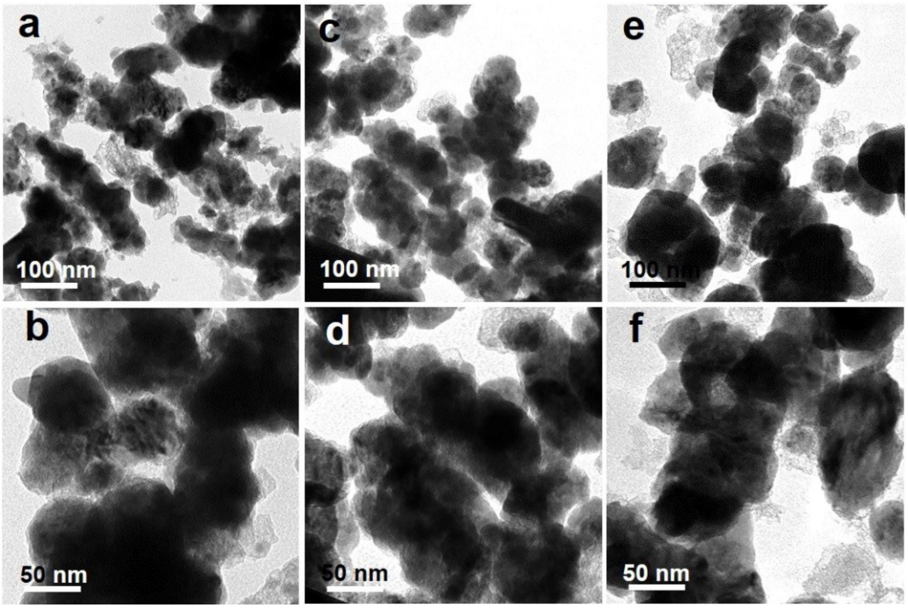
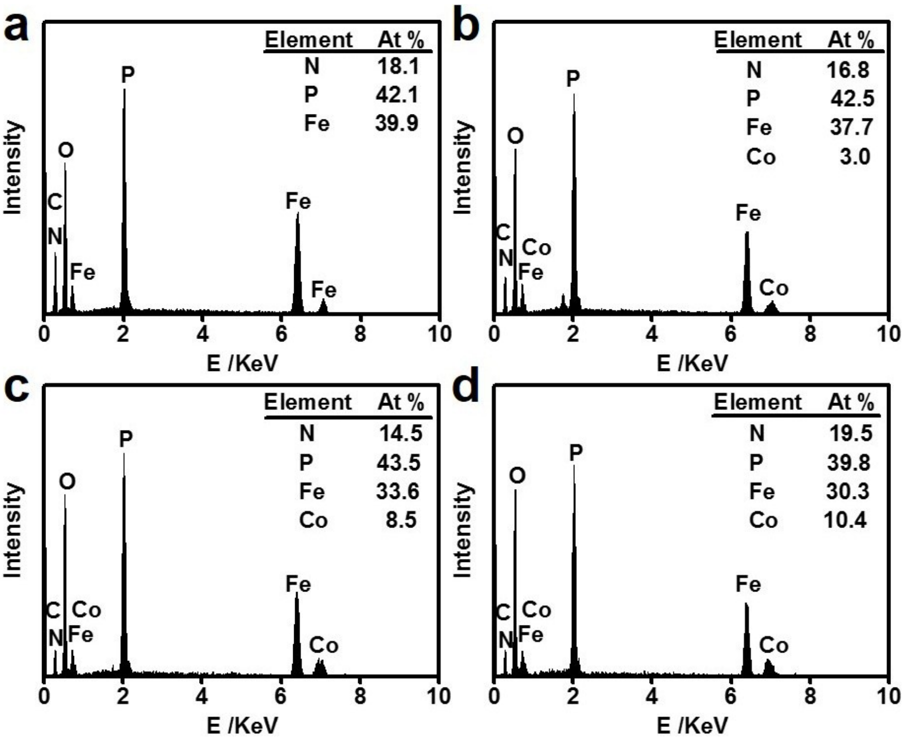


