Supporting information

Plasma-Assisted Nitrogen Doping in Ni-Co-P Hollow Nanocubes for Efficient Hydrogen Evolution Electrocatalysis

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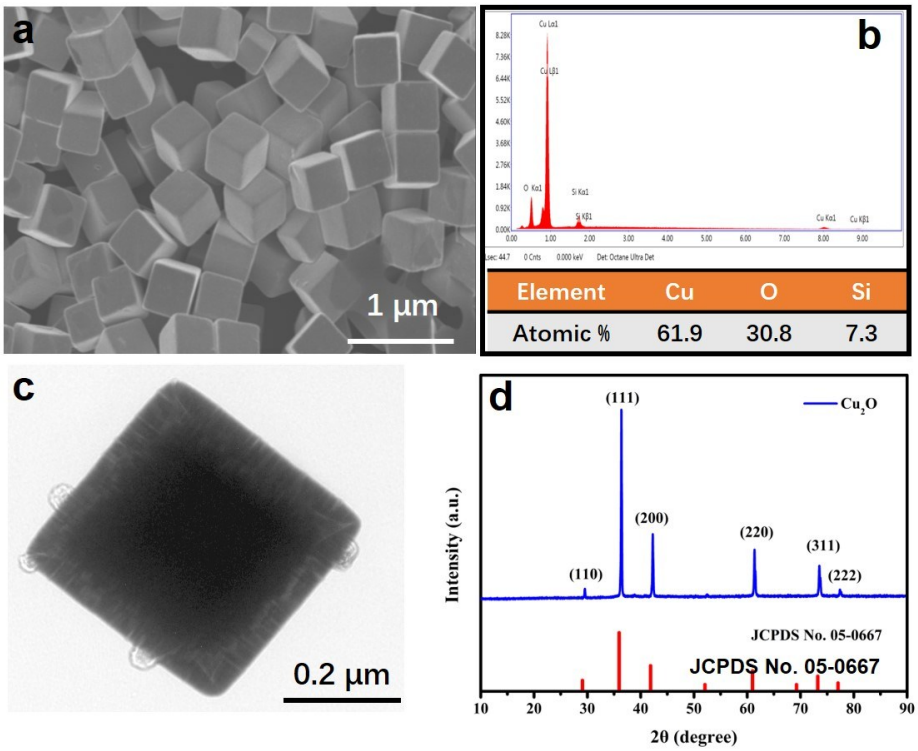


Figure S1. (a) SEM image (b) EDS (c) TEM image (d) XRD pattern of Cu_2O.

