Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Nickel Cobalt Phosphides Quasi-Hollow Nanocubes as an Efficient Electrocatalyst for Hydrogen Evolution in Alkaline Solution

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Experimental Section

Synthesis of Prussian blue analogues:

Synthesis of Ni-Co PBA nanocubes: In a typical procedure, 0.6 mmol of nickel nitrate and 0.9 mmol of sodium citrate were dissolved in 20 mL of deionized water (DIW) to form solution A. 0.4 mmol of potassium hexacyanocobaltate(III) was dissolved in 20 mL of DIW to form solution B. Then, solutions A and B were mixed under magnetic stirring for 3 min. The obtained mixed solution was aged for 18 h at room temperature. After collected by centrifugation and washed with water and ethanol, the precipitates were dried at 70 ^{o}C overnight.

Synthesis of Co-Co PBA microcubes: In a typical procedure, 0.6 mmol of cobalt acetate and 0.9 mmol of sodium citrate were dissolved in 20 mL of DIW to form solution A. 0.4 mmol of potassium hexacyanocobaltate(III) was dissolved in 20 mL of DIW to form solution B. Then, solutions A and B were mixed under magnetic stirring for 3 min. The obtained mixed solution was aged for 18 h at room temperature. After collected by centrifugation and washed with water and ethanol, the precipitates were dried at 70 ^{o}C overnight.

Synthesis of Ni-Ni PBA nanoplates: In a typical procedure, 0.4 mmol of nickel cloride and 0.3 mmol of sodium citrate were dissolved in 20 mL of DIW to form solution A. 0.4 mmol of potassium tetracyanonickelate(II) was dissolved in 20 mL of DIW to form solution B. Then, solutions A and B were mixed under magnetic stirring for 3 min. The obtained mixed solution was aged for 18 h at room temperature. After collected by centrifugation and washed with water and ethanol, the precipitates were dried at 70 ^{o}C overnight.

Synthesis of Co-Ni PBA stacked nanoplates: In a typical procedure, 0.8 mmol of cobalt cloride and 0.35 mmol of sodium citrate were dissolved in 20 mL of DIW to form solution A. 0.4 mmol of potassium tetracyanonickelate(II) was dissolved in 20 mL of DIW to form solution B. Then, solutions A and B were mixed under magnetic stirring for 3 min. The obtained mixed solution was aged for 18 h at room temperature. After collected by centrifugation and washed with water and ethanol, the precipitates were dried at 70 ^{o}C overnight.

Synthesis of metal phosphides: In a typical synthesis, the as-obtained PBA were phosphidated by thermal decomposition of NaH_2PO_2 under Ar gas flow. 20 mg PBA and 200 mg NaH_2PO_2 were put at two separate positions in a porcelain boat with NaH_2PO_2 at the upstream side of the tube furnace. Then, the samples were annealed at 300 °C for 2 h with a heating rate of 3 °C min^{-1} under Ar atmosphere with a flow rate of 60 sccm. The metal phosphides were obtained after cooling to ambient temperature under Ar gas. For the phosphidation of Ni-Co PBA and Co-Co PBA, the calcination temperatures of 400 and 500 °C were also used.

Materials Characterization: Powder X-ray diffraction (XRD) measurements of the samples were performed with a Rigaku D/MAX RINT-2000 X-Ray Diffractometer. Field-emission scanning electron microscope (FESEM; JEOL, JSM07600F) and transmission electron microscope (TEM; JEOL, JEM-2100F) were used to examine the morphology of the samples. The composition of the samples and elemental mapping was analyzed by energy-dispersive X-ray spectroscope (EDX) attached to the TEM instrument. X-ray photoelectron spectrometer (XPS, VG microtech ESCA2000) was used for the analysis of the composition of the as-synthesized samples.

Electrochemical Measurements: The HER activity was evaluated in a three-electrode configuration using a rotating disk electrode (RDE) (Autolab RDE/2, at a rotation speed of 1500 rpm) with an Autolab potentiostat/galvanostat (Model PGSTAT-72637) workstation at ambient temperature. A glassy carbon electrode (GCE) with a diameter of 3 mm was used as the support for the working electrode. The catalyst suspension was prepared by dispersing 5 mg of catalyst in 1 mL of solution containing 0.5 mL of DIW, 0.44 mL of ethanol and 60 µL of 0.5 wt.% Nafion solution followed by ultrasonication for 30 min. 4 µL of the catalyst suspension was pipetted onto the GCDE surface using a micropipettor and then dried at ambient temperature. The catalyst loading amount is 0.286 mg cm^{-2} on the GCE. A Ag/AgCl (KCl saturated) electrode was used as the reference electrode and a platinum disc electrode was used as the counter electrode. Potentials were referenced to a reversible hydrogen electrode (RHE): E(RHE) = E(Ag/AgCl) + (0.2 + 0.059 pH)V. Linear sweep voltammetry (LSV) was recorded in 1 M KOH (pH = 13.62) at a scan rate of 5 mV s^{-1} to obtain the polarization curves. The long-term stability tests were performed by continuous LSV scans and a sweep rate of 50 mV s^{-1} was used. All the data presented were corrected for i*R* losses and background current. EIS was performed at various overpotentials with frequency from 0.1 to 100,000 Hz and an amplitude of 5 mV.

