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Supporting Information

Pulse Electrodeposited CoFeNiP as Highly Active and Stable Electrocatalyst for Alkaline Water Electrolysis

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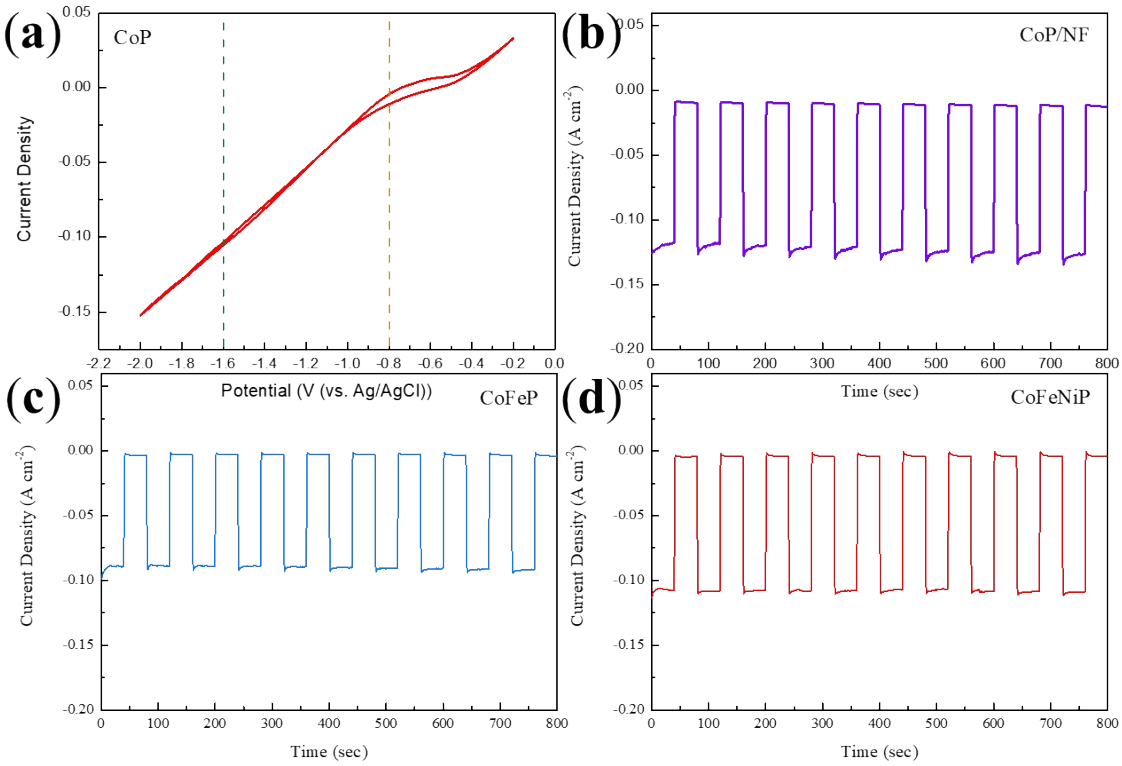

Figure S1. (a) The cyclic voltammetry curve at a range of -0.2 V ~ -2.0 V (vs. Ag/AgCl) on nickel foam at a plating solution of CoP. The pulsed electrodeposition curve of (b) CoP/NF, (c) CoFeP/NF and (d) CoFeNiP/NF.

