Electronic Supplementary Information

Construction of hierarchical Ni-Co-P hollow nanobricks with oriented nanosheets for efficient overall water splitting

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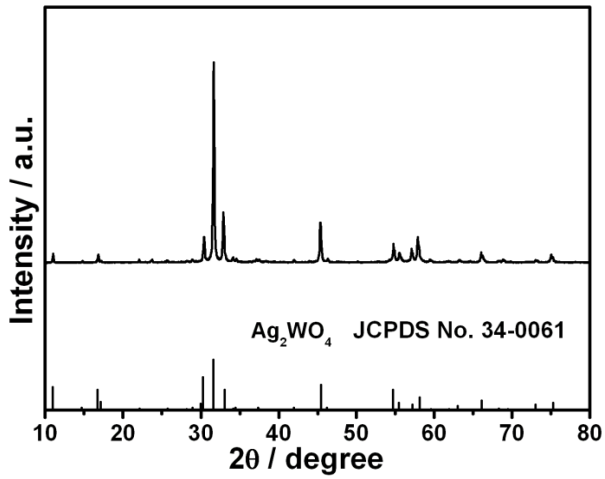


Fig. S1 XRD Pattern of the as-prepared Ag_2WO_4 solid nanobricks.

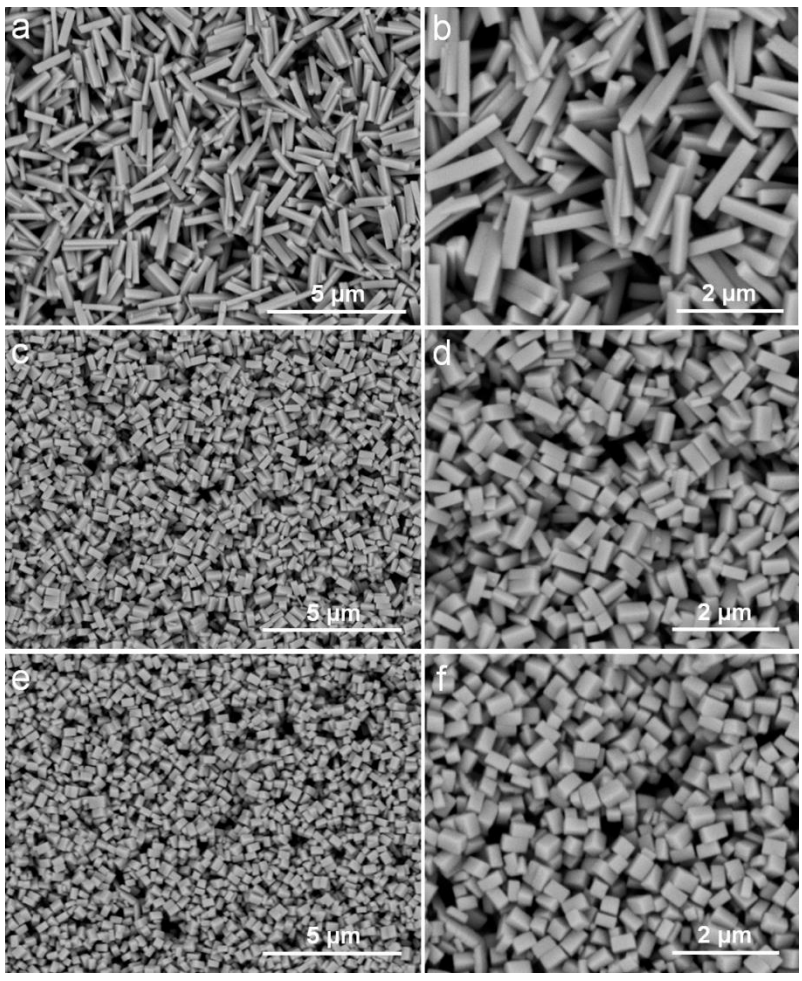


Fig. S2 FESEM images of Ag_2WO_4 obtained by using different amounts of PVP in both $AgNO_3$ and Na_2WO_4 solution: (a, b) 0.25 g, (c, d) 0.75 g, and (e, f) 1.0 g.