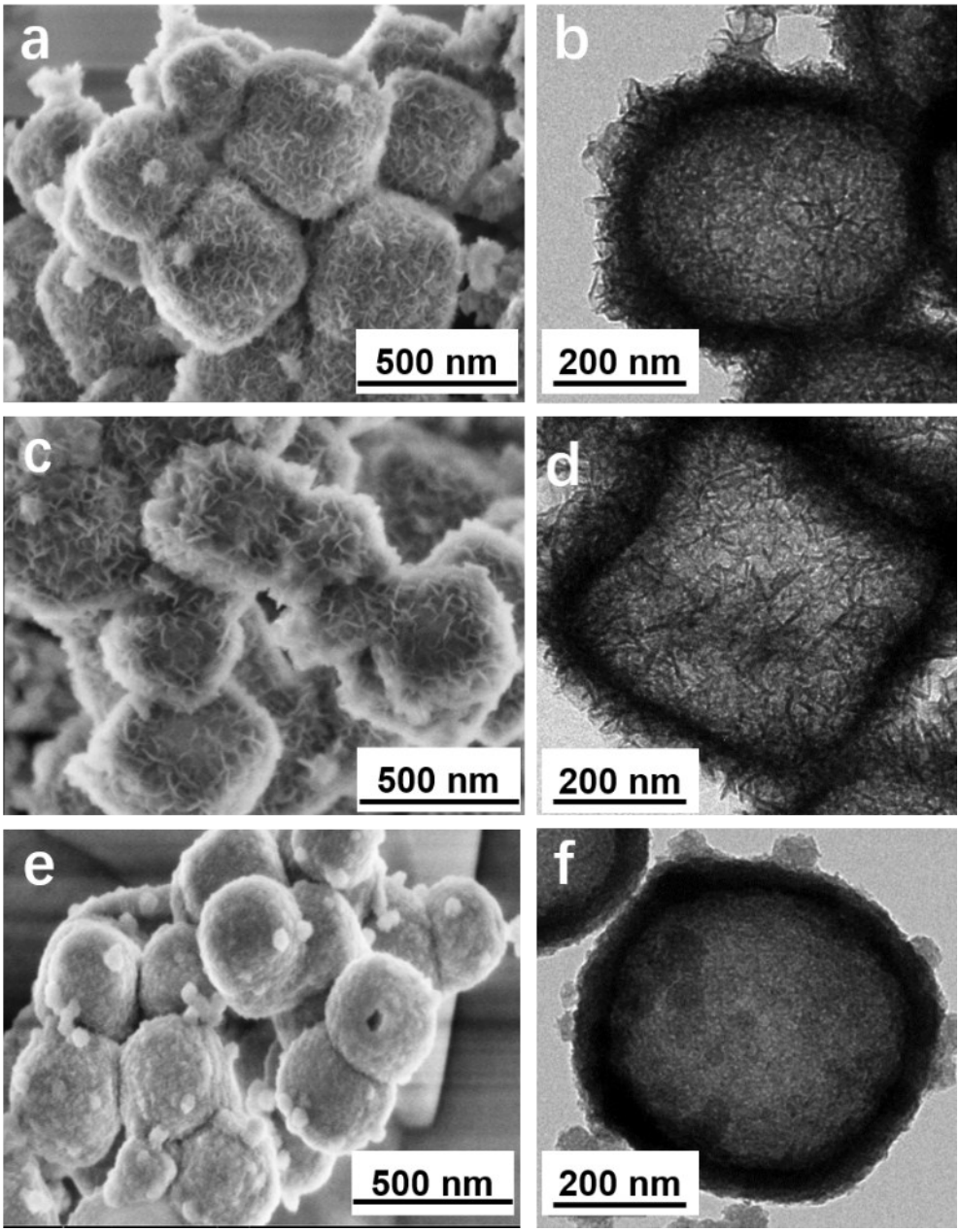
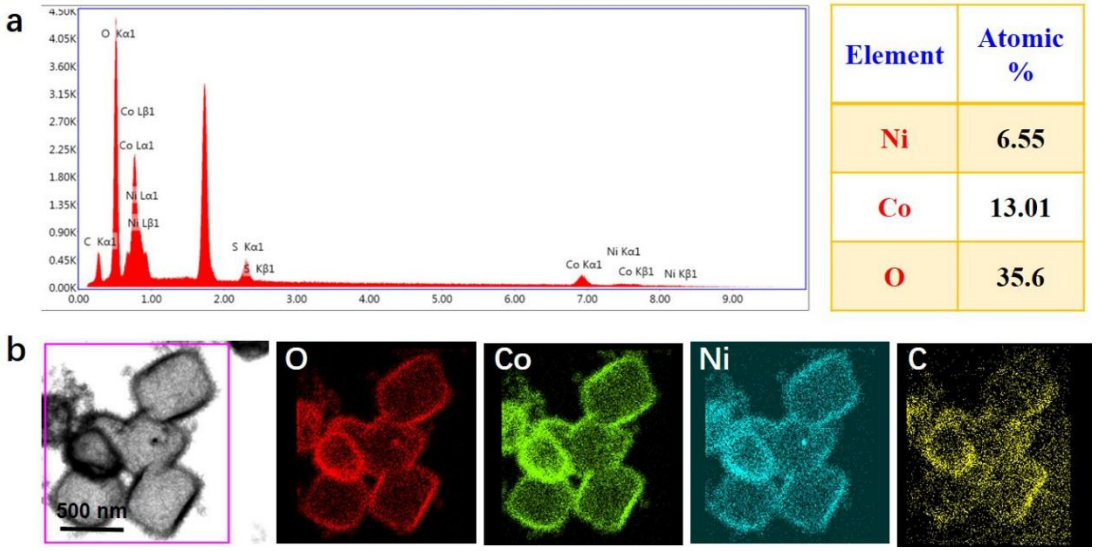


Figure S2. SEM and TEM images of Ni-Co LDHs with different molar ratio of Ni:Co (a, b)1:1, (c, d) 1:3 and (e, f) 3:1.



Element	Atomic %
Ni	6.55
Co	13.01
O	35.6

Figure S3. EDS and mapping images of Ni-Co LDHs.

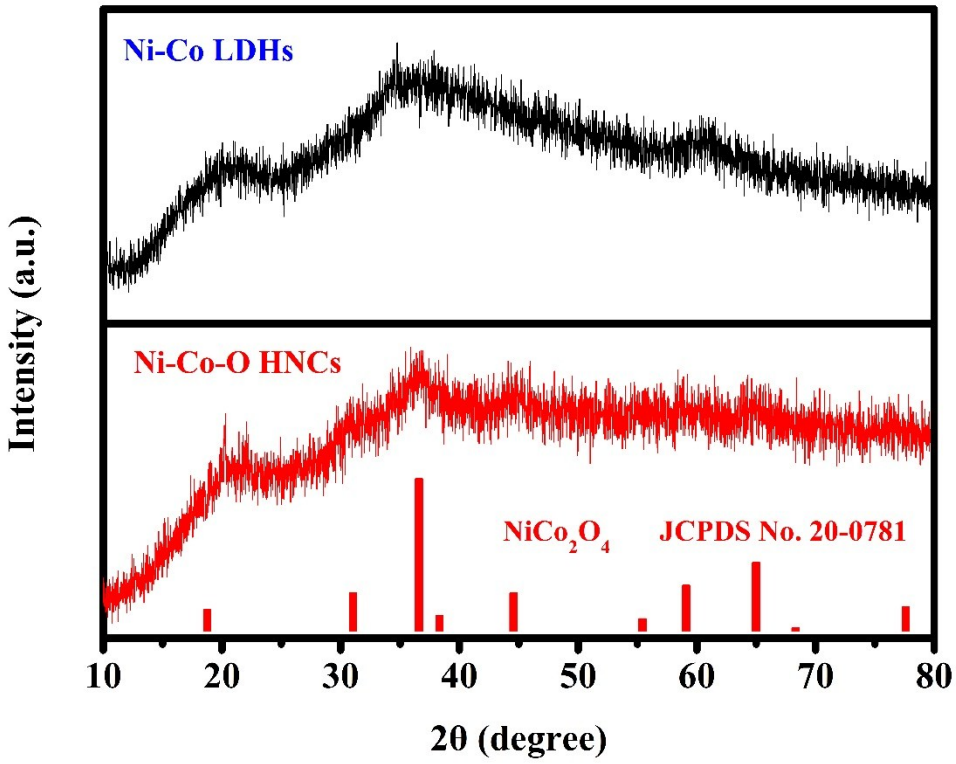


Figure S4. XRD patterns of Ni-Co LDHs and the corresponding Ni-Co-O HNCs.

