Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

Ternary Metal Phosphide Nanosheets as Highly Efficient Electrocatalyst for Water Reduction to Hydrogen over a Wide pH Range from 0 to 14

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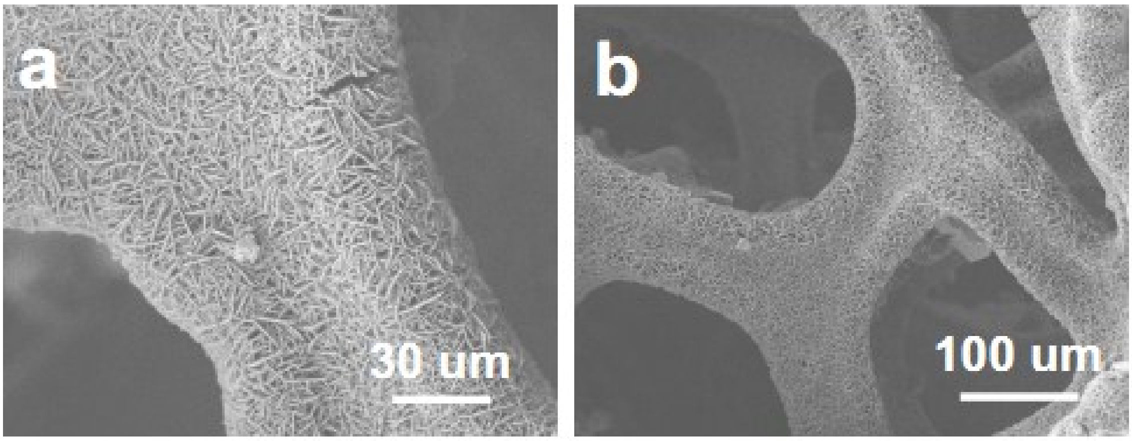

Figure S1. (a)-(b), SEM images of CoNiP@NF electrode with low-magnification.

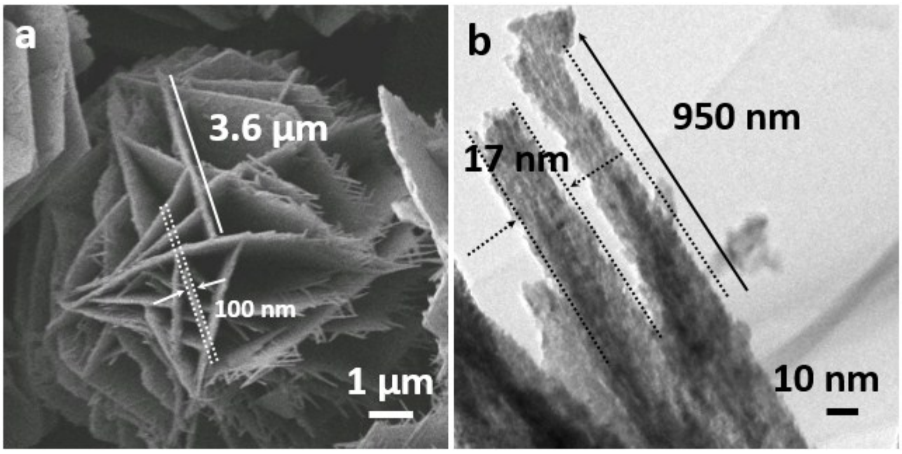

Figure S2. a, SEM image for CoNiP powder scraped from nickel foam; b, TEM image for CoNiP nanosheet.

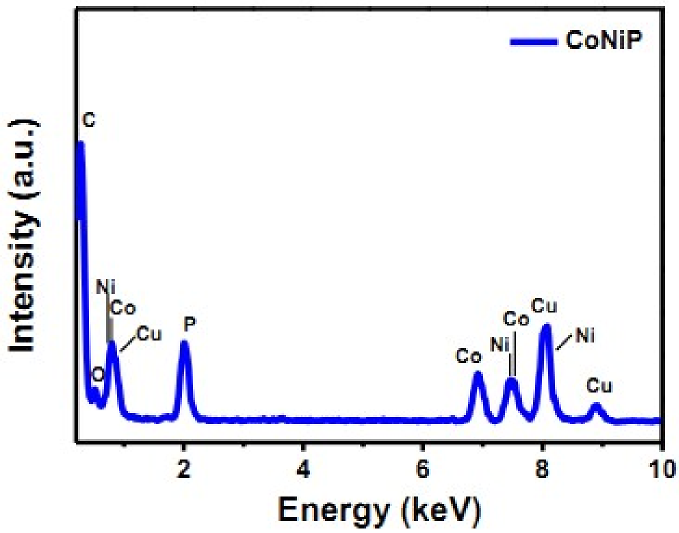

Figure S3. EDX spectrum of the as-prepared CoNiP nanosheet. The atomic ratio of the Co, Ni, and P is close to 1:1:1.