Figure S3. TEM images of (a, b) $Fe_2P_2O_7$@N-C, (c, d) $(Fe_{12}Co_1)P_2O_7$@N-C and (e, f) $(Fe_3Co_1)P_2O_7$@N-C.



a

Element	At %
N	18.1
P	42.1
Fe	39.9

b

Element	At %
N	16.8
P	42.5
Fe	37.7
Co	3.0

c

Element	At %
N	14.5
P	43.5
Fe	33.6
Co	8.5

d

Element	At %
N	19.5
P	39.8
Fe	30.3
Co	10.4

Figure S4. EDX patterns of (a) $Fe_2P_2O_7$@N-C, (b) $(Fe_{12}Co_1)P_2O_7$@N-C, (c) $(Fe_4Co_1)P_2O_7$@N-C and (d) $(Fe_3Co_1)P_2O_7$@N-C.

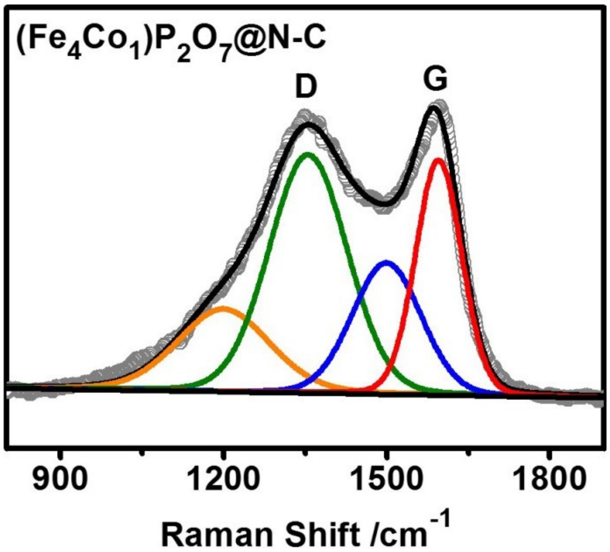


Figure S5. Raman spectrum of $(Fe_4Co_1)P_2O_7$@N-C.

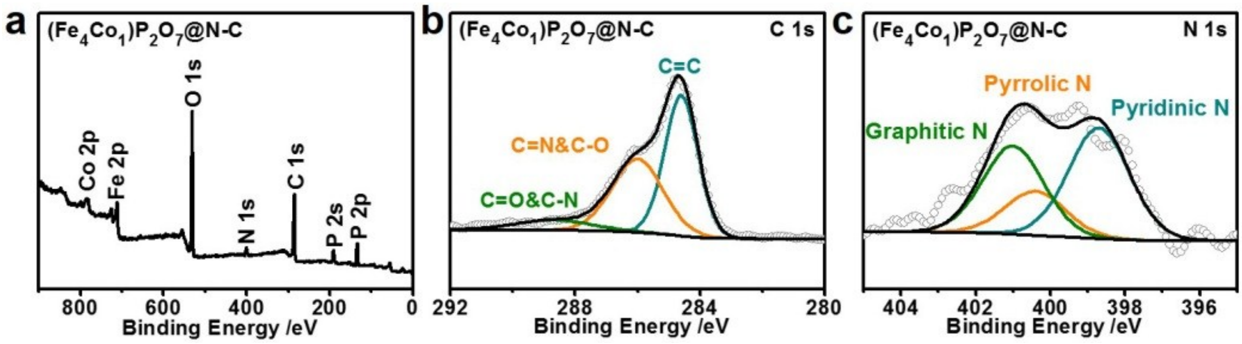


Figure S6. (a) The survey XPS spectrum and (b, c) the fine XPS spectra of C 1s and N 1s of $(Fe_4Co_1)P_2O_7$@N-C.