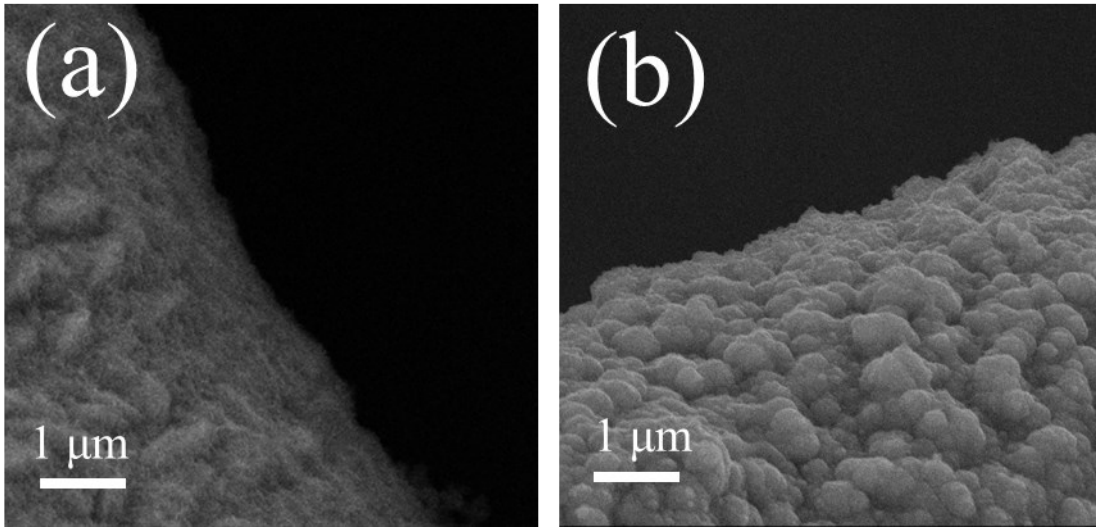

Figure S2. The SEM images of (a) CoP/NF and (b) CoFeP/NF catalyst.

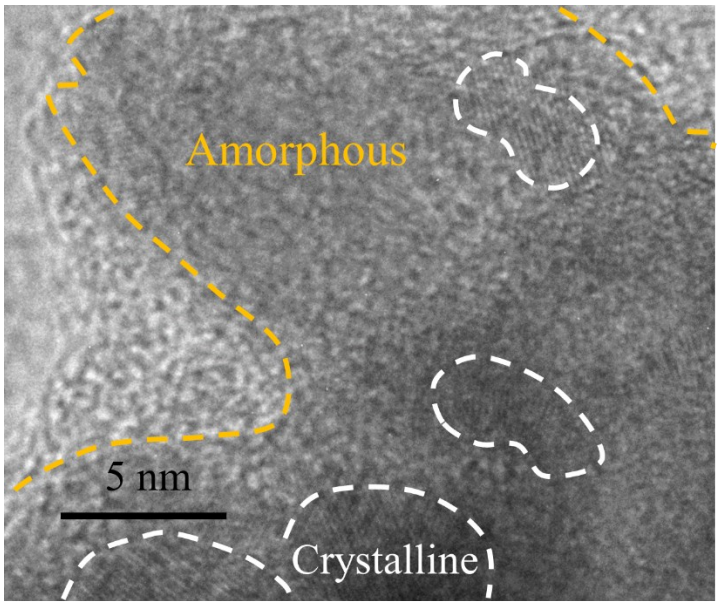

Figure S3. The HRTEM images of the CoFeNiP/NF

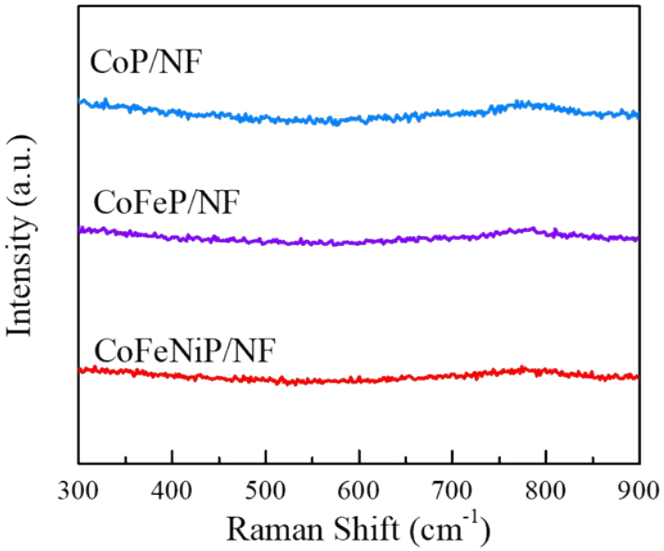

Figure S4. The Raman spectra for CoP/NF, CoFeP/NF and CoFeNiP/NF.