Table S1. Comparison of the HER activity for several reported non-noble metal-based electrocatalysts in alkaline solution.

Electrocatalysts	**η@10 mA cm^{-2} [mV]**	**Tafel slope (mV dec^{-1})**	**Ref.**
Ni-Co-P-300	**150**	**60.6**	**This work**
Co-P-300	**280**	**94.1**	**This work**
Ni-P	**350**	**132.3**	**This work**
Co-Ni-P	**167**	**71.2**	**This work**
Co-entrapped N-doped carbon nanotubes	**180**	**193**	**1**
Ni_2P nanoparticles	**~225**	**100**	**2**
CoP nanowire arrays	**209**	**129**	**3**
NiP_2 nanosheet arrays	**102**	**65**	**4**
Ni_5P_4 nanostructured films	**150**	**53**	**5**
WN nanorod arrays	**285**	**170**	**6**

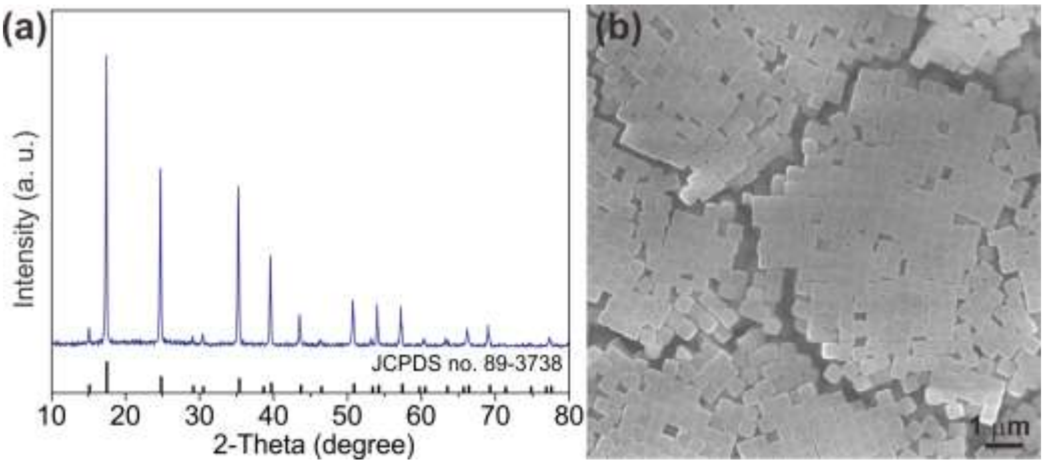


Fig. S1 XRD pattern (a) and large-scale SEM image (b) of Ni-Co PBA.

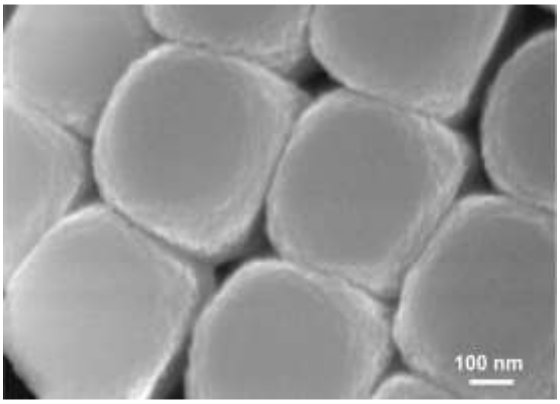


Fig. S2 High resolution SEM image of Ni-Co PBA.

