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Supporting Information

Facile synthesis of FeP/CoP confined in N, P co-doped carbon derived from MOFs for efficient pH-universal hydrogen evolution reaction

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S1. Figures in Supporting Information

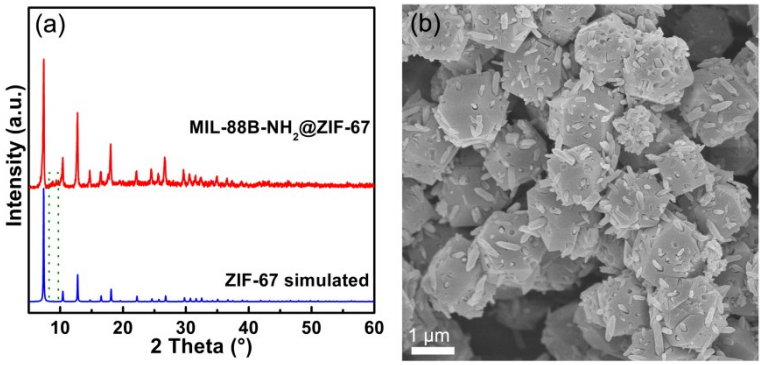

Fig. S1 (a) PXRD pattern and (b) SEM image of MIL-88B-NH_2@ZIF-67.

Fig. S1a shows the PXRD pattern of pre-prepared MIL-88B-NH_2@ZIF-67 is almost identical to that of simulated ZIF-67 and the weak peaks (green dotted line) at 8.7 and 9.4° correspond to MIL-88B-NH_2, which prove the successful fabrication of dual-metal-organic frameworks. In addition, it is found that numerous nanorods are randomly incorporated into the polyhedral ZIF-67 crystals as shown in **Fig. S1b**.

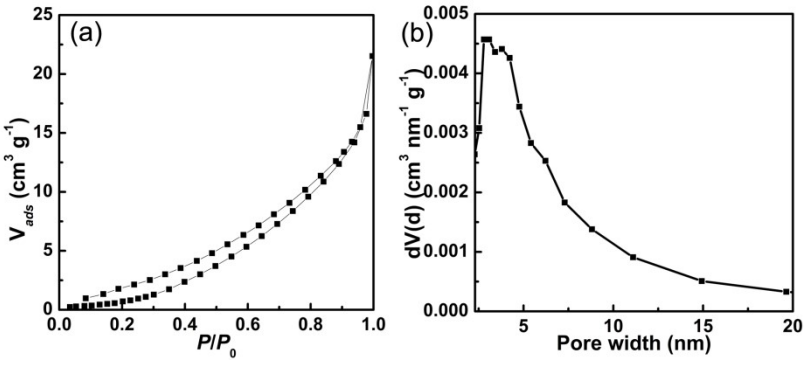

Fig. S2 (a) N_2 sorption isotherm and (b) corresponding pore size distribution of FeP/CoP@NPC.

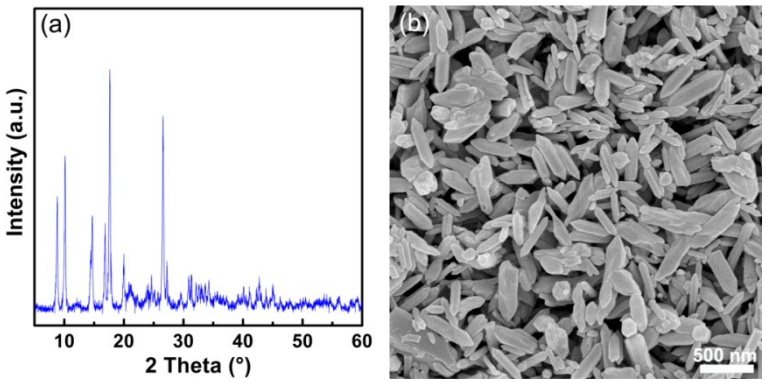

Fig. S3 (a) PXRD pattern and (b) SEM image of MIL-88B-NH_2.

In **Fig. S3a**, the PXRD pattern of the resultant MIL-88B-NH_2 is consistent with the simulated MIL-88B, indicative of high purity. Meanwhile, the rod-like MIL-88B-NH_2 were intuitively observed from **Fig. S3b**.