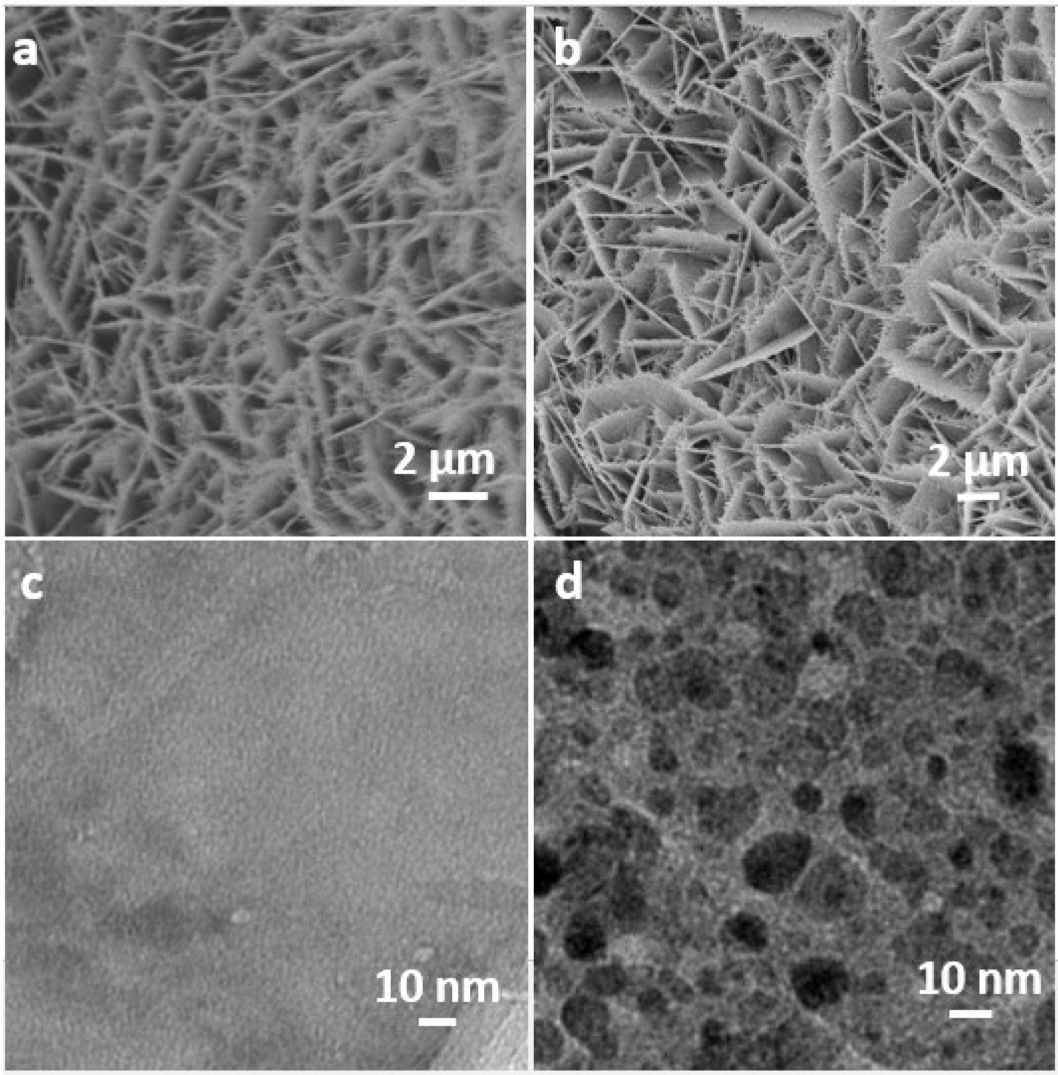

Figure S4. a, SEM image for CoNi(OH)xF precursor; b, SEM image for CoNiP; c, TEM image for CoNi(OH)xF precursor; d, TEM image for CoNiP.