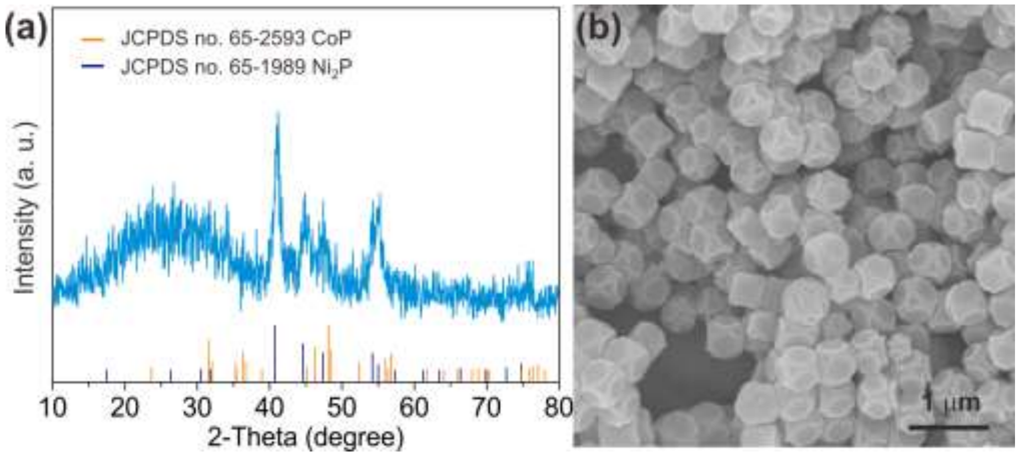
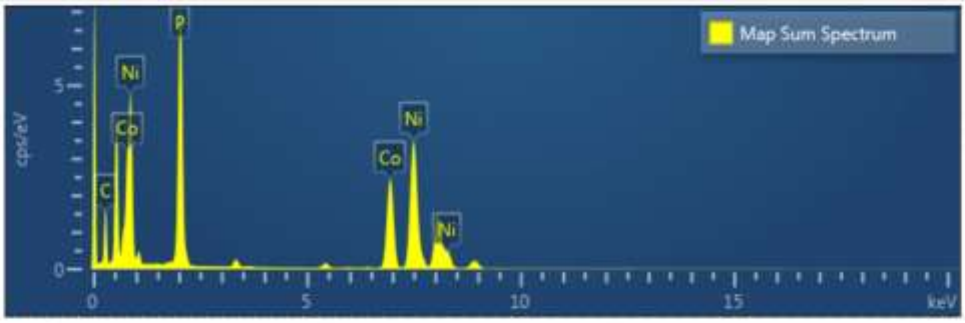
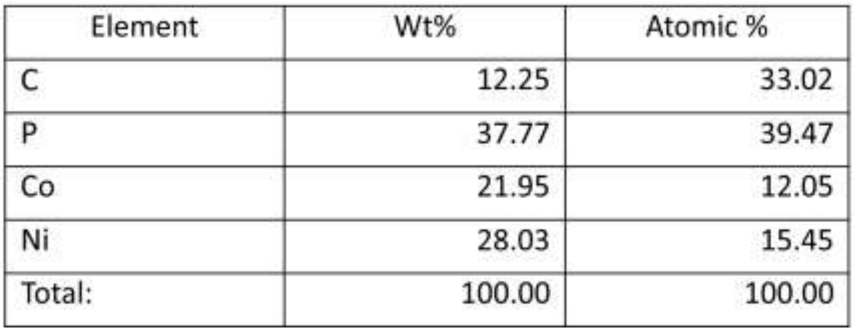


Fig. S3 XRD pattern (a) and large-scale SEM image (b) of Ni-Co-P nanocubes synthesized at 300 ^{o}C.





Element	Wt%	Atomic %
C	12.25	33.02
P	37.77	39.47
Co	21.95	12.05
Ni	28.03	15.45
Total:	100.00	100.00

Fig. S4 EDX spectrum of Ni-Co-P nanocubes synthesized at 300 °C.

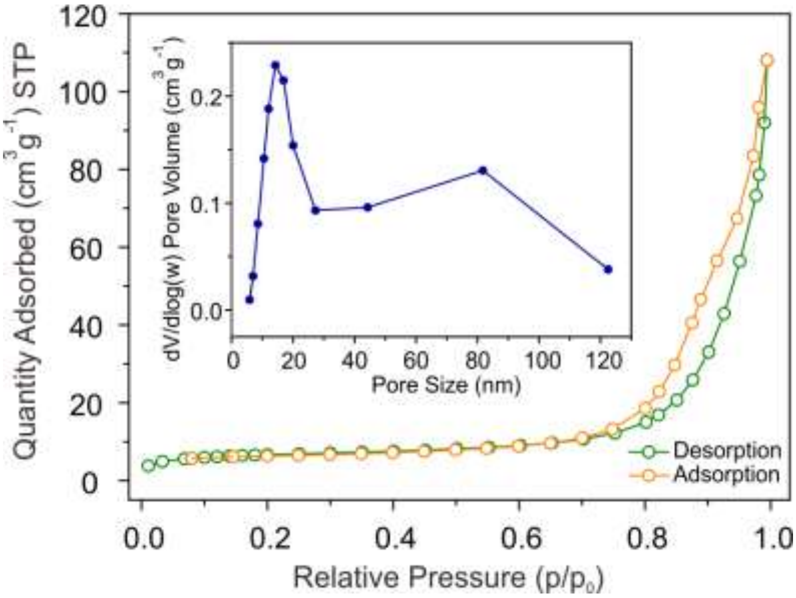


Fig. S5 N_2 adsorption-desorption isotherms and pore size distribution (inset) of Ni-Co-P-300 quasi-hollow nanocubes.