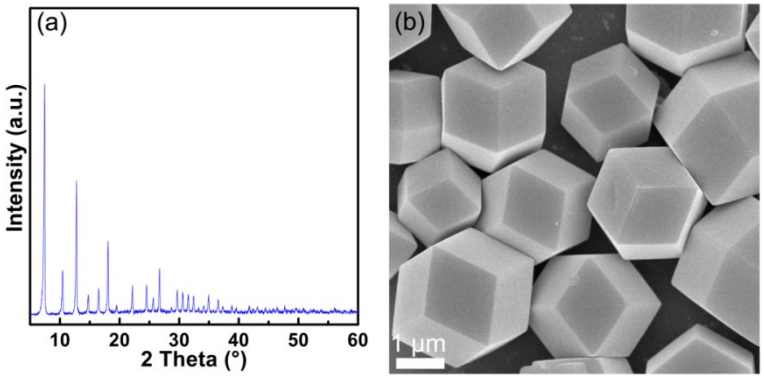

Fig. S4 (a) PXRD pattern and (b) SEM image of ZIF-67.

As shown in **Fig. S4a**, the PXRD pattern of the obtained ZIF-67 is in accordance with the simulated ZIF-67, confirming good crystallinity. The corresponding SEM image in **Fig. S4b**

reflects a rhombic polyhedral shape.

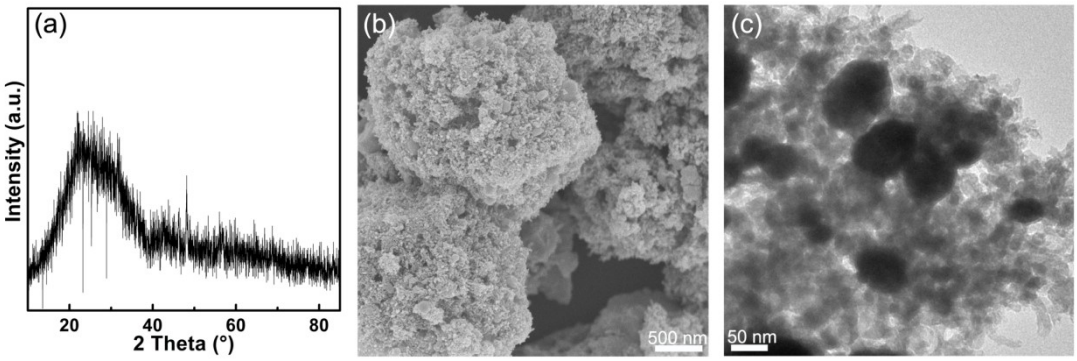

Fig. S5 (a) PXRD pattern, (b) SEM, and (c) TEM images of CoP@NPC.