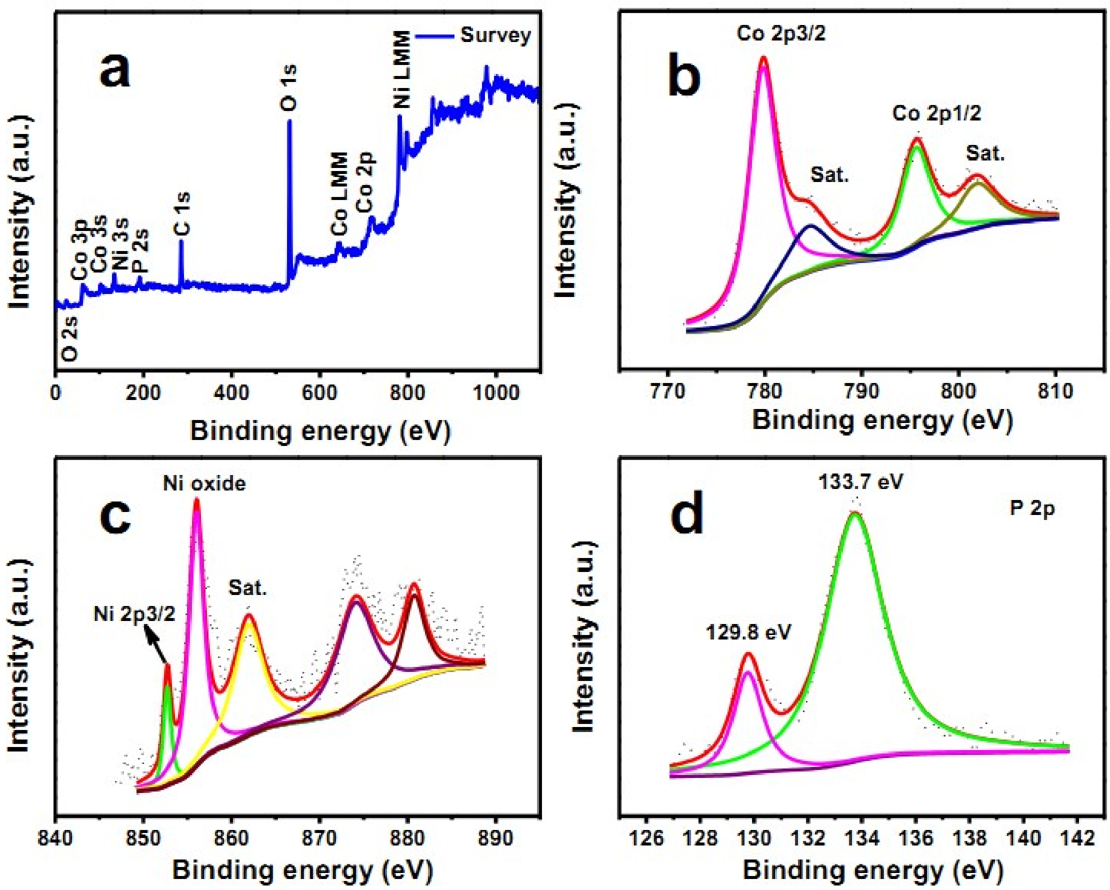

Figure S5. XPS spectra of the CoNiP@NF electrode. (a) the suvery scan of the CoNiP@NF electrode. (b) high-resolution spectrum of Co 2p. (c) high-resolution spectrum of Ni 2p; (d) high-resolution spectrum of P 2p.

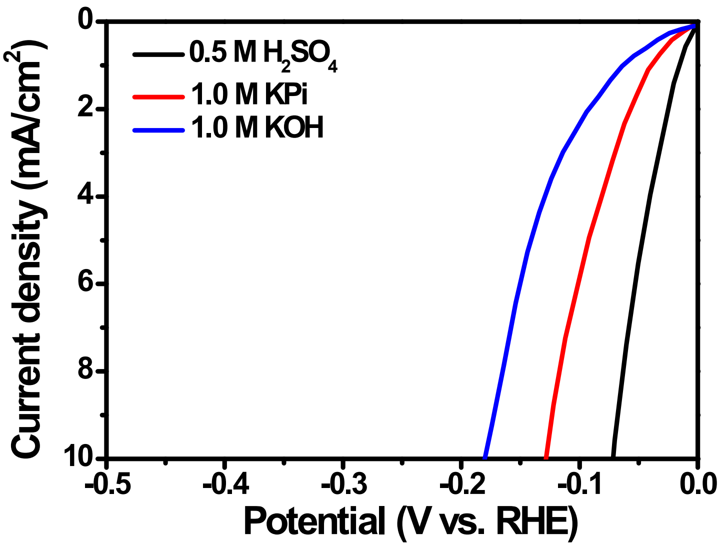

Figure S6. Polarization curves of CoNiP@Ti electrode in 0.5 M H_2SO_4 (black, pH = 0.26), 1.0 M KPi (red, pH = 7.0) and 1.0 M KOH (blue, pH = 13.6), respectively, with a scan rate of 5 mV s^{-1}. The working electrode was a Ti sheet electrode and the mass loading of CoNiP powder was 1.0 mg/cm^2.

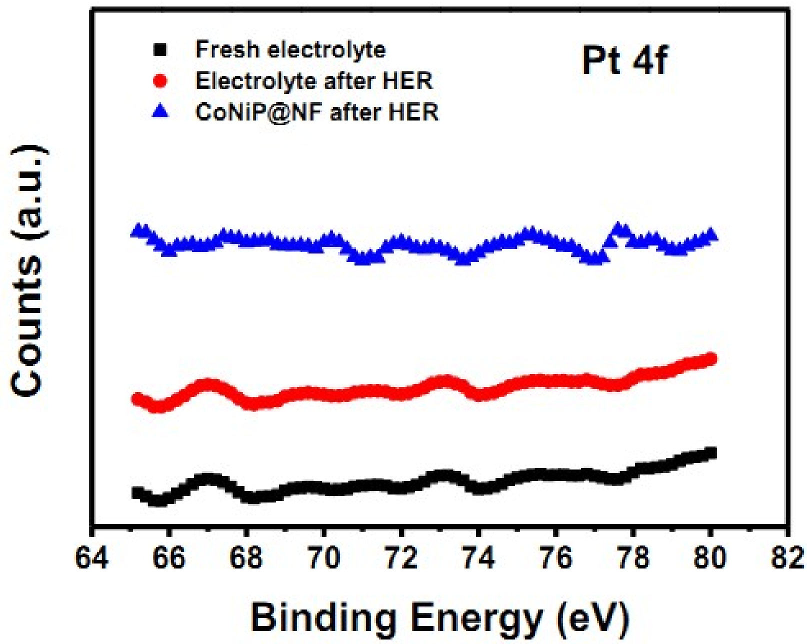

Figure S7. XPS specta of Pt 4f. Black: the sample was obtained from the fresh electrolyte; red: the sample was obtained from the electrolyte after HER tests; blue: the sample was obtained from the CoNiP@NF electrode after HER tests.