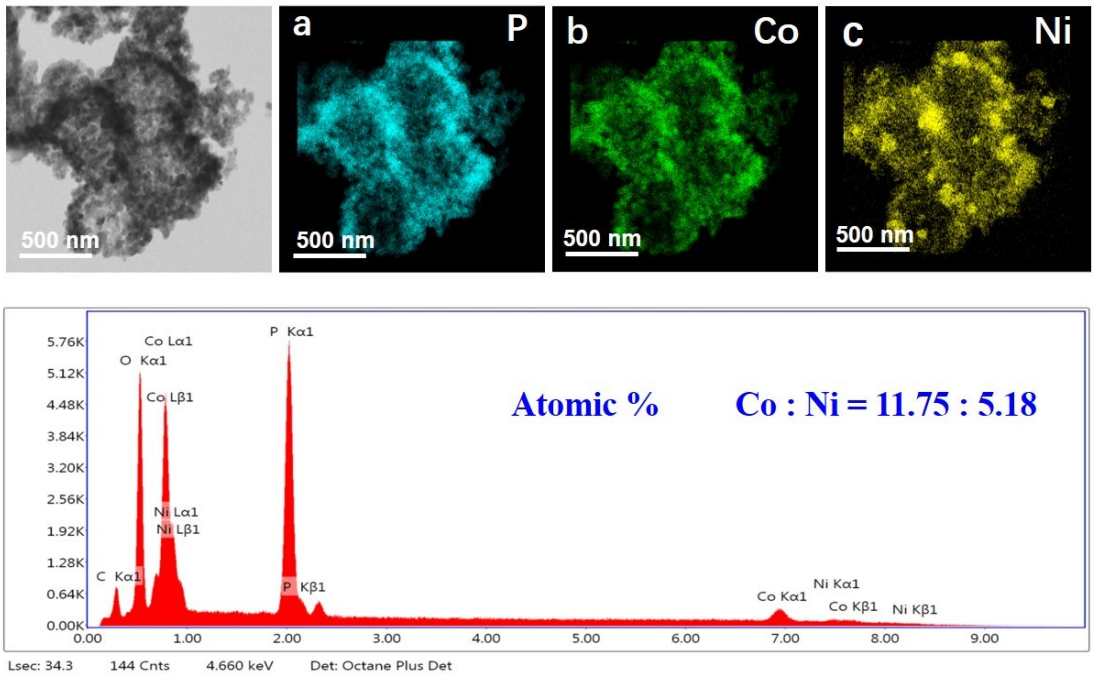


Figure S5. TEM image and EDS elemental mapping of Ni-Co-P HNCs.

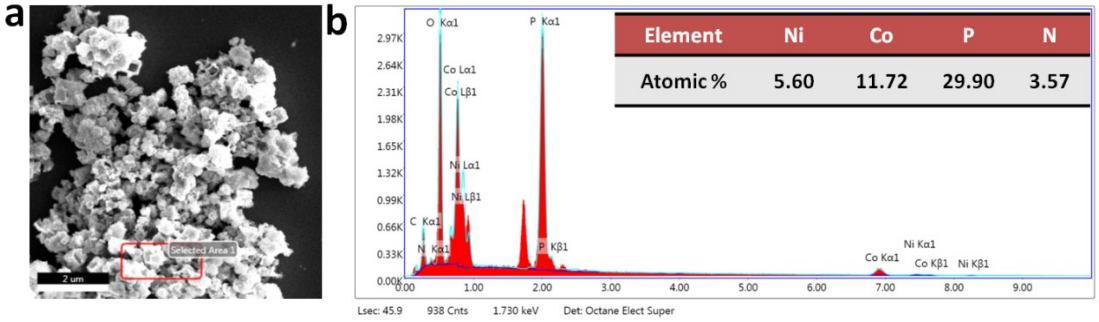


Figure S6. (a) SEM image and (b) EDS N-Ni-Co-P HNCs.

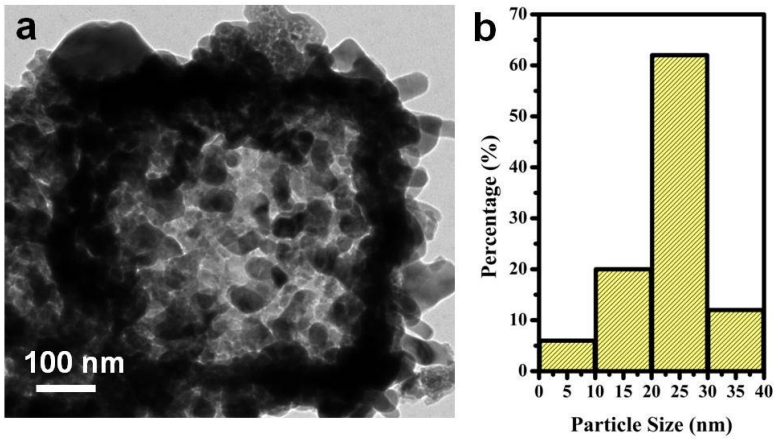


Figure S7. (a)TEM image and (b) coral-horned nanoparticle size statistics of N-Ni-Co-P HNCs.