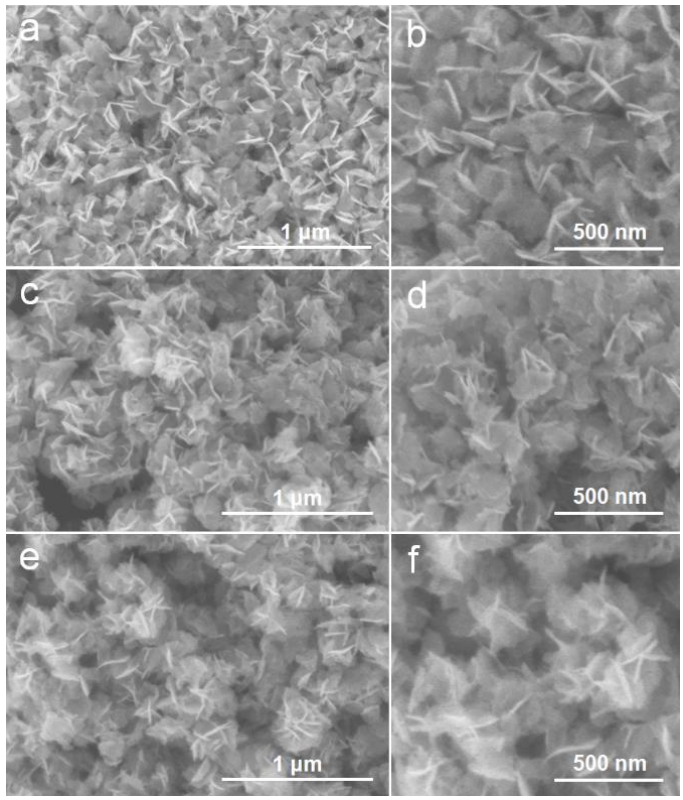


Fig. S3 FESEM images of (a, b) Ni-Co precursor nanosheets, (c, d) Ni-Co-O nanosheets, and (e, f) Ni-Co-P nanosheets.

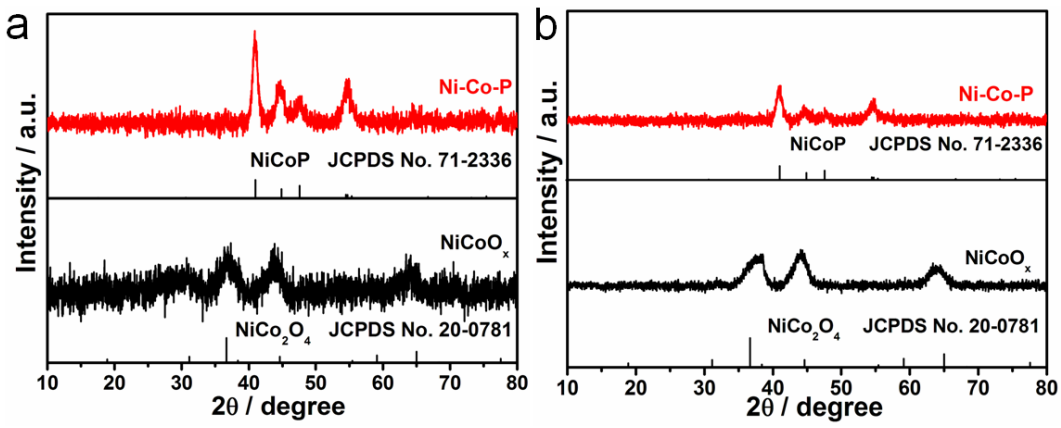
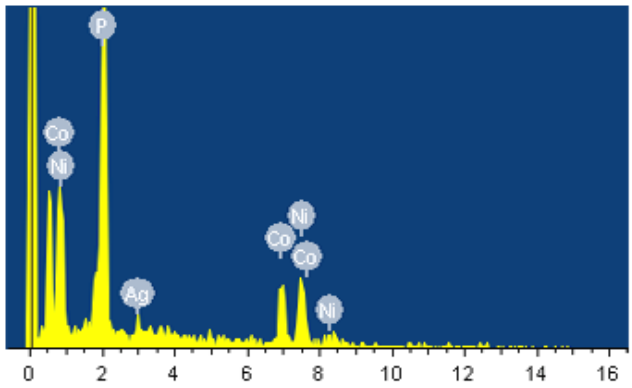


Fig. S4 XRD patterns of the as-prepared hierarchical (a) Ni-Co-O and Ni-Co-P HNBs and (b) Ni-Co-O and Ni-Co-P nanosheets.

a



b

Element	Atomic percentage (%)
P K	55.39
Co L	18.82
Ni L	24.01
Ag L	1.78

Fig. S5 (a) EDX spectrum and (b) atomic percentage of the as-prepared Ni-Co-P HNBs.