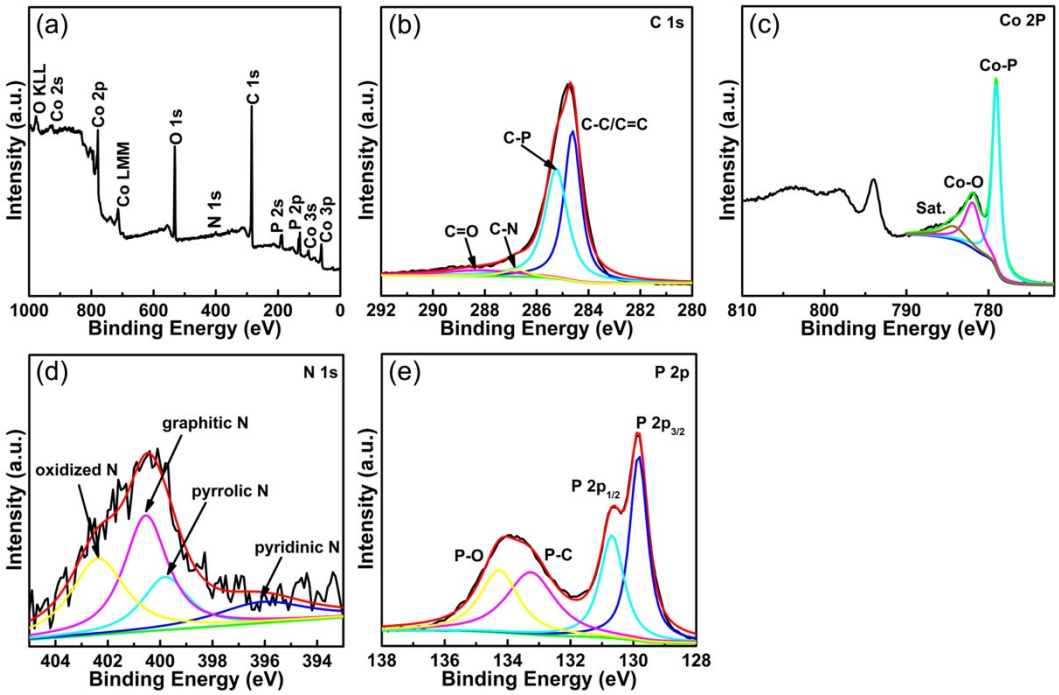

Fig. S6 (a) XPS survey spectrum, (b-e) high-resolution spectra of C 1s, N 1s, Co 2p, and P 2p of CoP@NPC, respectively.

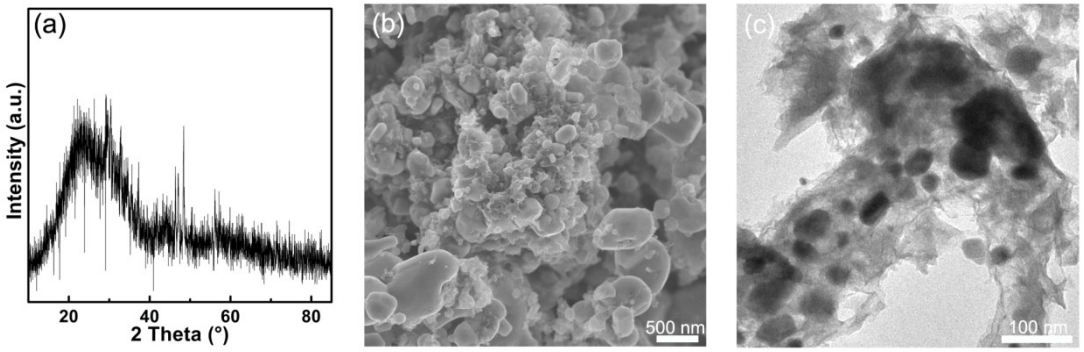

Fig. S7 (a) PXRD pattern, (b) SEM, and (c) TEM images of FeP@NPC.