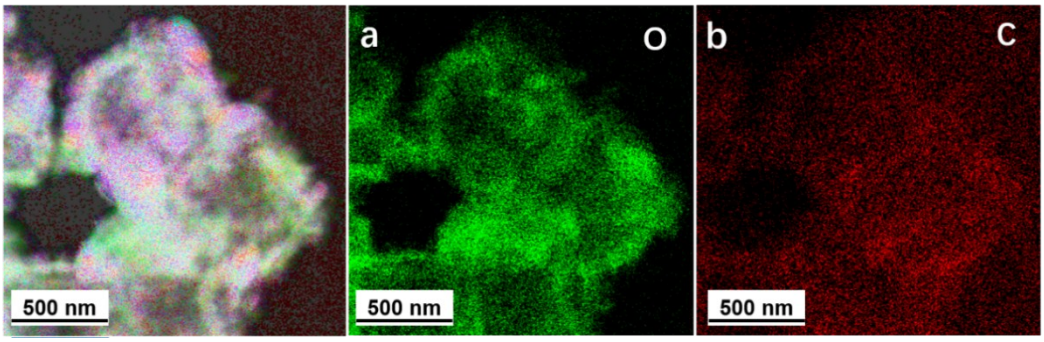


Figure S8. EDX elemental mapping for (a) O, (b) C of N-Ni-Co-P HNCs, corresponding to Figure 3g in the text.

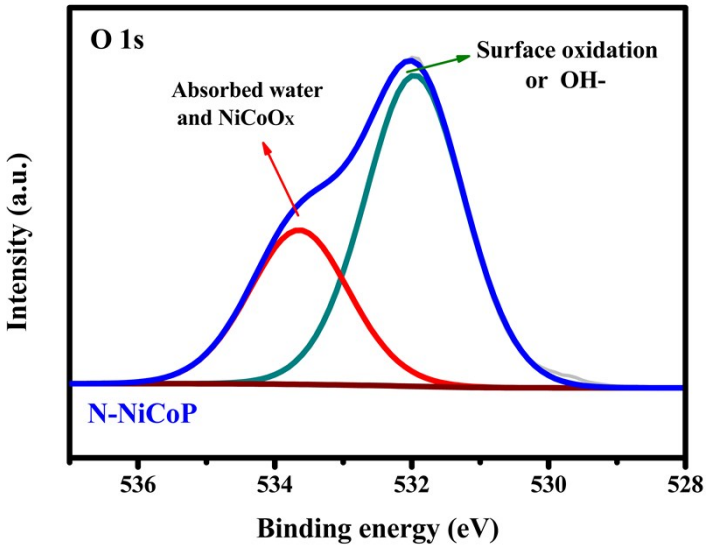


Figure S9. XPS spectrum of O 1s in N-Ni-Co-P HNCs.

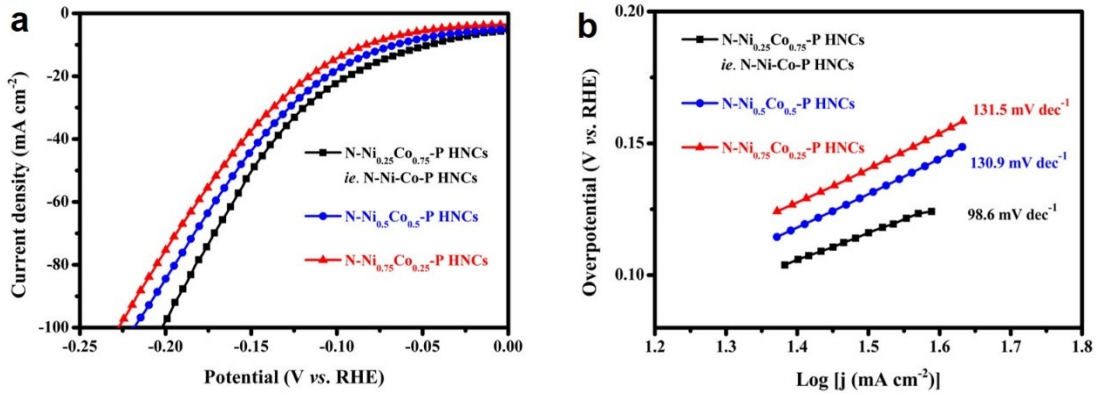


Figure S10. (a) The LSV curves of catalysts with different Ni/Co ratios, (b) The calculated Tafel slopes of the catalysts.