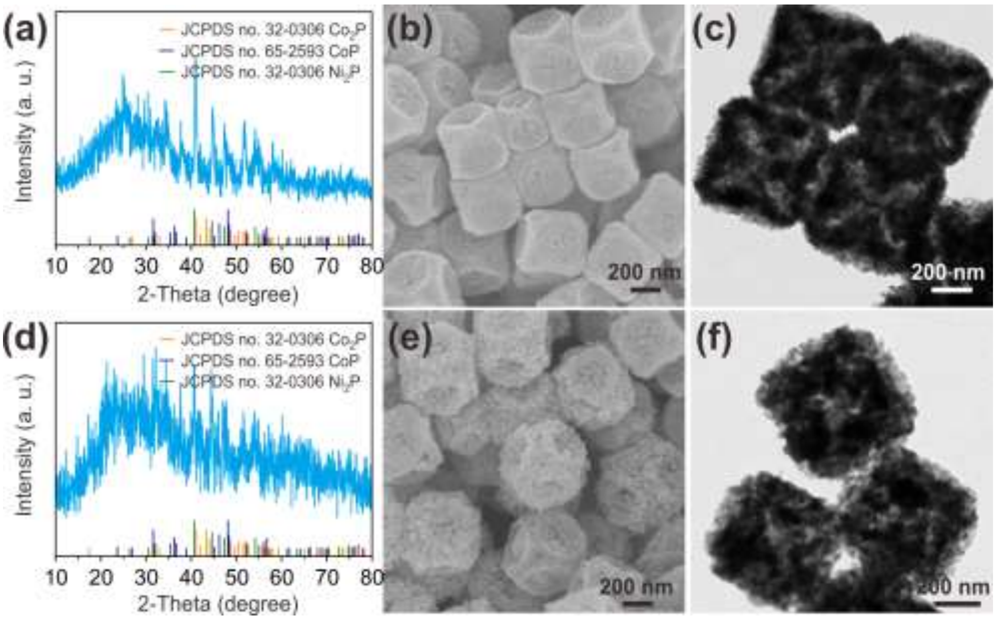


Fig. S6 XRD patterns (a, d), SEM images (b, e) and TEM images (c, f) of Ni-Co-P nanocubes synthesized at 400 ^{o}C and 500 ^{o}C, respectively. Fig. S4a and d demonstrate that Ni-Co-P-400 and Ni-Co-P-500 are composed of Ni_2P, CoP and Co_2P. FESEM (Fig. S4b and e) and TEM (Fig. S4c and f) images reveal that the cubic structure can still be maintained after phosphidation at high temperature.

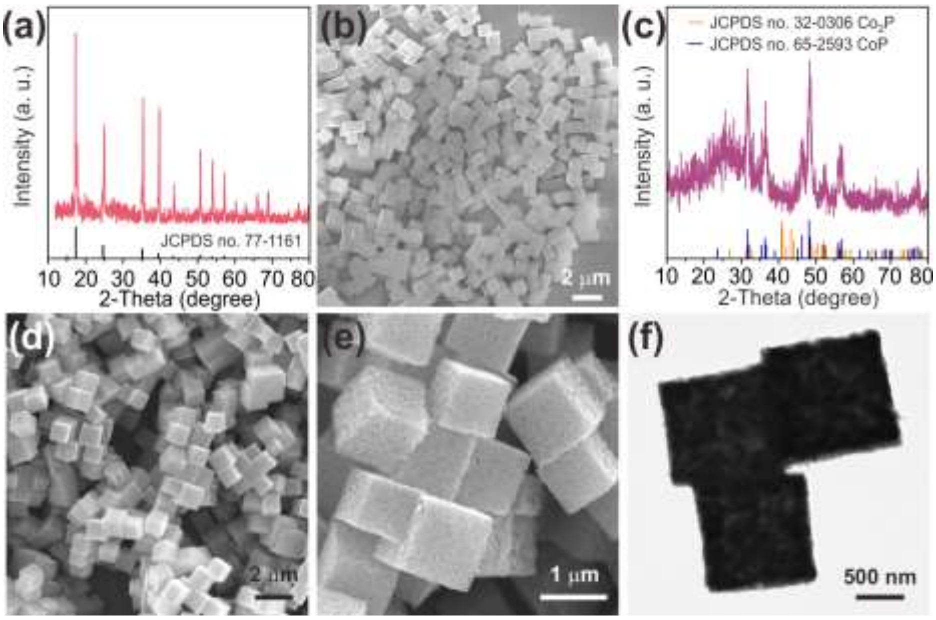


Fig. S7 XRD pattern (a) and large scale SEM image (b) of Co-Co PBA; XRD pattern (c), SEM images (d, e), and TEM image (f) of Co-P microcubes synthesized at 300 °C.