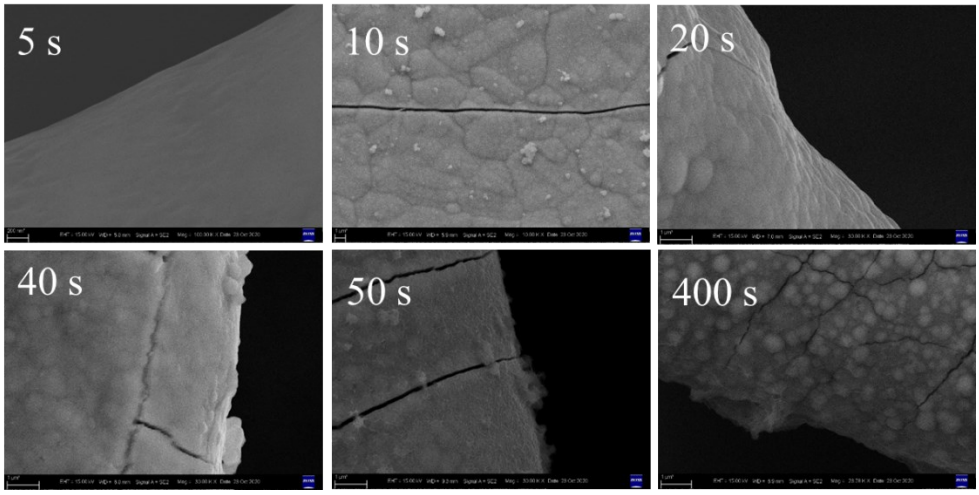

Figure S5. The SEM images for CoFeNiP prepared at different pulse frequencies (5, 10, 20, 40, 50, 400 s)