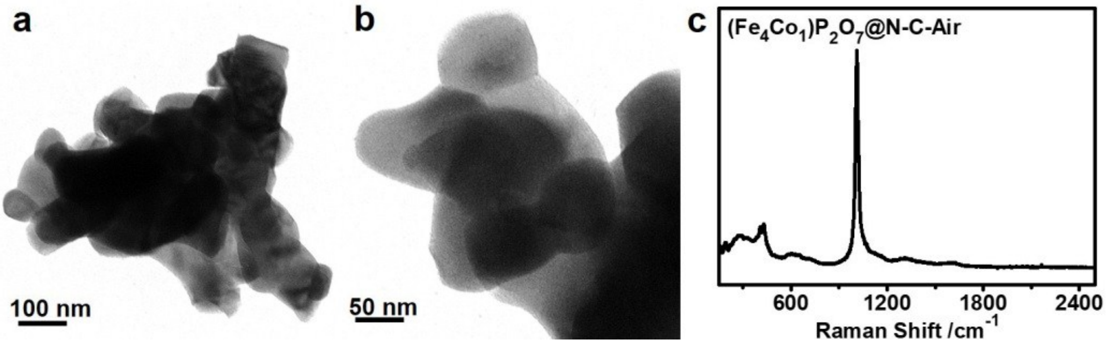


Figure S7. (a, b) TEM images and (c) Raman spectrum of $(Fe_4Co_1)P_2O_7$@N-C-Air.

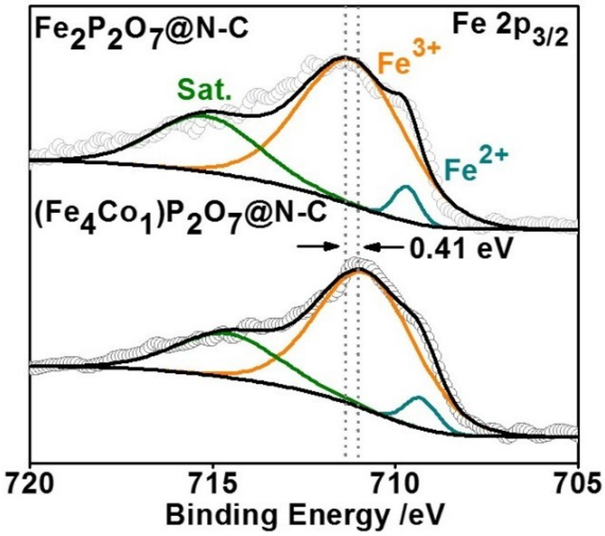


Figure S8. Fe 2p XPS spectra comparisions of $Fe_2P_2O_7$@N-C and $(Fe_4Co_1)P_2O_7$@N-C.

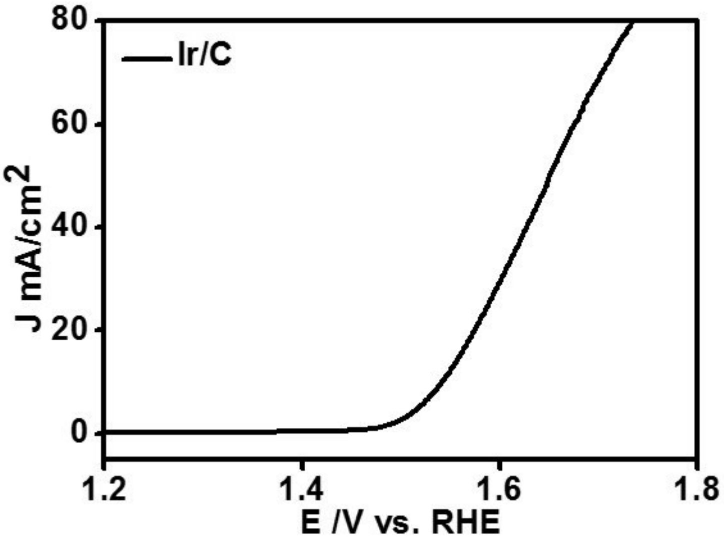


Figure S9. OER polarization curve of Ir/C in 1 M KOH.