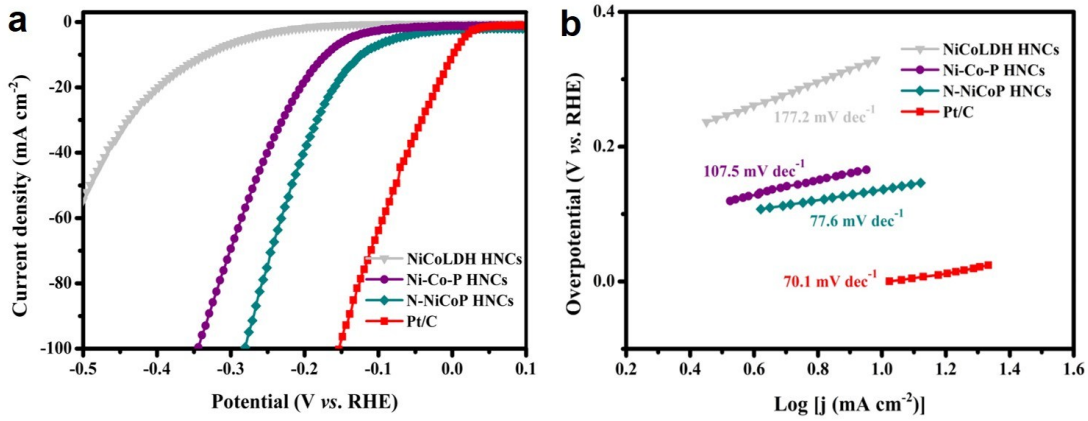


Figure S11. (a) LSV curves and (b) Tafel plots of the as-obtained catalysts on GCE.

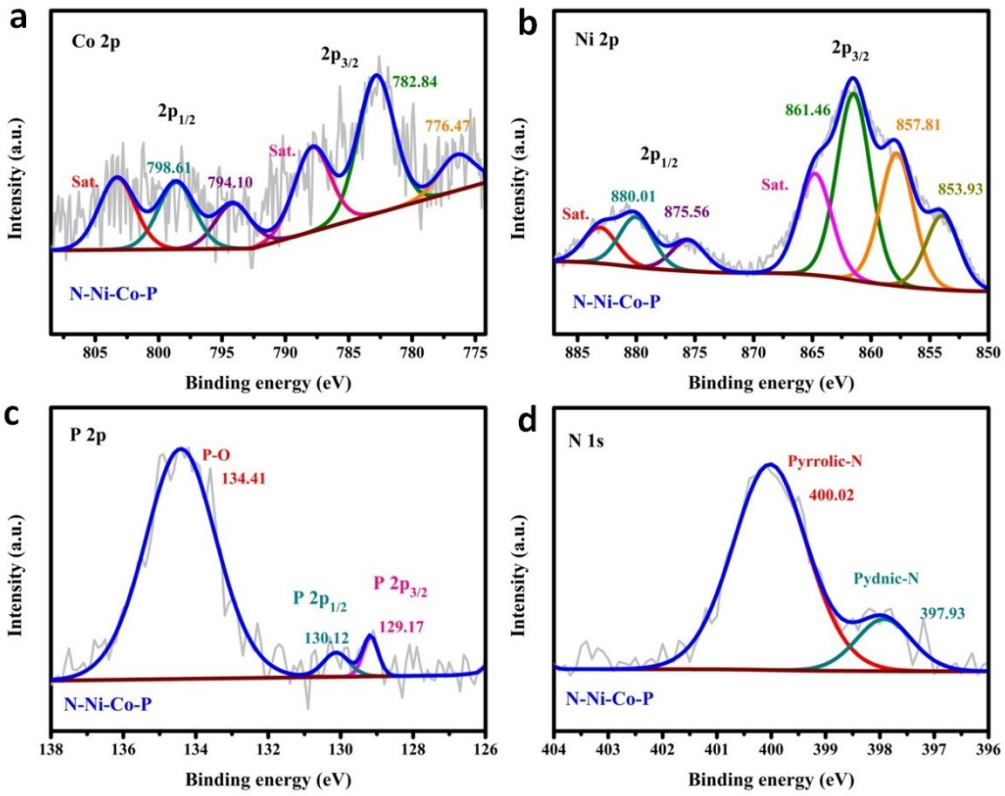


Figure S12. XPS spectra of (a) Co 2p, (b) Ni 2p, (c) P 2p and (d) N 1s of N-Ni-Co-P HNCs after the HER durability test.

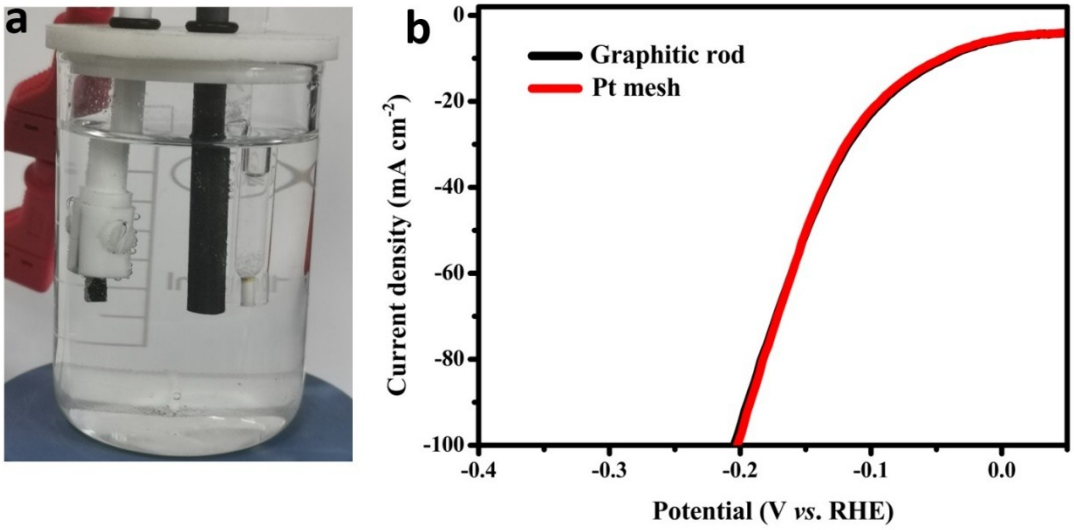


Figure S13. (a) Optical photo showing three-electrode test system (graphite rod as the electrode counter), (b) Catalytic performance of N-Ni-Co-P HNCs using a graphitic rod or a Pt mesh as the counter electrode in 1.0 M KOH, respectively.