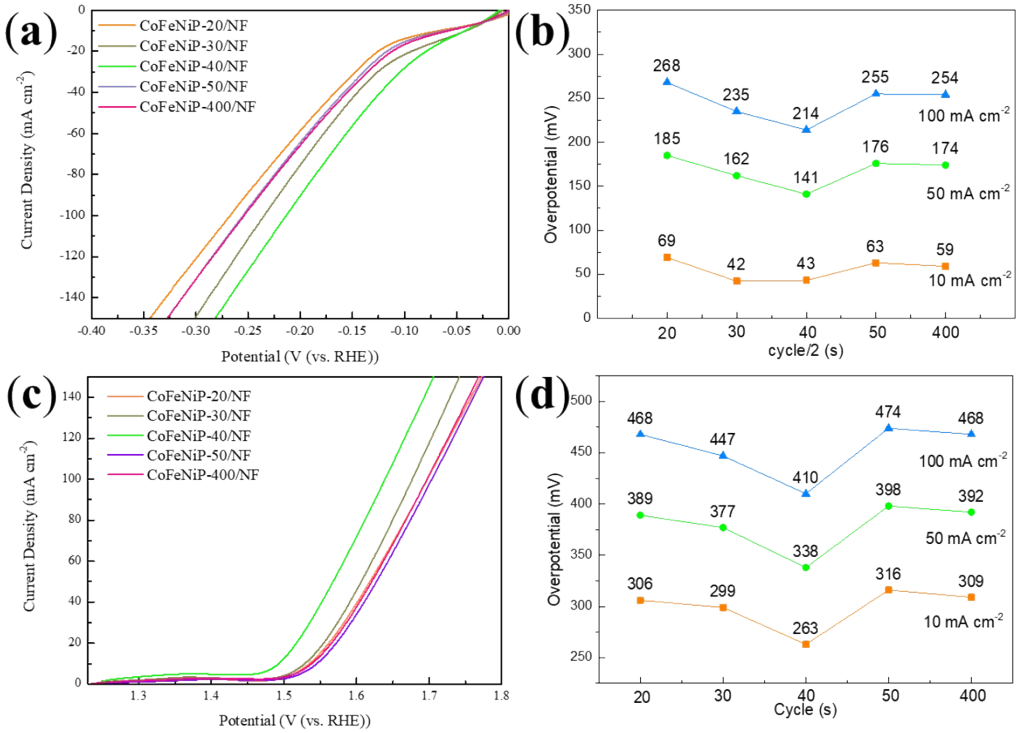

Figure S6. The effect of pulse frequency on the electrocatalyst performance. Polarization curves without iR correction for CoFeNiP-20/NF, CoFeNiP-30/NF, CoFeNiP-40/NF, CoFeNiP-50/NF and CoFeNiP-400/NF (set the electrodeposition time at one potential every cycle as 20, 30, 40,50 and 400 s) for (a) HER and (c) OER, and corresponding overpotential-cycle/2 plots (b) and (d).

□	Co	Fe	Ni
CoFeP/NF	75.4%	23.1%	
CoFeNiP-0.01/NF	70.5%	22.5%	1.4%
CoFeNiP-0.03/NF	64.4%	20.8%	5.6%
CoFeNiP-0.05/NF	61.5%	19.7%	17.1%
CoFeNiP-0.07/NF	59.1%	18.8%	20.3%