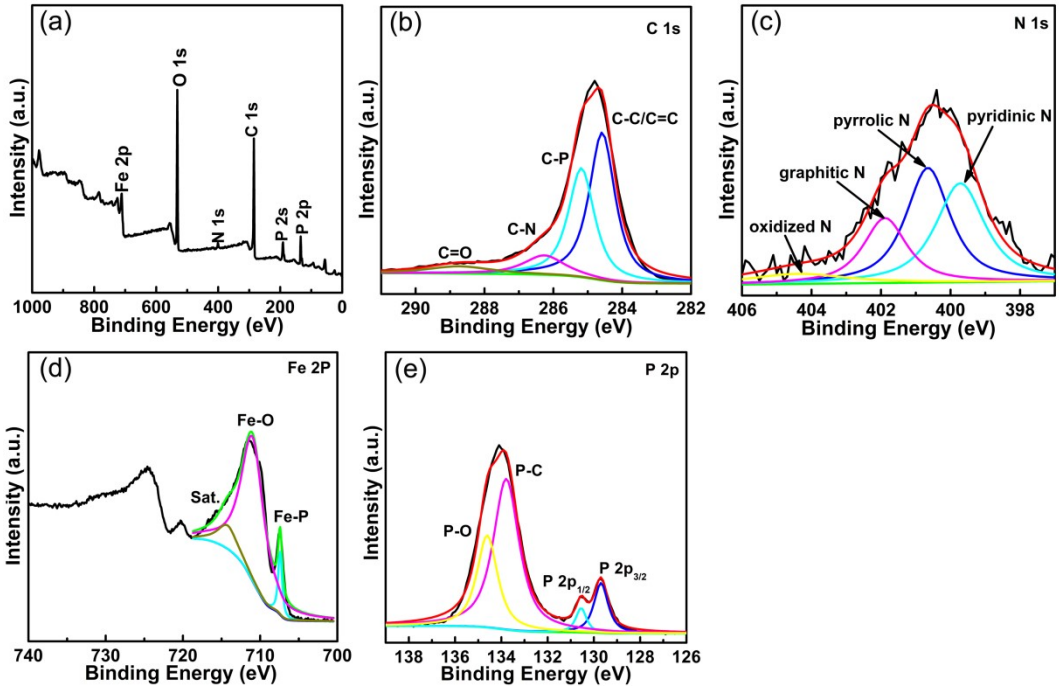

Fig. S8 (a) XPS survey spectrum, (b-e) high-resolution spectra of C 1s, N 1s, Fe 2p, and P 2p of FeP@NPC, respectively.

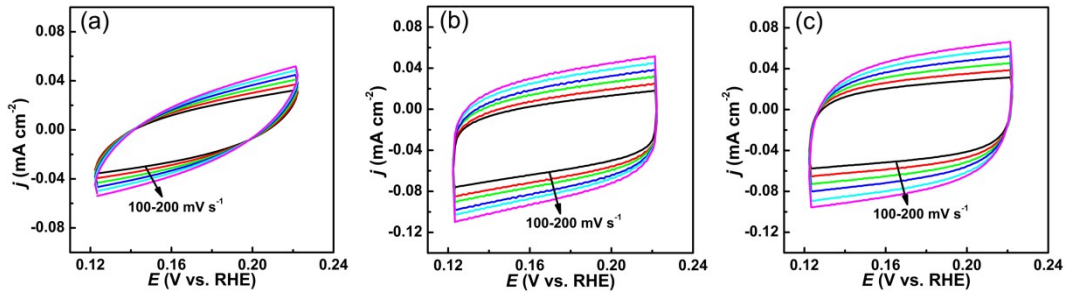

Fig. S9 (a-c) CV curves of CoP@NPC, FeP@NPC, and FeP/CoP@NPC in 0.5 M H_2SO_4.

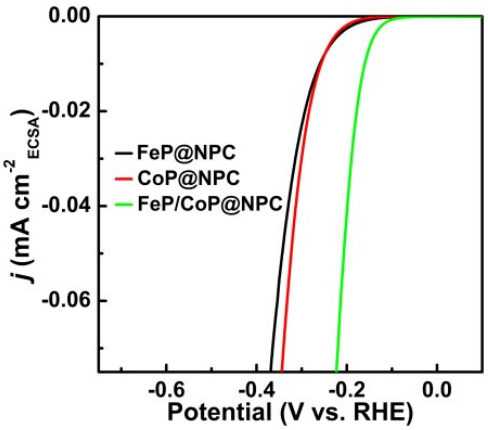

Fig. S10 HER activity of different catalysts in 0.5 M H_2SO_4 normalized by ECSA.

Calculation of ECSA:

$$\mathrm{ECSA} = \frac{C_{dl}}{C_s} = \frac{C_{dl}}{40\,\mu\mathrm{F\,cm^{-2}}\ \mathrm{cm_{ECSA}^{-2}}}$$

In 0.5 M H_2SO_4:

For FeP, $$\mathrm{ECSA} = \frac{562\,\mu\mathrm{F\,cm^{-2}}}{40\,\mu\mathrm{F\,cm^{-2}}\ \mathrm{cm_{ECSA}^{-2}}} = 14.1\,\mathrm{cm_{ECSA}^{2}}$$

For CoP, $$\mathrm{ECSA} = \frac{311\,\mu\mathrm{F\,cm^{-2}}}{40\,\mu\mathrm{F\,cm^{-2}}\ \mathrm{cm_{ECSA}^{-2}}} = 7.78\,\mathrm{cm_{ECSA}^{2}}$$