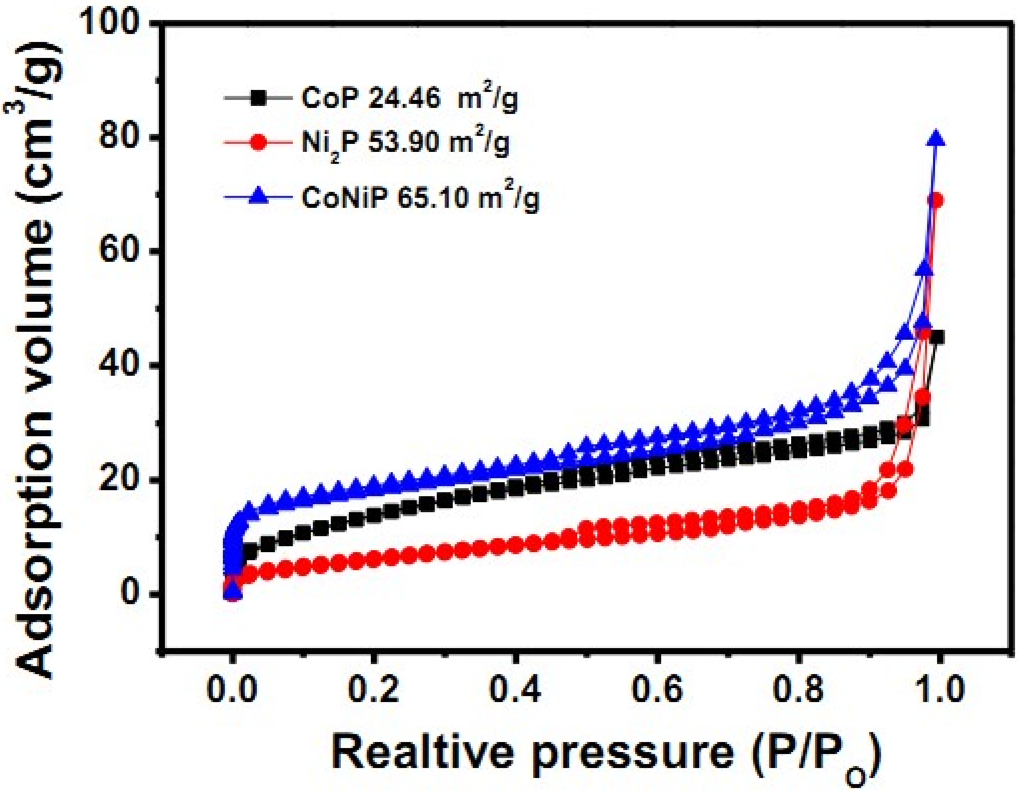

Figure S8. Nitrogen adsorption/desorption isotherm of the as-prepared CoP nanowires (black), Ni_2P nanosheets (red) and CoNiP nanosheets (blue).