Table S1. The metal element content (wt. %) for CoFeP/NF and CoFeNiP/NF

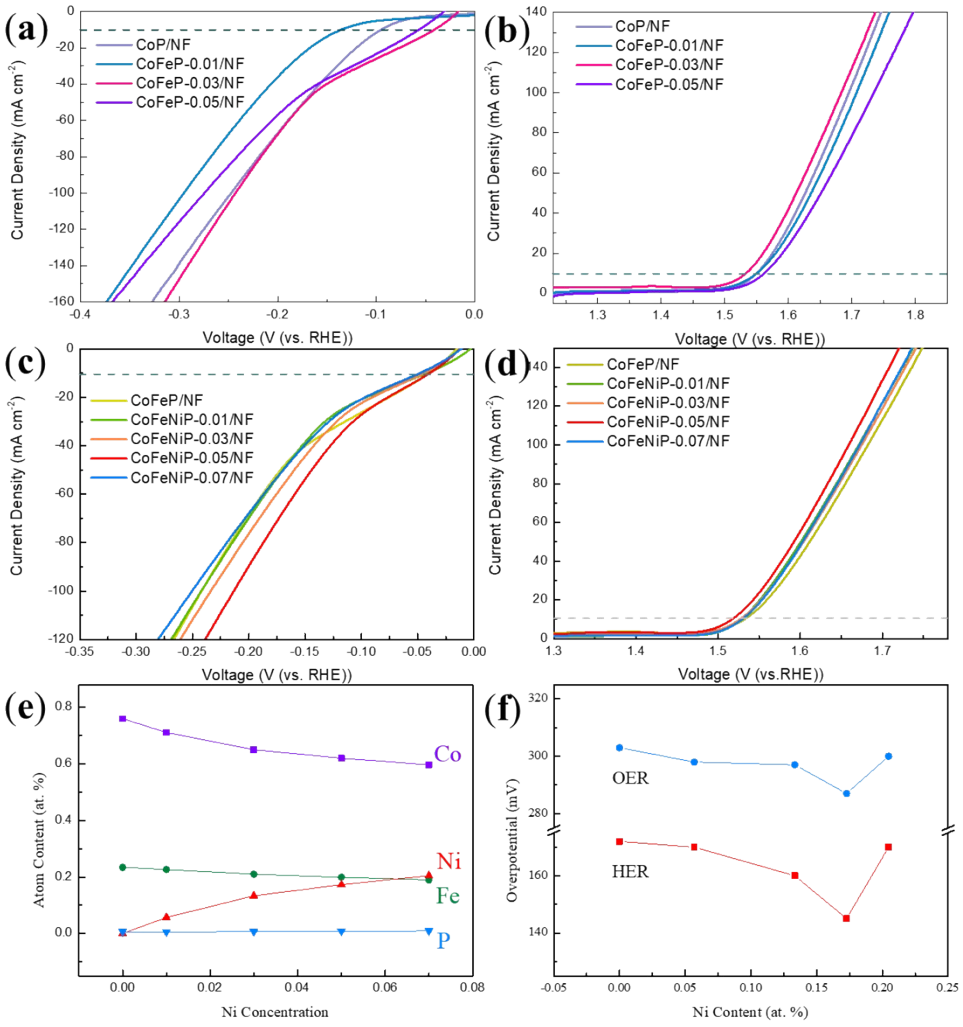

Figure S7. Polarization curves without iR correction of CoFeP-0.01/NF, CoFeP-0.02/NF,CoFeP-0.03/NF and CoFeP-0.05/NF for (a) HER and (b) OER. Polarization curves of CoFeNiP-0.01/NF, CoFeNiP-0.02/NF,CoFeNiP-0.03/NF and CoFeNiP-0.05/NF for (c) HER and (d) OER. All polarization were tested at a scan rate of 5 mV s^{-1} in 1 M KOH solution. (e) The real atom content of Co, Fe, Ni and P in the electroplated CoFeNiP-x/NF catalysts in the plating electrolyte containing 0 M, 0.01 M, 0.03 M, 0.05 M and 0.07 M Ni concentration, respectively. (f) The relationship between the Ni content in CoFeNiP-x/NF and the electro-catalytic activity for HER (overpotential at 50 mA cm^{-2}) and OER (overpotential at 10 mA cm^{-2}).

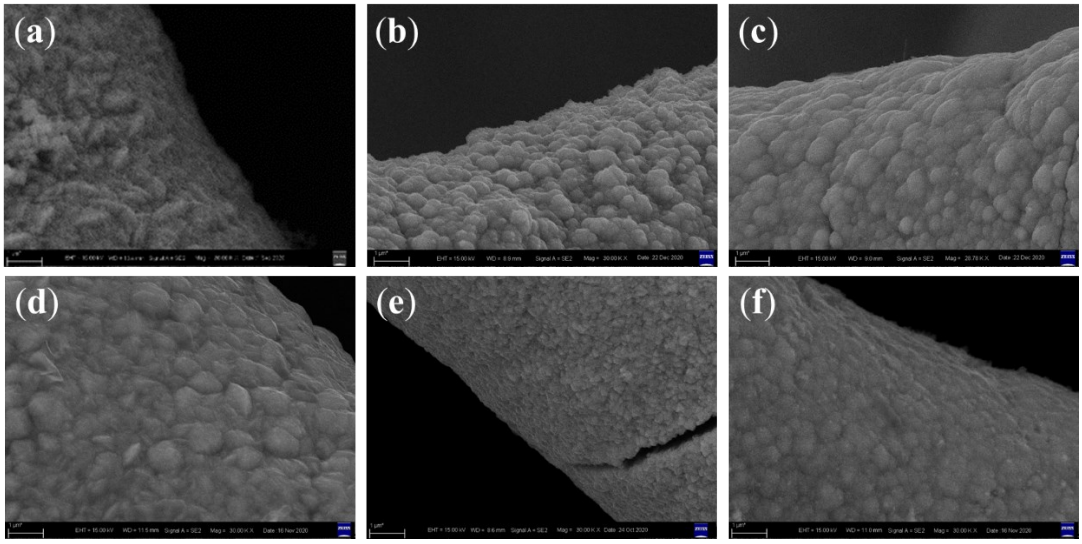

Figure S8. The SEM images for (a)(d) CoP/NF, (b)(e) CoFeP/NF and (c)(f) CoFeNiP/NF before and after HER.