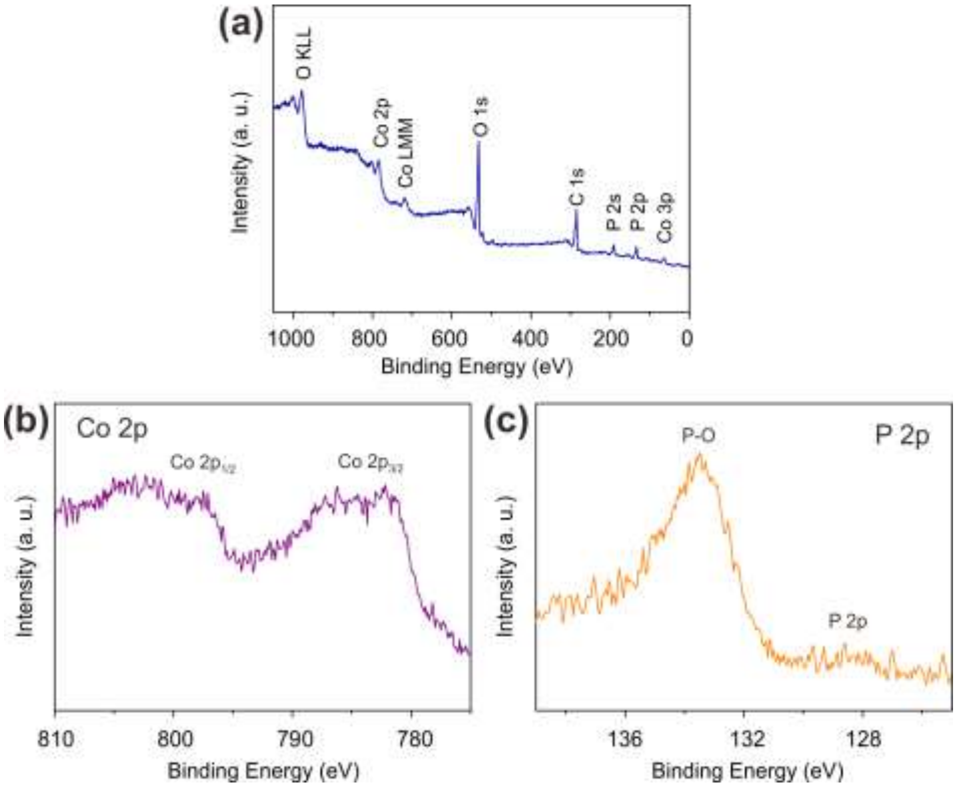


Fig. S8 XPS spectra of Co-P microcubes synthesized at 300 °C: survey (a) and high resolution spectra of Co 2p (b) and P 2p (c).

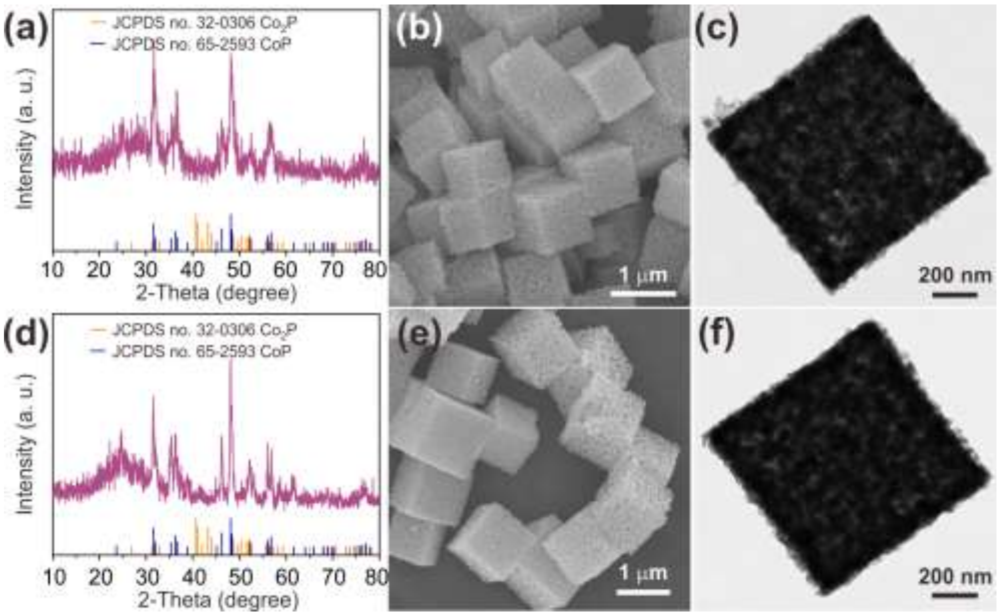


Fig. S9 XRD patterns (a, d), SEM images (b, e) and TEM images (c, f) of Co-P microcubes synthesized at 400 ^{o}C (a-c) and 500 ^{o}C (d-f). Both Co-P-400 and Co-P-500 are composed of Co_2P and CoP with porous microcube structure.