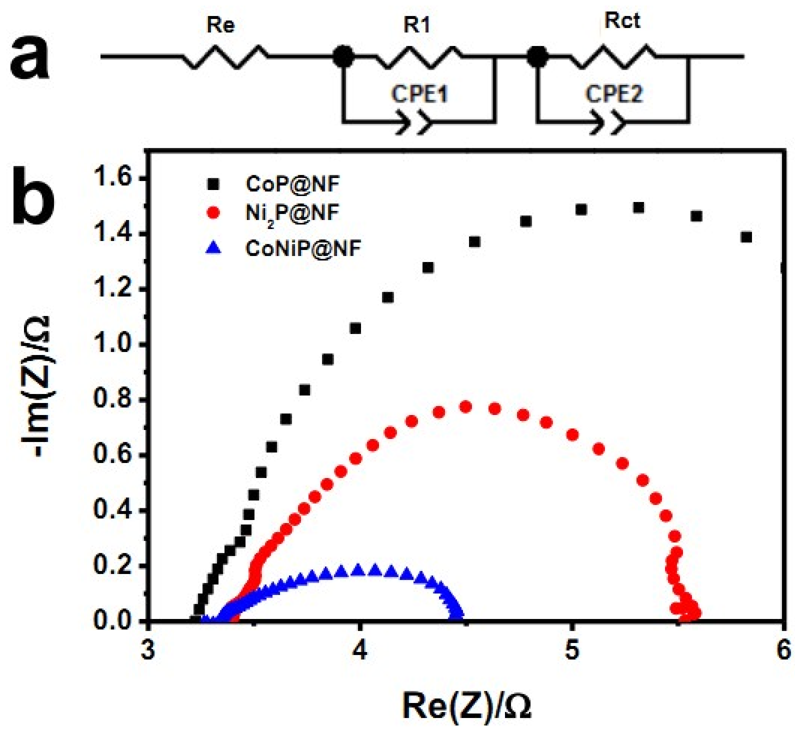

Figure S9. (a) The equivalent circuit for fitting the Nyquist plots in Figure S5b. Re represents the ohmic resistance arising from the electrolyte and all contacts. The time constant R1-CPE1 may be related to the interfacial resistance resulting from the electron transport between the metal phosphides and the porous underneath. R_{ct}-CPE2 reflects the charge transfer resistance (R_{ct}) at the interface between the metal phosphide and the electrolyte. (b) Nyquist plots of the CoP@NF (blank), Ni_2P@NF (red), and CoNiP@NF (blue) electrodes measured at open circuit in the frequency range of 10^5-0.05 Hz. The applied potential was -100 mV vs. RHE in 0.5 M H_2SO_4.

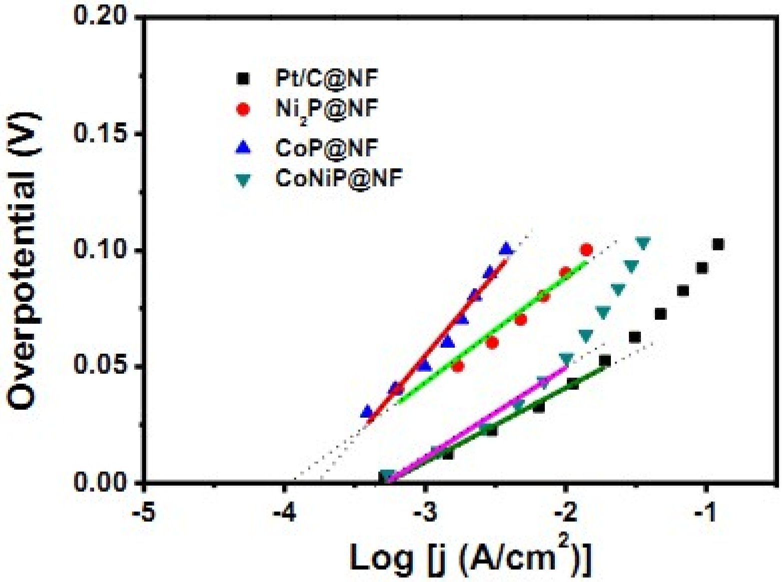

Figure S10. The Tafel plots used for calculating exchange current density (j_0) of various samples by extrapolation method.