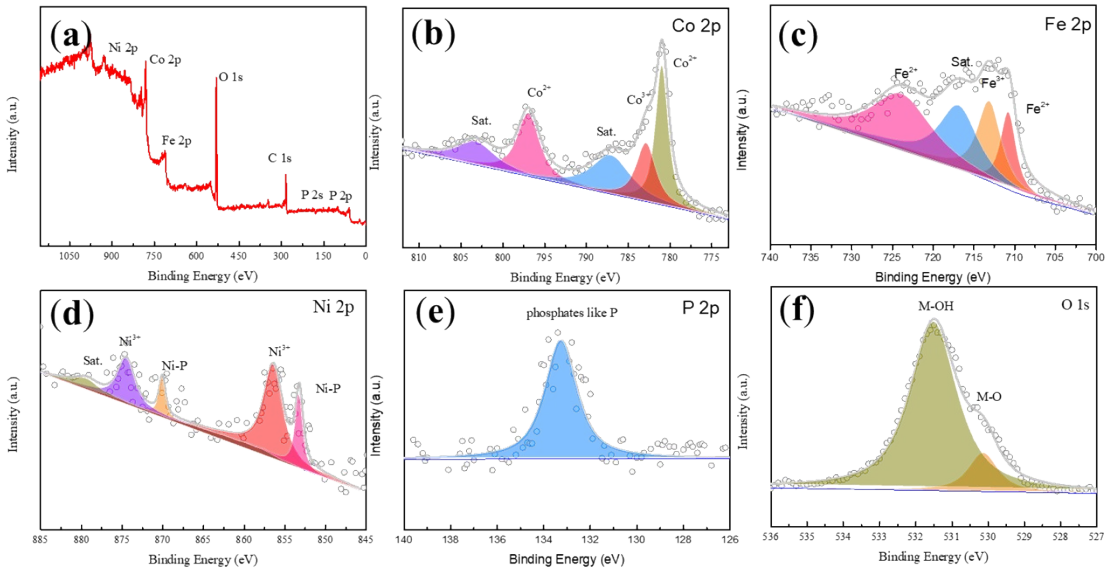

Figure S9. The XPS survey spectrum and high resolution spectra of (b) Co 2p, (c) Fe2p, (d) Ni 2p, (e) P 2p and O 1s for the CoFeNiP/NF after HER performance.

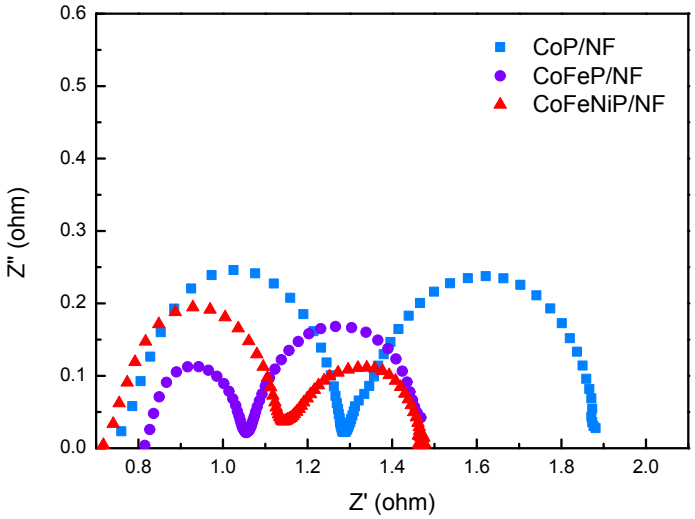

Figure S10. Nyquist plots of CoP/NF, CoFeP/NF and CoFeNiP/NF for OER.