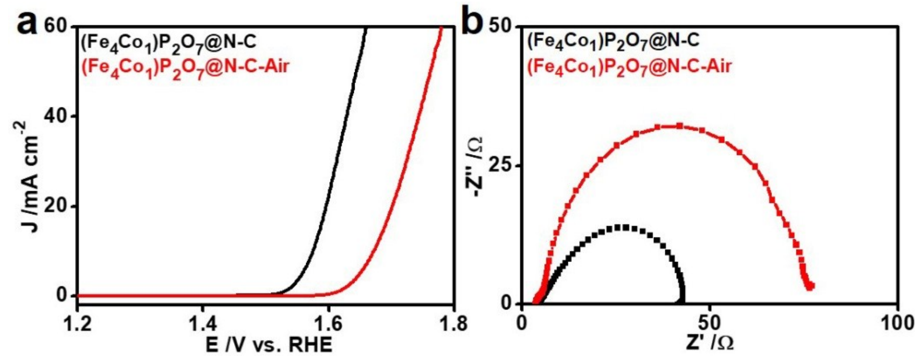


Figure S10. (a) OER polarization curves and (b) Nyquist plots recorded at the overpotential of 450 mV of $(Fe_4Co_1)P_2O_7$@N-C and $(Fe_4Co_1)P_2O_7$@N-C-Air in 1 M KOH.

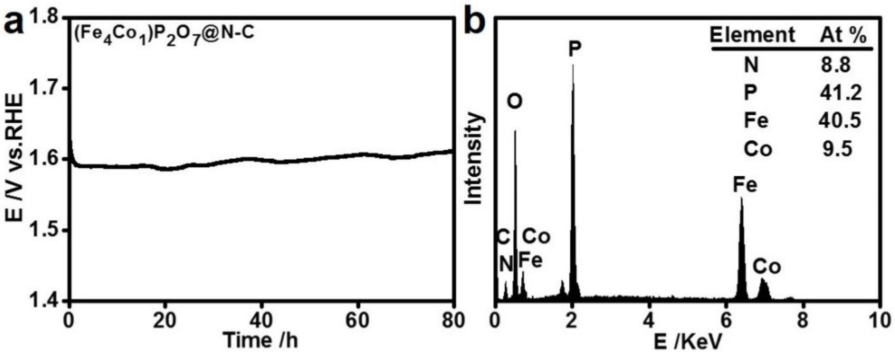


Figure S11. (a) Chronopotentiometry curve under the current density of 10 mA cm^{-2} and (b) EDX analysis after stability test of (Fe$_4$Co$_1$)P$_2$O$_7$@N-C.