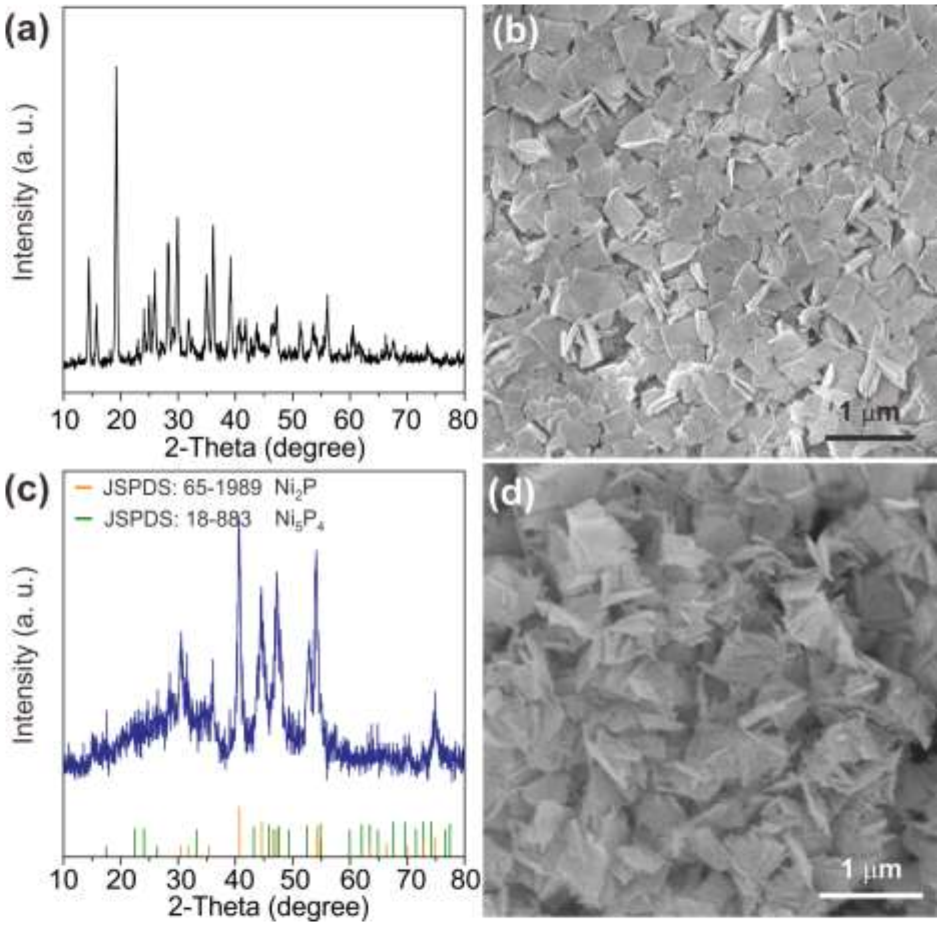


Fig. S10 XRD patterns (a, c) and large-scale SEM images (b, d) of Ni-Ni PBA (a, b) and Ni-P nanoplates (c, d).

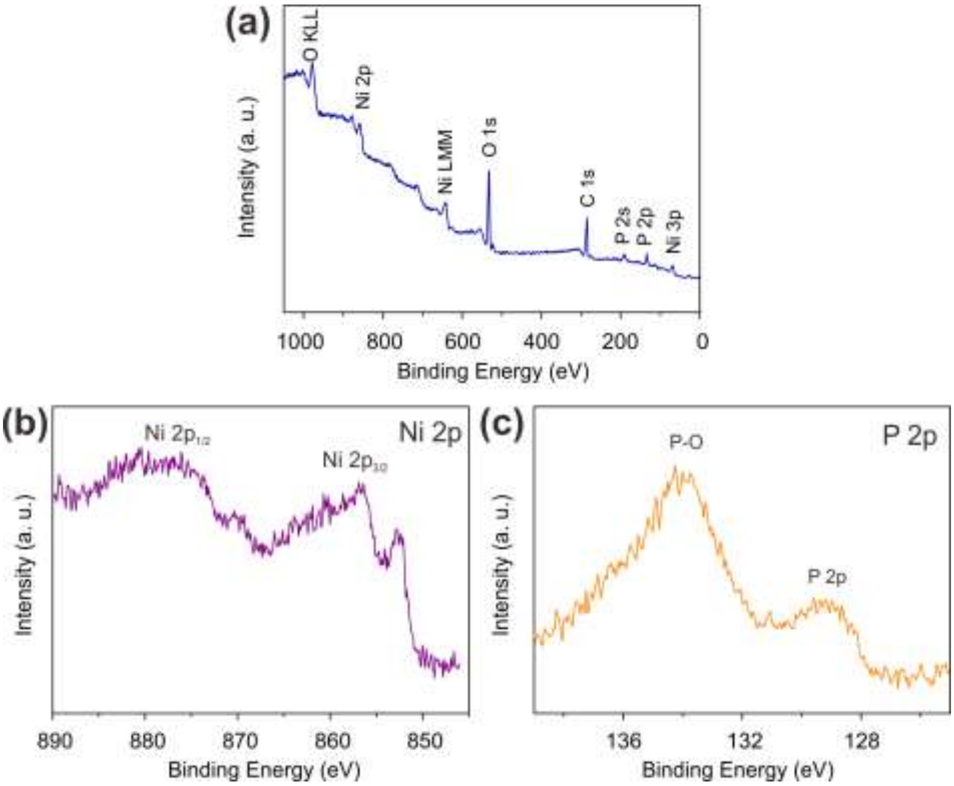


Fig. S11 XPS spectra of Ni-P nanoplates: survey (a) and high resolution spectra of Ni 2p (b) and P 2p (c).