For FeP/CoP@NPC, $\mathrm{ECSA} = \frac{685\ \mu\mathrm{F\,cm^{-2}}}{40\ \mu\mathrm{F\,cm^{-2}}\ \mathrm{cm_{ECSA}^{-2}}} = 17.1\mathrm{cm_{ECSA}^{2}}$

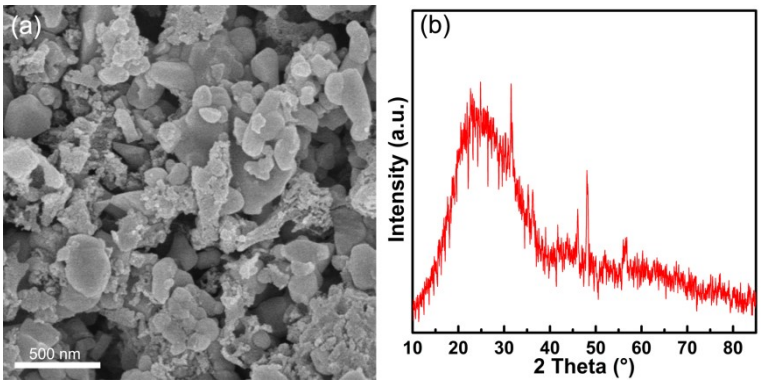

Fig. S11 (a) SEM and (b) PXRD pattern of FeP/CoP@NPC after long-term stability test in 0.5 M H_2SO_4.

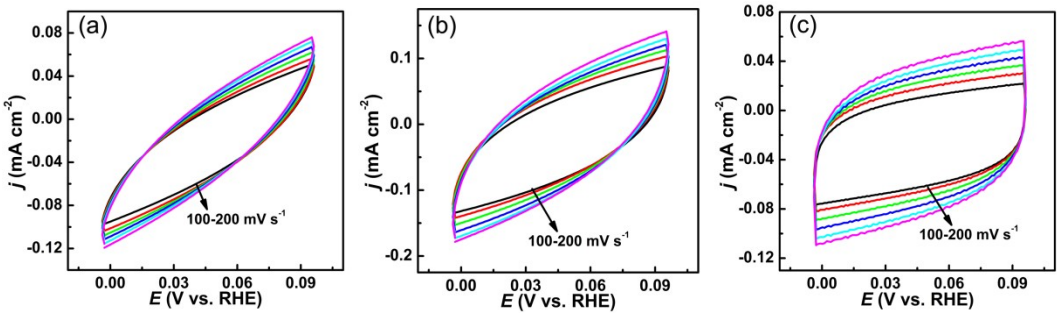

Fig. S12 (a-c) CV curves of CoP@NPC, FeP@NPC, and FeP/CoP@NPC in 1.0 M PBS.

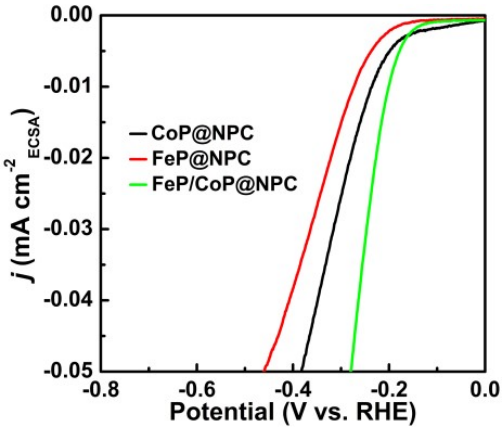

Fig. S13 HER activity of different catalysts in 1.0 M PBS normalized by ECSA.