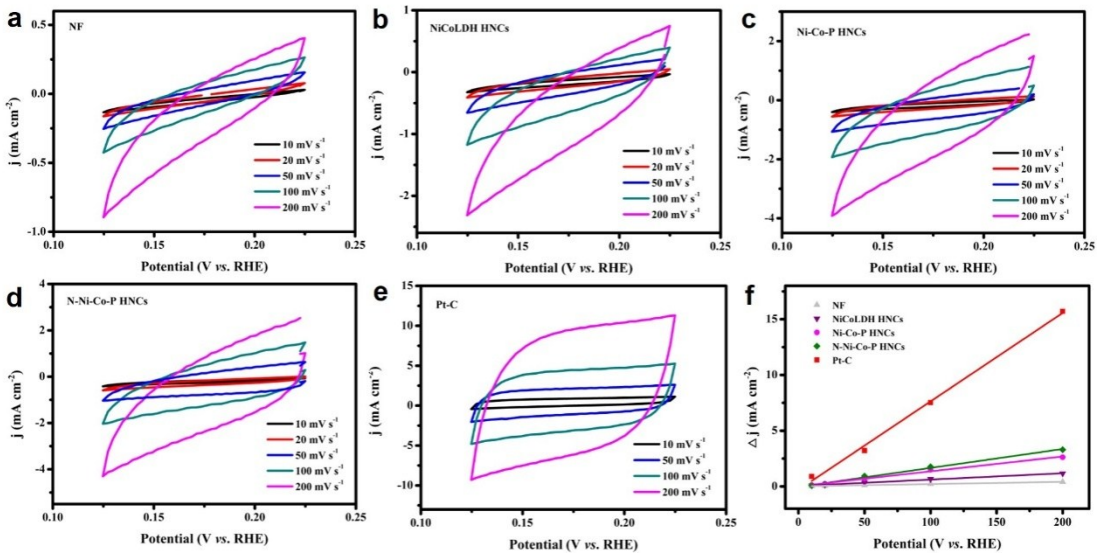


Figure S14. The electrochemical double-layer capacitance (C_{dl}) measurements with different scanning rates of 10, 20, 50, 100 and 200 mV s^{-1} for (a) bare NF, (b) Ni-Co LDH HNCs, (c) Ni-Co-P HNCs (d) N-Ni-Co-P HNCs, (e) Pt-C, (f) The Double-layer capacity currents vs. scan rates of the as-prepared samples.

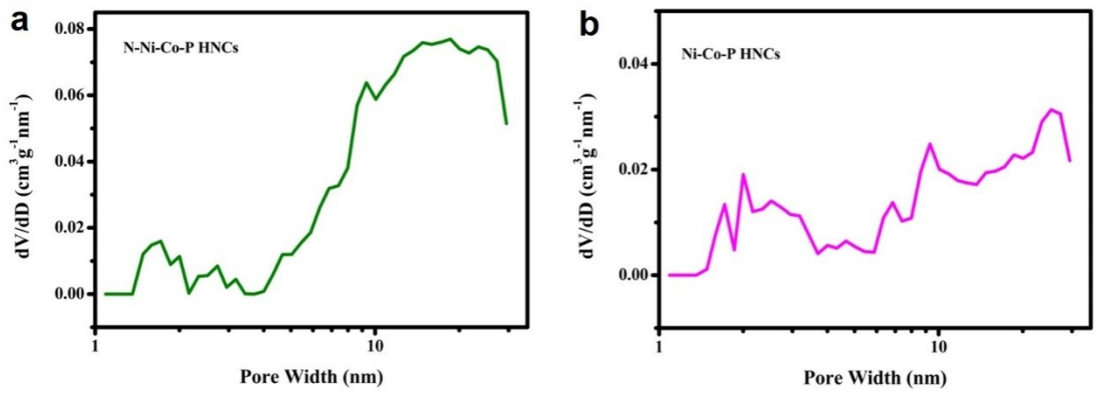


Figure S15. Pore-size distribution of (a) N-Ni-Co-P HNCs, (b) Ni-Co-P HNCs.

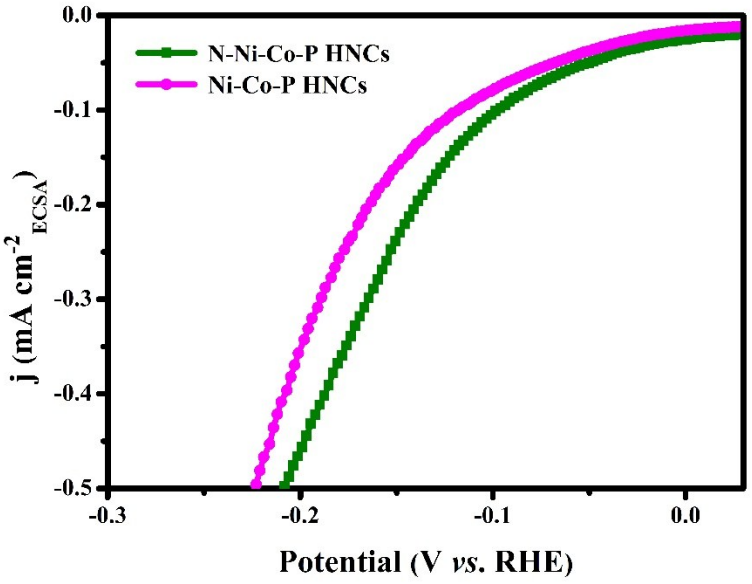


Figure S16. HER polarization curves of N-Ni-Co-P HNCs and Ni-Co-P HNCs catalysts normalized by ECSA.