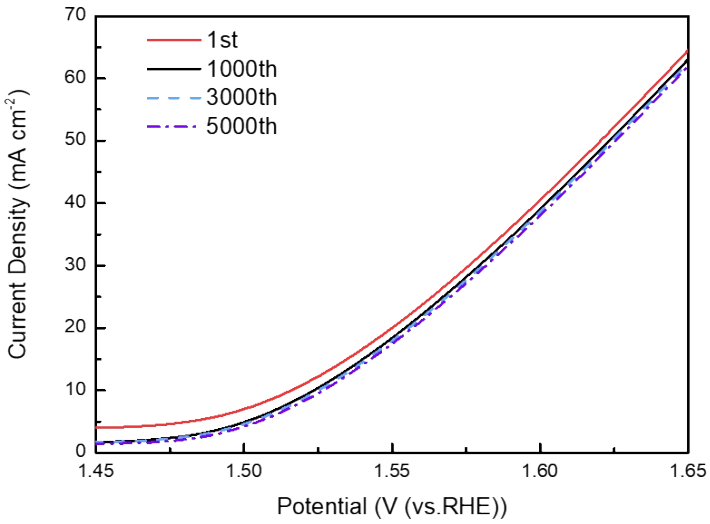

Figure S11. Polarization curves of the CoFeNiP/NF recorded after 1, 1000, 3000 and 5000 continuous CV cycles in the range of 1.225-1.625 V versus RHE at 100 mV s^{-1}. All polarization were tested at a scan rate of 5 mV s^{-1} in 1 M KOH solution.

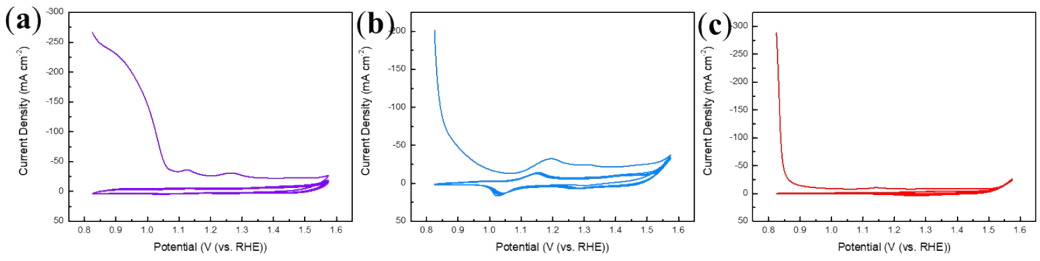

Figure S12. The cyclic voltammetry curve from 0.875 to 1.575 V with 10 cycles at a scan rate of 20 mV s^{-1} for CoP/NF, CoFeP/NF and CoFeNiP/NF in alkaline solution.

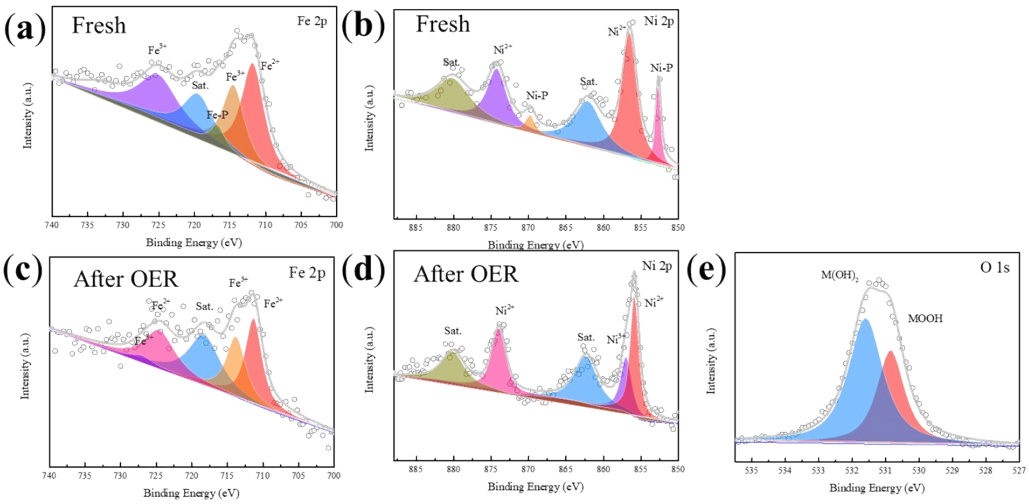

Figure S13. The XPS analysis of (a)(c) Fe 2p and (b)(d) Ni 2p spectra for the CoFeNiP/NF before and after OER. (e) The XPS spectra of O 1s for CoFeNiP/NF after OER.