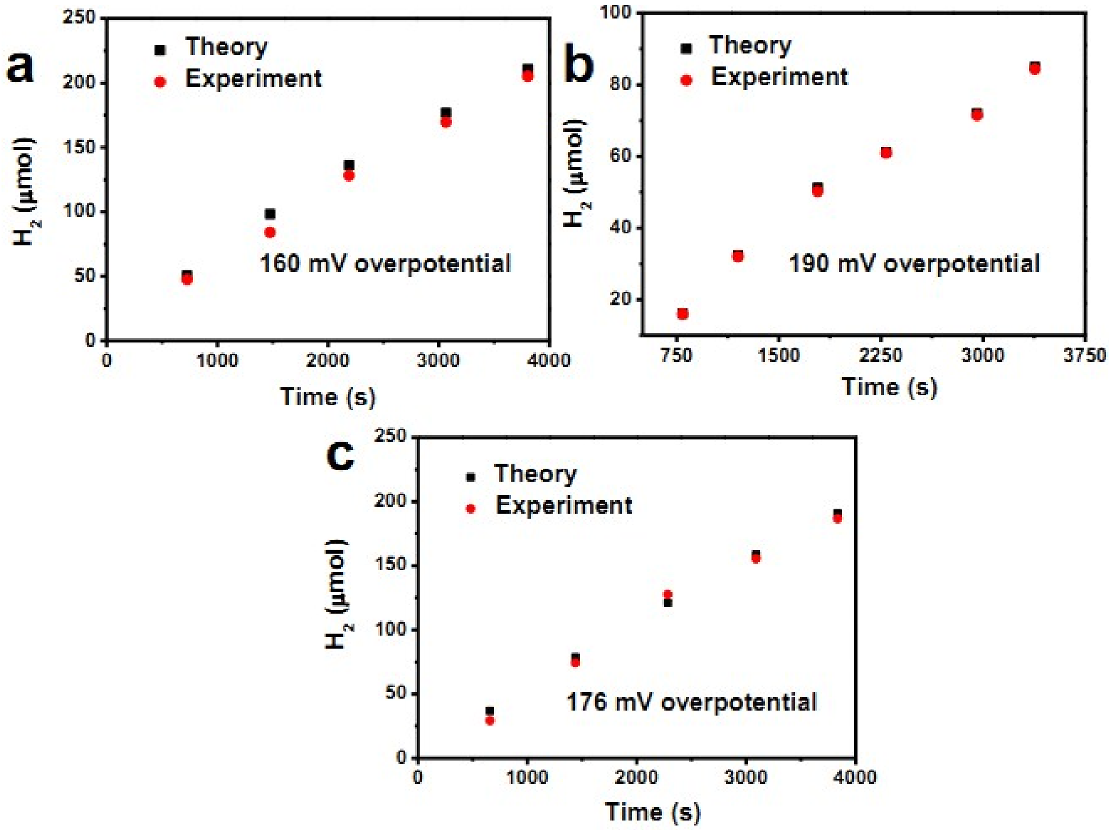

Figure S11. (a) The theoretical (black dot) and experimentally observed (red dot) H_2 production in 0.5 M H_2SO_4 solution using CoNiP@NF as the cathode. (b) The theoretical (black dot) and experimentally observed (red dot) H_2 production in 1.0 M KPi solution using CoNiP@NF as the cathode. (c) The theoretical (black dot) and experimentally observed (red dot) H_2 production using CoNiP@NF as the cathode.

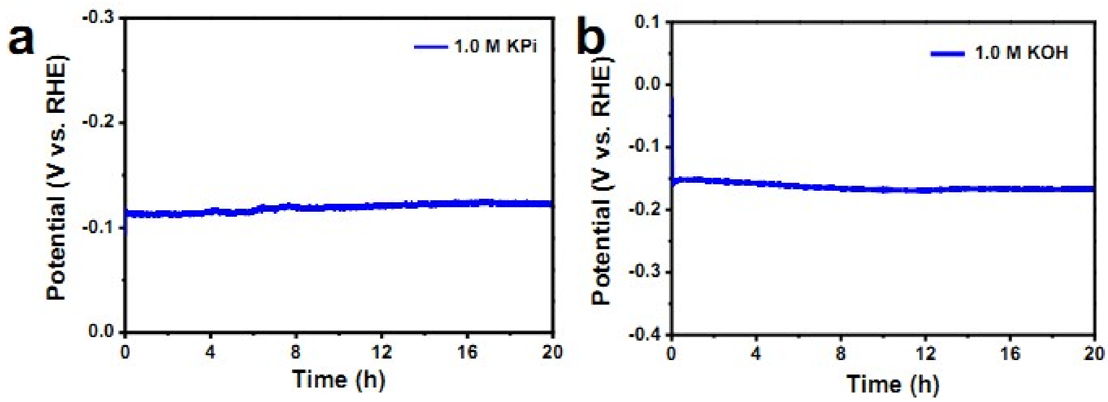

Figure S12. (a) Chronopotentiometry method to obtain 10 mA/cm^2 using the CoNiP@NF electrode in 1.0 M KPi for 20 hours. (b) Chronopotentiometry method to obtain 10 mA/cm^2 using CoNiP@NF electrode in 1.0 M KOH for 20 hours.

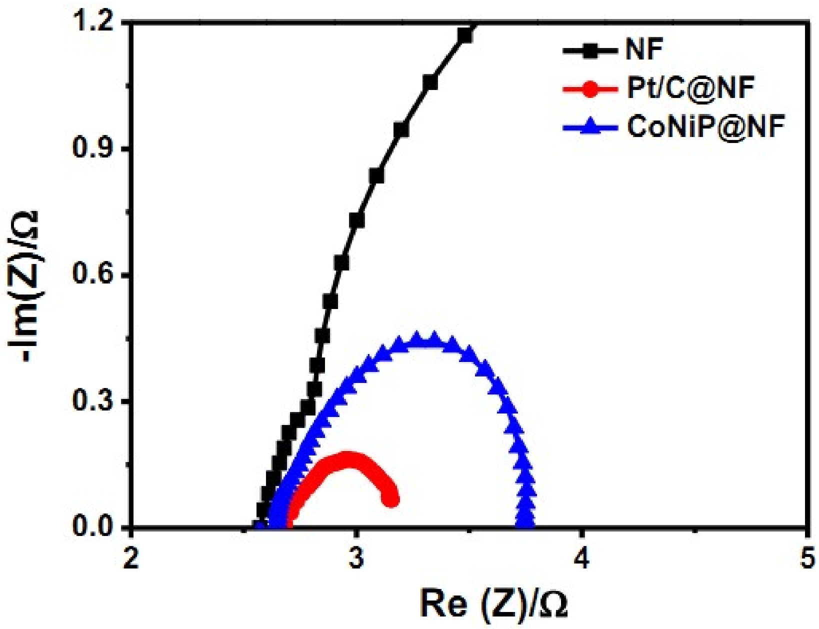

Figure S13. Nyquist plots of the NF (blank), Pt/C@NF (red), and CoNiP@NF (blue) electrodes measured at open circuit in the frequency range of 10^5-0.05 Hz. The applied potential was -300 mV vs. RHE.