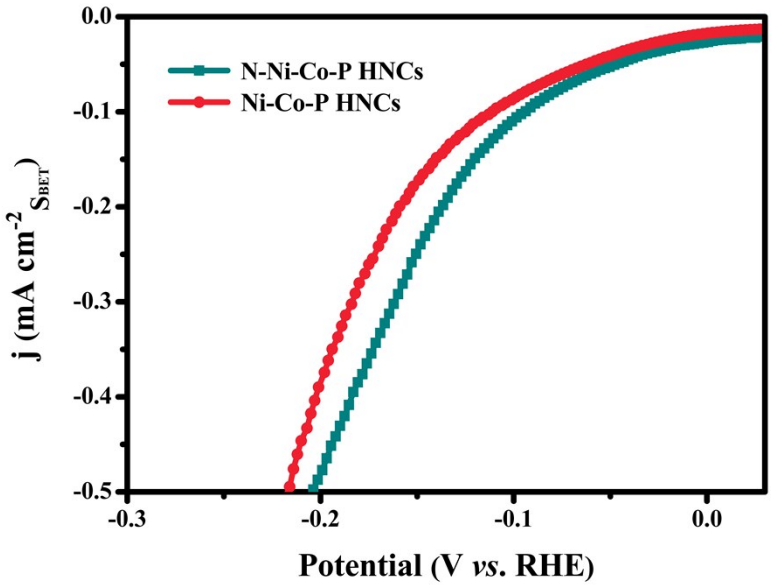


Figure S17. HER polarization curves of N-Ni-Co-P HNCs and Ni-Co-P HNCs catalysts normalized by S_{BET} surface area.

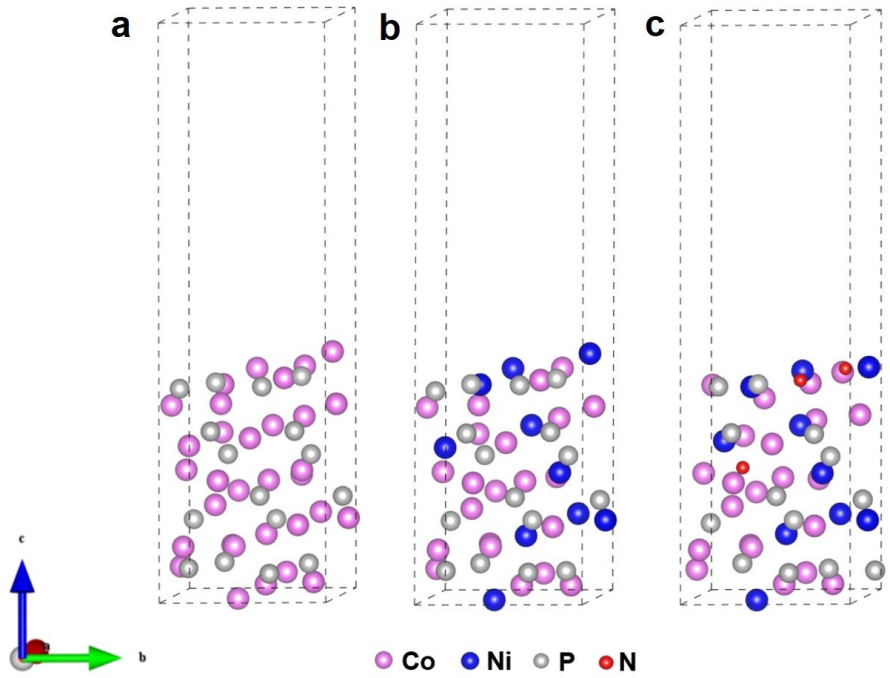


Figure S18. The crystal models of (a) Co_2P, (b) Ni-Co-P and (c) N-Ni-Co-P.