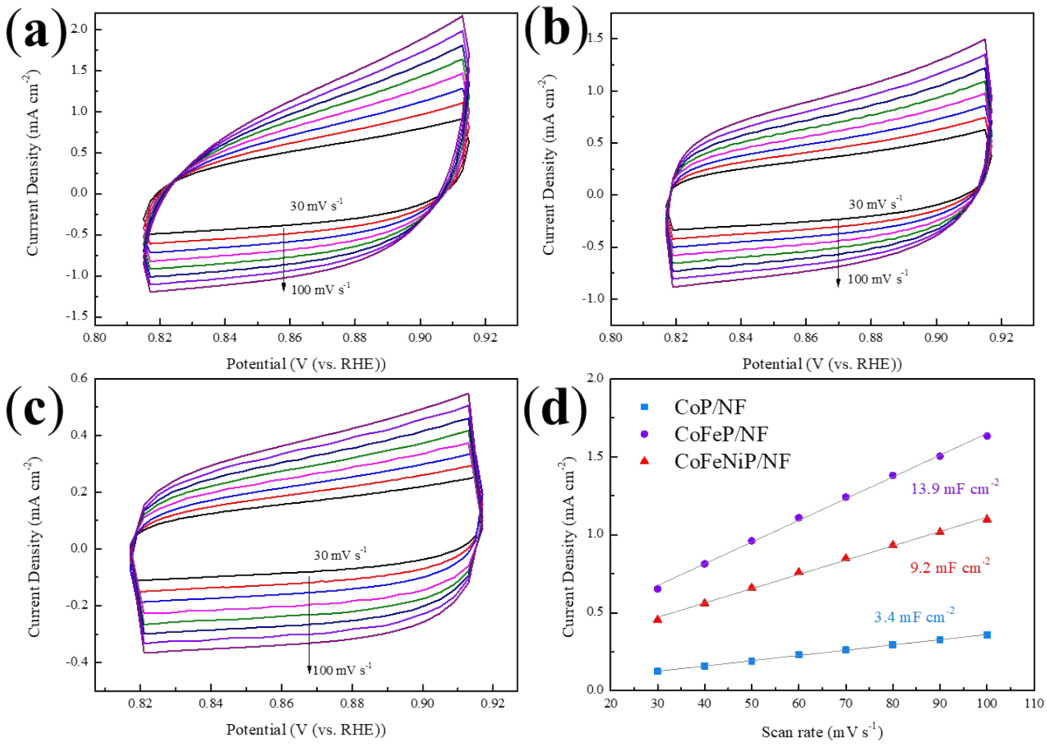

Figure S14. The cyclic voltammetry curve for (a) CoP/NF, (b) CoFeP/NF and (c) CoFeNiP/NF from 0.819-0.917 V (vs. RHE) at scan rate at 30, 40, 50, 60, 70, 80,90 and 100 mV s^{-1}. (d) Plots of current densities (at 0.87V vs. RHE) as a function of scan rates.

Table S2. Comparisons of HER and OER performances of CoFeNiP/NF with other Co-based phosphides catalysts in 1 M KOH.

Composition	Synthesis	Morphology	Performance(mV)		Tafel Slope (mV dec^{-1})		Reference
			HER	OER	HER	OER	
$Co_{0.9}Fe_{0.1}P$/CNT	1.solvothermal 2.phosphating	nanoplate	88	250	75	40	1
Fe-Co_2P	liquid reaction	nanorod	156		90		2
Fe-CoP/HPFs	1. solvothermal 2. phosphating	hollow polyhedron	173		87		3
$Co_{0.6}Fe_{0.4}P$	1.PBAtemplate 2.etching 3.phosphating	nanoframe	133	298	61	48	4
Co_xFe_{1-x}-P	galvanostatic electrodeposition	film	169	290	56.9	39.2	5
CoFeP	1. hydrothermal 2. phosphating	hollow microball	177	350	72	59	6
CoFeP-0.03	pulse electrodeposition	nanoplate	56	303	42	70	This work
CoFeNiP-0.05	pulse electrodeposition	nanoplate	40	287	30	67	
FeCoNiP@NC	1. solvothermal 2.phosphating	nanoparticle	187	266	52.2	35.6	7
$NiCoFe_xP$	1. hydrothermal 2.phosphating	nanoplate	39	275	112	147	8

Reference

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