In 1.0 M PBS:

For FeP, $\mathrm{ECSA} = \frac{496\,\mu\mathrm{F\,cm^{-2}}}{40\,\mu\mathrm{F\,cm^{-2}}\ \mathrm{cm_{ECSA}^{-2}}} = 12.4\,\mathrm{cm_{ECSA}^{2}}$

For CoP, $\mathrm{ECSA} = \frac{175\,\mu\mathrm{F\,cm^{-2}}}{40\,\mu\mathrm{F\,cm^{-2}}\ \mathrm{cm_{ECSA}^{-2}}} = 4.38\,\mathrm{cm_{ECSA}^{2}}$

For FeP/CoP@NPC, $\mathrm{ECSA} = \frac{525\,\mu\mathrm{F\,cm^{-2}}}{40\,\mu\mathrm{F\,cm^{-2}}\ \mathrm{cm_{ECSA}^{-2}}} = 13.1\,\mathrm{cm_{ECSA}^{2}}$

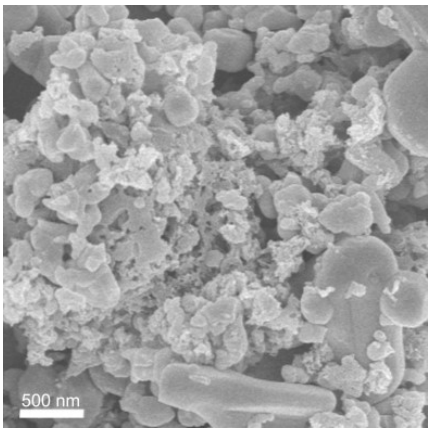

Fig. S14 SEM image of FeP/CoP@NPC after stability test in 1.0 M PBS.

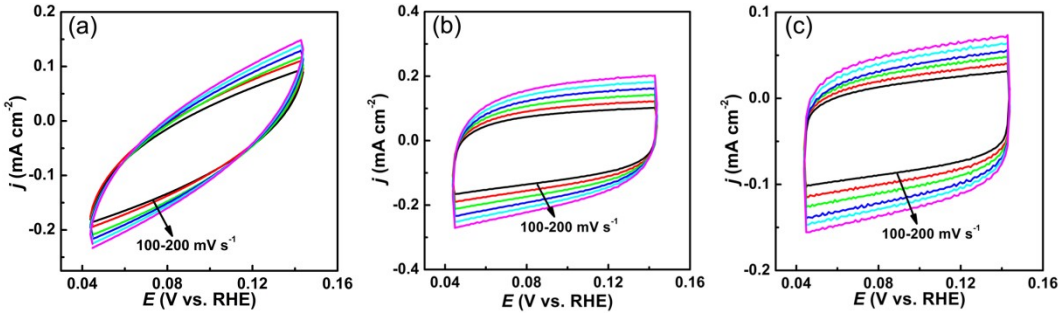

Fig. S15 (a-c) CV curves of CoP@NPC, FeP@NPC, and FeP/CoP@NPC at in 1.0 M KOH.

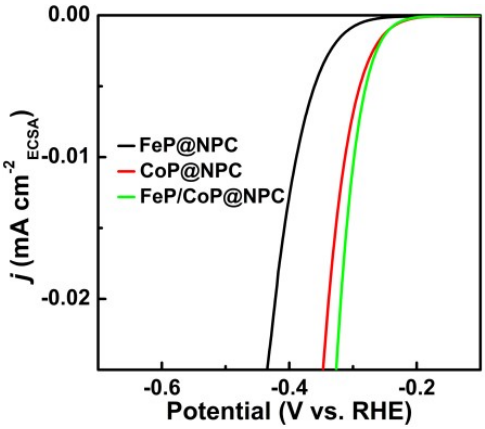

Fig. S16 HER activity of different catalysts in 1.0 M KOH normalized by ECSA.

In 1.0 M KOH:

For FeP, $\mathrm{ECSA} = \frac{1670\,\mu\mathrm{F\,cm^{-2}}}{40\,\mu\mathrm{F\,cm^{-2}}\ \mathrm{cm}_{ECSA}^{-2}} = 41.75\,\mathrm{cm}_{ECSA}^{2}$

For CoP, $\mathrm{ECSA} = \frac{442\,\mu\mathrm{F\,cm^{-2}}}{40\,\mu\mathrm{F\,cm^{-2}}\ \mathrm{cm}_{ECSA}^{-2}} = 11.05\,\mathrm{cm}_{ECSA}^{2}$

For FeP/CoP@NPC, $\mathrm{ECSA} = \frac{760\,\mu\mathrm{F\,cm^{-2}}}{40\,\mu\mathrm{F\,cm^{-2}}\ \mathrm{cm}_{ECSA}^{-2}} = 19\,\mathrm{cm}_{ECSA}^{2}$