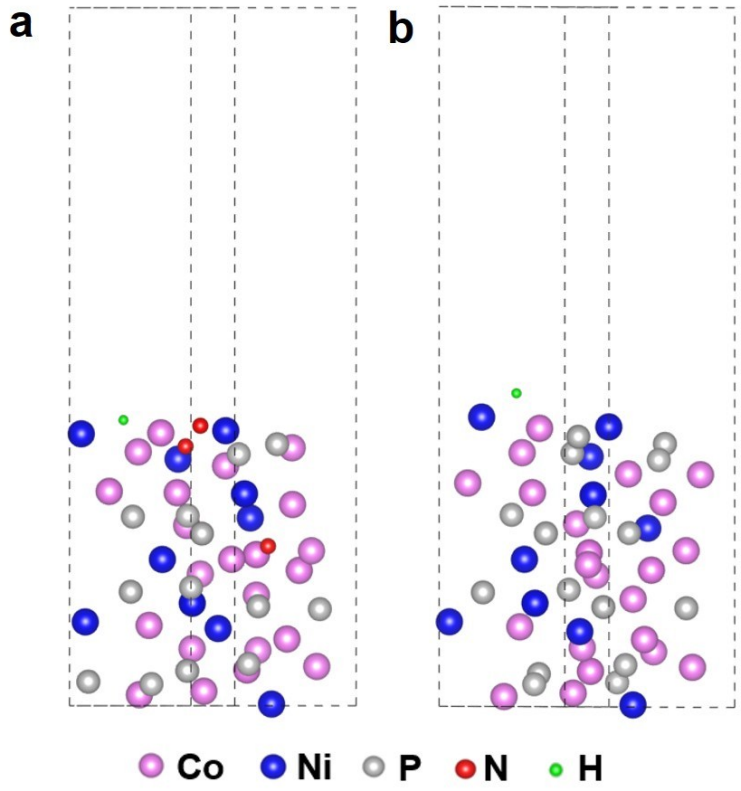


Figure S19. The optimized structure of H* on (111) facet of (a) N-Ni-Co-P and (b) Ni-Co-P.

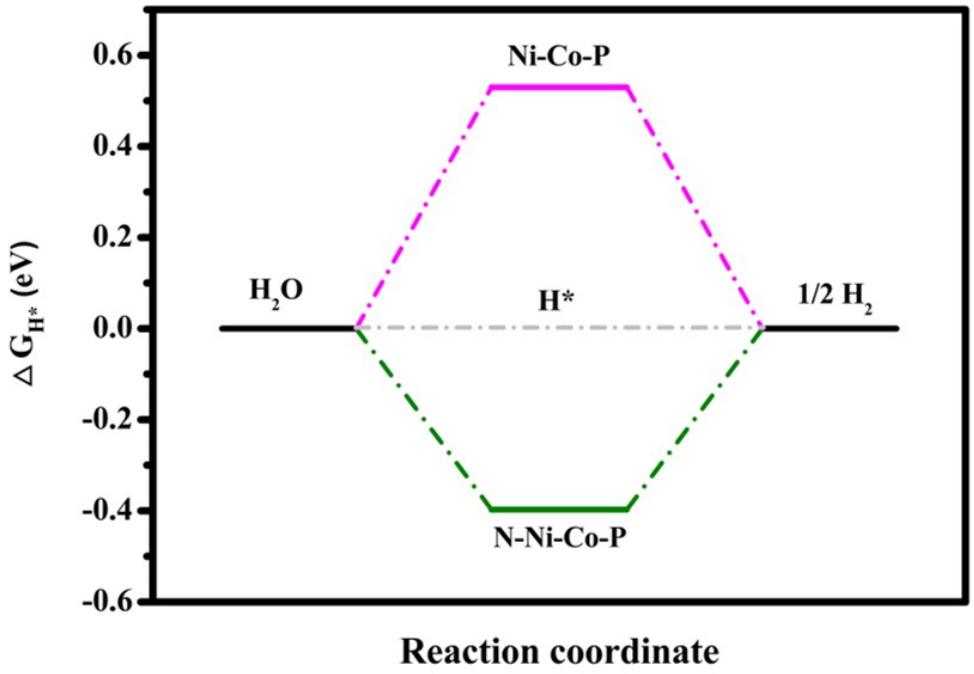


Figure S20. The calculated HER free-energy diagram (FED) on N-Ni-Co-P (001) and Ni-Co-P (001) surface.

The d band center (ε_d) in Figure 8b can be calculated from the following formula [1]:

$$\varepsilon_d = \frac{\int_{-\infty}^{\infty} x\rho(x)dx}{\int_{-\infty}^{\infty} \rho(x)dx} \quad (1)$$

in which x and ρ(x) represent the energy (eV) and d-pdos of Co in Figure 8b.

Table S1. Comparison of HER activity of various TMPs based catalysts

Catalyst	η_{10}/mV	η_{50}/mV	Electrolyte	Reference
N-Ni-Co-P HNCs	47.9	150.5	1M KOH	This work
$Ni_{12}P_5/Ni_3(PO_4)_2$-HS	114		1M KOH	R2
C@Ni_8P_3	110		1M KOH	R3
Ni-Co-P-NF	85		1M KOH	R4
NiCo-LDH/NF	162		1M KOH	R5
NiCoP/CC	62		1M KOH	R6
Ni-Co-P HNBs	107		1M KOH	R7
N-NiCoP/NCF	78		1M KOH	R8
Ni-NiCoP	90	168	1M KOH	R9
Porous Ni-NiCoP	61		1M KOH	R10
NiCoP-CoP/NF	73		1M KOH	R11
S:CoP@NF	109		1M KOH	R12
$Ni_{1.8}Cu_{0.2}$-P/NF	78		1M KOH	R13
CoP/NiCoP/NC	75		1M KOH	R14
Ni_2P/NiCoP@NCCs	116		1M KOH	R15
NiCoP-NWAs/NF	104		1M KOH	R16
Ni-Fe-P@C NRs	79		1M KOH	R17

Table S2. C_{dl}, ECSA, BET and S_{BET} of N-Ni-Co-P HNCs and Ni-Co-P HNCs.

Catalyst	C_{dl} (mF cm^{-2})	ECSA (cm^2)	BET(m^2 g^{-1})	S_{BET}(cm^2)
N-Ni-Co-P HNCs	8.52	42.60	20.87	41.74
Ni-Co-P HNCs	6.67	33.35	15.06	30.12

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