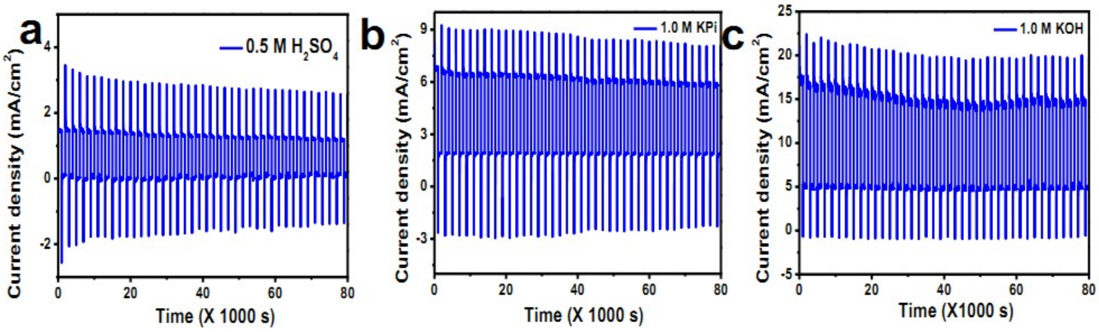

Figure S14. (a) Time-dependence of catalytic currents during electrolysis for HER under different overpotentials in 0.5 M H_2SO_4 after 80 cycles (> XX hours). (b) Time-dependence of catalytic currents during electrolysis for HER under different overpotentials in 1.0 M KPi after 80 cycles. (c) Time-dependence of catalytic currents during electrolysis for HER under different overpotentials in 1.0 M KOH after 80 cycles.

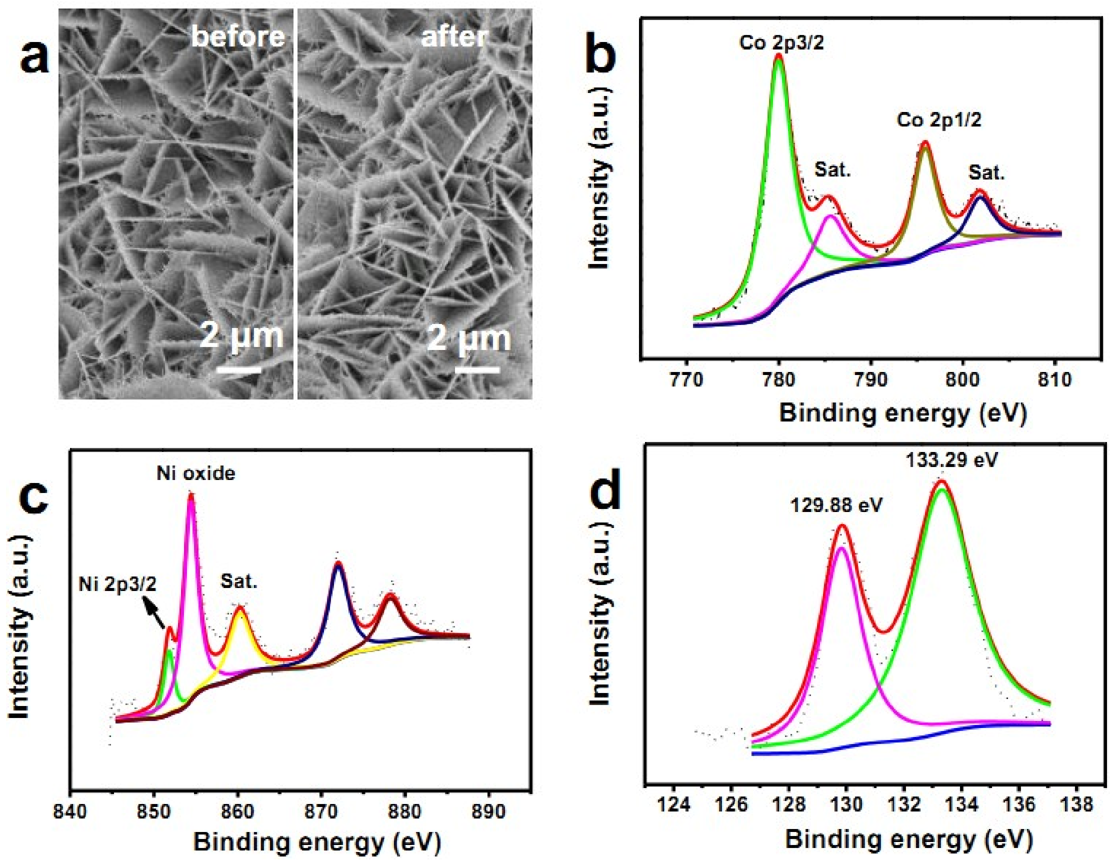

Figure S15. (a) SEM images of the CoNiP@NF electrode before (left) and after electrolysis (right) for HER in 1.0 M KOH. (b, c, d) XPS spectrum of CoNiP@NF electrode after electrolysis in 1.0 M KOH for 30 h. b, high-resolution of Co 2p; c, high-resolution of Ni 2p; d, high-resolution of P 2p.

Table S1. The solution resistances using different catalysts for electrocatalysis.

Catalysts	0.5 M H_2SO_4	1.0 M KPi	1.0 M KOH
CoNiP@NF	3.5 ohm	15.0 ohm	4.0 ohm
CoP@NF	4.0 ohm	-	-
Ni_2P@NF	3.8 ohm	-	-

Table S2. Comparison of various solid-state HER catalysts in acid solutions (0.5 M H_2SO_4).