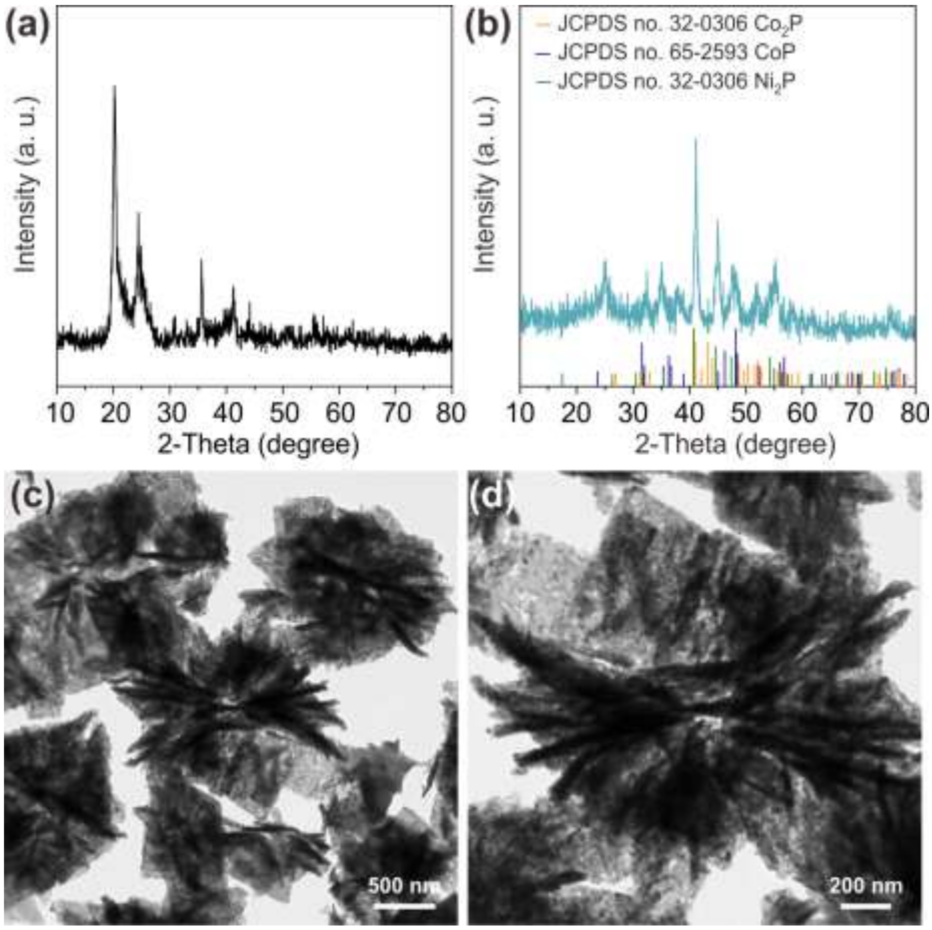


Fig. S12 XRD patterns (a, b) and TEM images (c, d) of Co-Ni PBA (a), and Co-Ni-P stacked nanoplates (b-d).

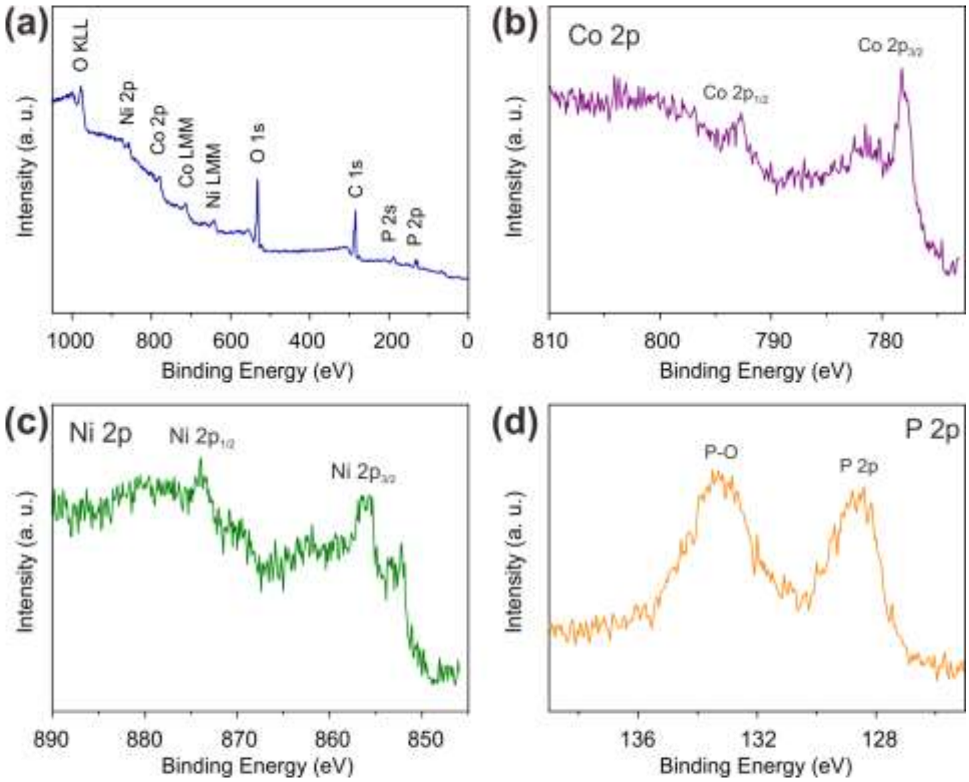


Fig. S13 XPS spectra of Co-Ni-P stacked nanoplates: survey (a) and high resolution spectra of Co 2p (b), Ni 2p (c) and P 2p (d).