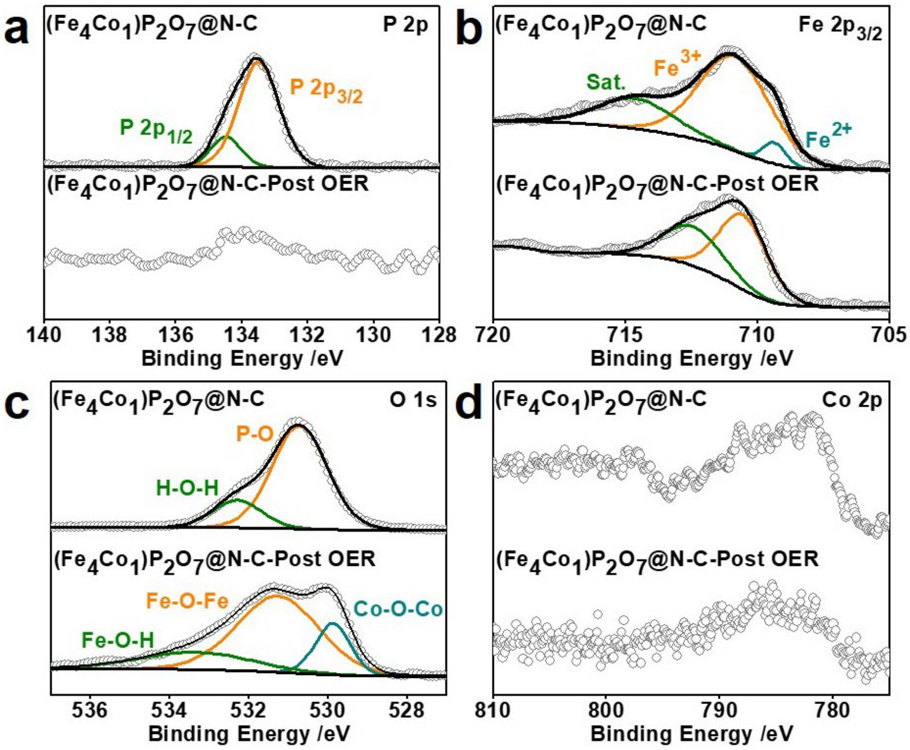


Figure S12. XPS spectra of (Fe$_4$Co$_1$)P$_2$O$_7$@N-C before and after OER stability test: (a) P 2p, (b) Fe 2p, (c) O 1s and (d) Co 2p.

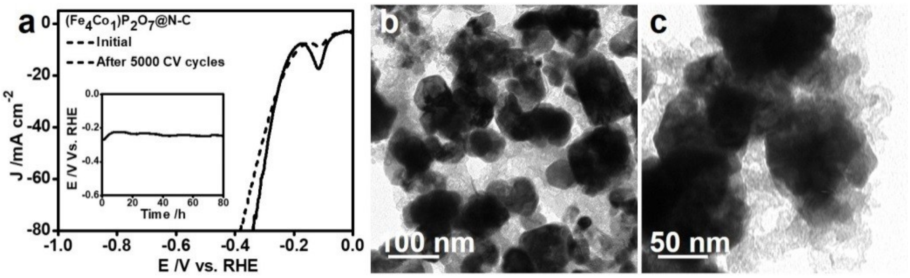


Figure S13. (a) The polarization curves before and after 5000 CV cycles and the chronopotentiometry curves measured at the current density of 10 mA cm^{-2} (inset) of $(Fe_4Co_1)P_2O_7$@N-C. (b, c) TEM images after the stability test.

Table S1. Summary of different OER catalysts.

Catalyst	**Overpotential /mV (J = 10 mA cm^{-2})**	**Electrolyte**	**Reference**
$(Fe_4Co_1)P_2O_7$@N-C	**341**	**1 M KOH**	**This work**
CoP hollow polyhedra	400	1 M KOH	1
Co_2P/NPCNT	370	1 M KOH	2
$Co_{0.5}Fe_{0.5}S$@N-MC	410	1 M KOH	3
Fe/FeC_3@N-graphitic layer	580	0.1 M KOH	4
Co@Co_3O_4/NC-2	402	0.1 M KOH	5
N/Co-doped PCP//NRGO	430	0.1 M NaOH	6
Co-P/NC	354	1 M KOH	7

Mn_xO_y/NC	450	0.1 M KOH	8

Table S2. Summary of different HER catalysts.

Catalyst	Overpotential /mV (J = 10 mA cm^{-2})	Electrolyte	Reference
$(Fe_4Co_1)P_2O_7$@N-C	**201**	**1 M KOH**	**This work**
Co-Fe-P-1.7	295	1 M KOH	9
CoP nanowire	335	1 M KOH	10
Ni_2P	220	1 M KOH	11
Co/CoP-5	253	1 M KOH	12
$Cu_{0.3}Co_{2.7}P$/NC	220	1 M KOH	13
Co-NG	270	1 M NaOH	14
FeP NAs/CC	218	1 M KOH	15
Ni_2S_3/NF	223	1 M KOH	16

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