Catalyst	Onset η (mV) (1.0 mA/cm^2)	Tafel slope (mV/dec)	η_{10} (mV)[a]	j_0 (A/cm^2)[b]	References
CoNiP@NF	30	39	60	5.4×10^{-4}	This work
CoNiP@Ti[c]	-	-	75	3.6×10^{-4}	
MnO_2@PC-RGO	-	41	64	4.8×10^{-4}	*Angew. Chem. Int. Ed.*, **2015,** *54,* 1.
CoNi@NC	-	104	142	-	*Angew. Chem. Int. Ed.*, ***2015,*** *54, 2100.*
CoP/CC	38	51	67	2.9×10^{-4}	*J. Am. Chem. Soc.* **2014**, *136*, 7587.
Co_2P/Ti	-	71	167	-	*Nano Energy*, **2014,** *9,* 373.
$CoSe_2$ nanobelts	50	48	-	8.4×10^{-6}	*Angew. Chem. Int. Ed.*, **2013,** *52,* 8546.
CoP/CNT	40	54	122	1.3×10^{-4}	*Angew. Chem. Int. Ed.*, **2014,** *53,* 6710.
MoS_2 nanosheets	200	54	195	-	*J. Am. Chem. Soc.* **2013**, *135*, 10274.
FeP nanosheets	100	67	240	-	*Chem. Commun.* **2013,** ***49,*** 6656.
Ni_2P nanoparticles	-	46	116	3.3×10^{-5}	*J. Am. Chem. Soc.* **2013**, *135*, 9267.
Ni_5P_4-Ni_2P-NS	54	79.1	120	1.2×10^{-4}	*Angew. Chem. Int. Ed.*, **2015,** *54,* 8188.
WS_2 nanosheets	80-100	60	-	2.0×10^{-5}	*Nat. Mater.*, **2013,** *12* 850.

[a] The potentials are versus RHE; [b] j_0 values were calculated from Tafel curves; [c] The CoNiP powder was deposited on Ti sheet electrode with a mass loading of 1.0 mg/cm^2.

Table S3. Comparison of various solid-state HER catalysts in neutral solutions (pH = 7.0).

Catalyst	Onset η (mV) (1 mA/cm^2)	Tafel slope (mV/dec)	η_2(mV)[a]	η_{10}(mV)[b]	References
CoNiP@NF	32	103	35	120	This work
CoNiP@Ti[c]	-	-	55	130	
CoP/CC	45	93	65	106	*J. Am. Chem. Soc.* **2014**, *136*, 7587.
H_2-CoCat	50	140	385	-	*Nat. Mater.* **2012,** *11,* 802.
Co-NRCNTs	-	-	380	-	*Angew. Chem. Int. Ed.,* **2014,** *53,* 4372.
CoS/FTO	43	93	83	-	*J. Am. Chem. Soc.* **2013**, *135*, 17699.
$CuMoS_4$	135	95	210	-	*Energy Environ. Sci.* **2012,** *5,* 8912.

[a]-[b] The potentials are versus RHE. [c] The CoNiP powder was deposited on Ti sheet electrode with a mass loading of 1.0 mg/cm^2.

Table S4. Comparison of various solid-state HER catalysts in basic solutions (1.0 M KOH).

Catalyst	Onset η (mV) (1.0 mA/cm^2)	Tafel slope (mV/dec)	η_2(mV)[a]	η_{10}(mV)[a]	References
CoNiP@NF	35	113	82	155	This work
CoNiP@Ti[c]	-	-	94	184	
CoP/CC	80	129	-	209	*J. Am. Chem. Soc.* **2014**, *136*, 7587.
Ni wire	190	-	-	350	*ACS Catal.* **2013,** *3,* 166.
CoS/FTO	-	-	-	480[d]	*J. Am. Chem. Soc.* **2013**, *135*, 17699.
Co-NRCNTs	50-100	-	-	370	*Angew. Chem. Int. Ed.,* **2014,** *53,* 4372.
CoOx@CN	85	115	-	232[e]	*J. Am. Chem. Soc.* **2015**, *137*, 2688.
NiO/Ni-CNT	-	82	-	80[f]	*Nat. Commun,* **2014,** *5,* 4695.
$Fe_{0.9}Co_{0.1}S_2$/C NT	-	46	-	120[g]	*J. Am. Chem. Soc.* **2015**, *137*, 1587.
Co-P film	-	42	-	94	*Angew. Chem. Int. Ed.,* **2015,** *54,* 6251.

[a]-[b] The potentials are versus RHE; [c] The CoNiP powder was deposited on Ti sheet electrode with a mass loading of 1.0 mg/cm^2; [d] this overpotential value is corresponding to the current density reached 1.0 mA/cm^2; [e] The catalyst amount is 0.12 mg/cm^2; [f] The catalyst amount is 0.28 mg/cm^2; [g] the overpotential value is corresponding to the current density at 20 mA/cm^2.