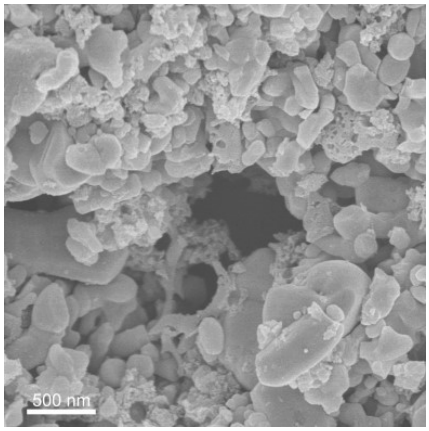

Fig. S17 SEM image of FeP/CoP@NPC after stability test in 1.0 M KOH.

S2. Tables in Supporting Information

Table S1. Comparison of catalytic performance of FeP/CoP@NPC and other reported materials toward HER in acidic conditions.

Catalysts	Tafel slope [mV dec^{-1}]	η_{10} (mV)	References
FeP/CoP@NPC	**53.6**	**198**	**This work**
Yb-MoP@NC	68.44	148.53	*Appl. Catal. B Environ.* 2021, 299, 120657.
$FeCoP_2$@NPPC	54	114	*ACS Appl. Mater. Interfaces* 2021, 13, 8832.
MoP@NPCS	58	113	*Appl. Catal. B Environ.* 2020, 263, 118352.
CoP-InNC@CNT	62	153	*Adv. Sci.* 2020, 7, 1903195.
CoP-CNT/NG	69.1	155	*Int. J. Hydrogen Energy* 2019, 44, 30053.
Mo_2N-Mo_2C/HGr-2	55	157	*Adv. Mater.* 2018, 30, 1704156.
MoP@PC	59.3	258	*ACS Appl. Mater. Interfaces*2018, 10, 17140.
$Mo_{0.5}W_{0.5}S_2$	55	138	*ACS Catal.* 2018, 8, 9529.

Table S2. Comparison of catalytic performance of FeP/CoP@NPC and other reported materials toward HER in neutral conditions.

Catalysts	Tafel slope [mV dec^{-1}]	η_{10} (mV)	References
FeP/CoP@NPC	**75.3**	**286**	**This work**
Yb-MoP@NC	168.37	250.1	*Appl. Catal. B Environ.* 2021, 299, 120657.
MoP@NC	95	191	*Appl. Catal. B Environ.* 2020, 263, 118358.
MoP/NPG	102	150	*Appl. Catal. B Environ.* 2020, 260, 118196.
Mo-WP	90	216	*Appl. Catal. B Environ.* 2019, 251, 162.
Ni_2P@NPCNFs	230.3	185.3	*Angew. Chem. Int. Ed.* 2018, 130, 1963.
CoP_3 CPs/CFP	113	179	*Phys. Chem. Chem. Phys.* 2017, 19, 2104.

Table S3. Comparison of catalytic performance of FeP/CoP@NPC and other reported materials toward HER in alkaline conditions.

Catalysts	Tafel slope [mV dec^{-1}]	η_{10} (mV)	References
FeP/CoP@NPC	**58.8**	**339**	**This work**
CoP@FeCoP/NC	56.34	141	*Chem. Eng. J.* 2021, 403, 126312.
Yb-MoP@NC	70.84	136.5	*Appl. Catal. B Environ.* 2021, 299, 120657.
FeCo/Co_2P@NPCF	120	260	*Adv. Energy Mater.* 2020, 10, 1903854.
Mo-Ni_3S_2/Ni_xP_y/NF	68.4	109	*Adv. Energy Mater.* 2020, 10, 1903891
NiFeP@C	75.8	160	*ACS Appl. Mater. Interfaces* 2020, 12, 19447
NiFeP/NCH	125	216	*J. Am. Chem. Soc.* 2019, 141, 7906.
CoP/CN@MoS_2	88	149	*ACS Appl. Mater. Interfaces* 2019, 11,
Fe-CoP	92	78	*Adv. Sci.* 2018, 5, 1800949.