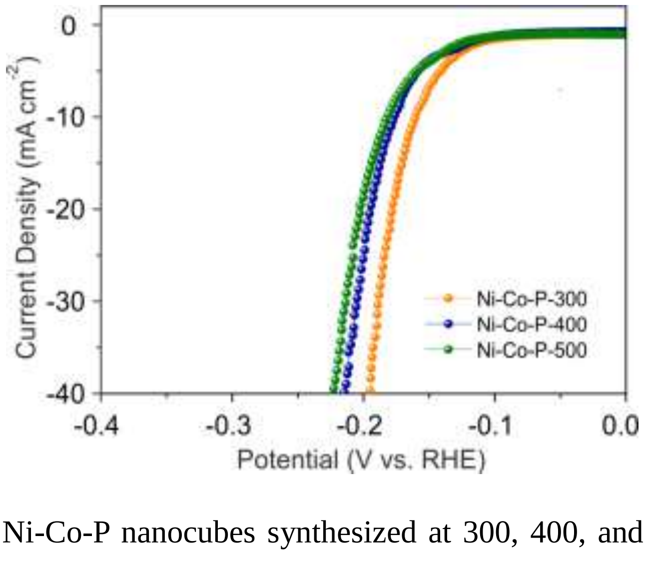


Fig. S14 LSV curves of Ni-Co-P nanocubes synthesized at 300, 400, and 500 ^{o}C. **Their different HER performances may be attributed to the morphology and composition differences.**

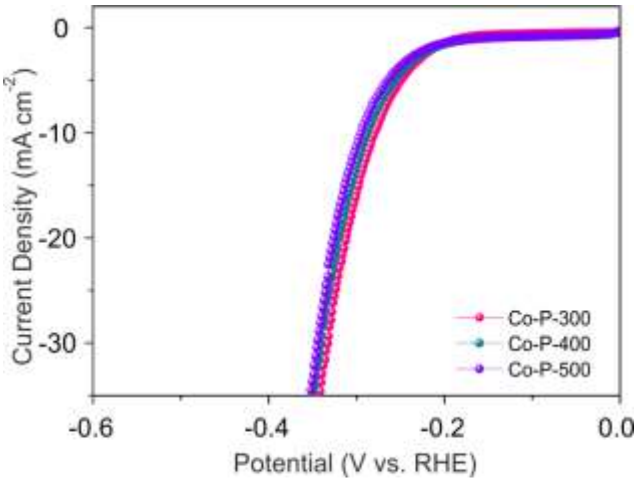


Fig. S15 LSV curves of Co-P microcubes synthesized at 300, 400, and 500 °C.

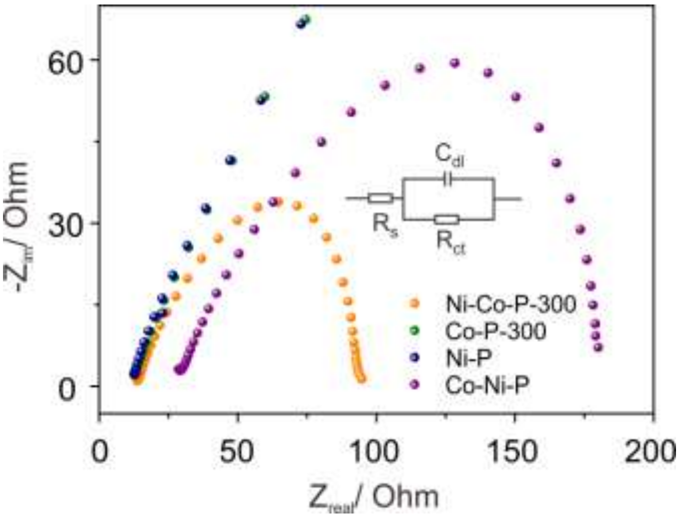


Fig. S16 Enlarged EIS Nyquist plots of Ni-Co-P-300 nanocubes, Co-P-300 microcubes, Ni-P nanoplates and Co-Ni-P stacked nanoplates in 1 M KOH at an overpotential of 160 mV.

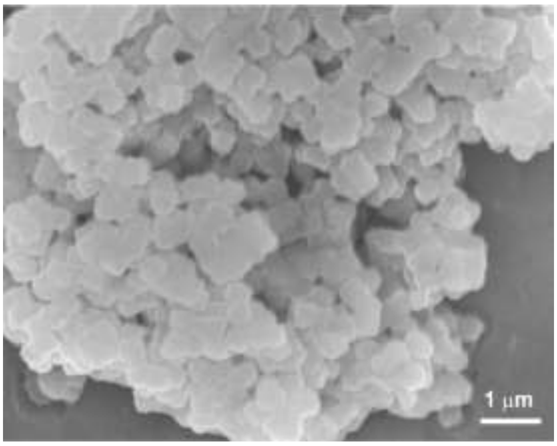


Fig. S17 SEM image of Ni-Co-P-300 after stability test.

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