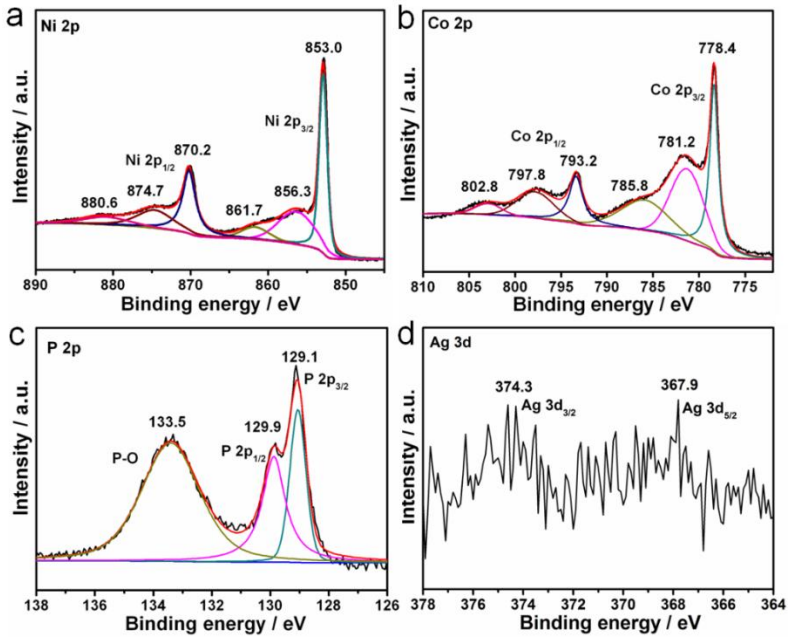


Fig. S6 High-resolution XPS spectra of the Ag-incorporated Ni-Co-P HNBs: (a) Ni 2p, (b) Co 2p, (c) P 2p, and (d) Ag 3d.

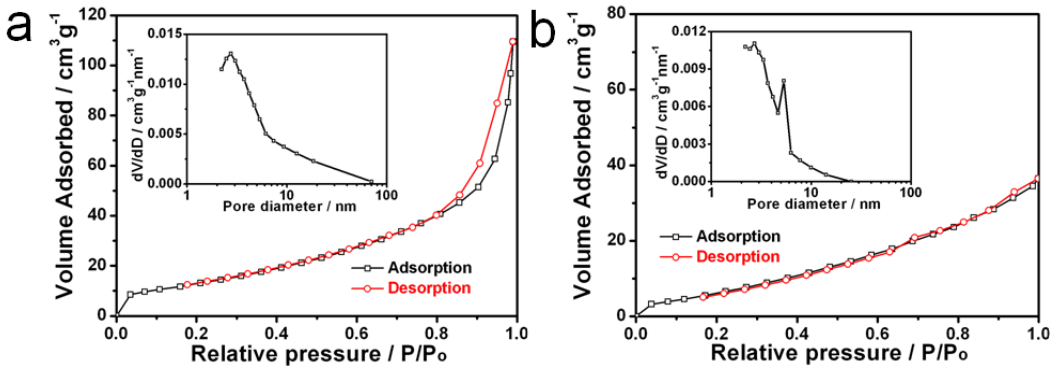


Fig. S7 N_2 adsorption-desorption isotherms and pore-size distribution curves of the as-prepared (a) hierarchical Ni-Co-P HNBs and (b) Ni-Co-P nanosheets.

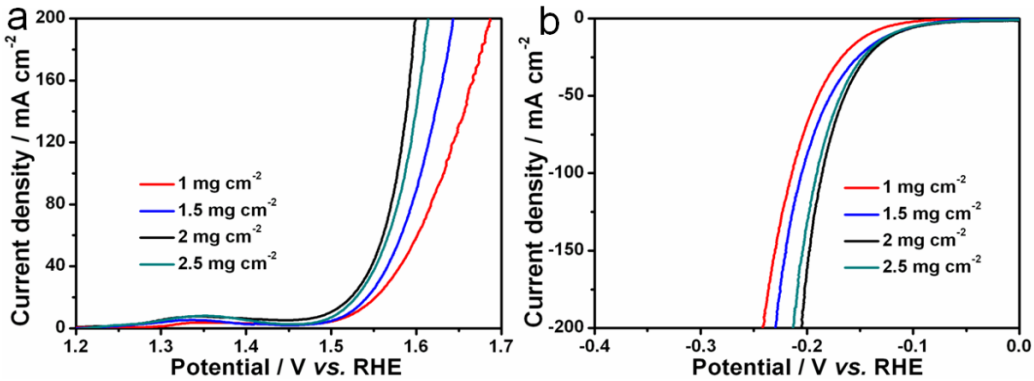


Fig. S8 Polarization curves of the hierarchical Ni-Co-P HNBs with the different mass loading on Ni foam substrate for (a) OER and (b) HER.

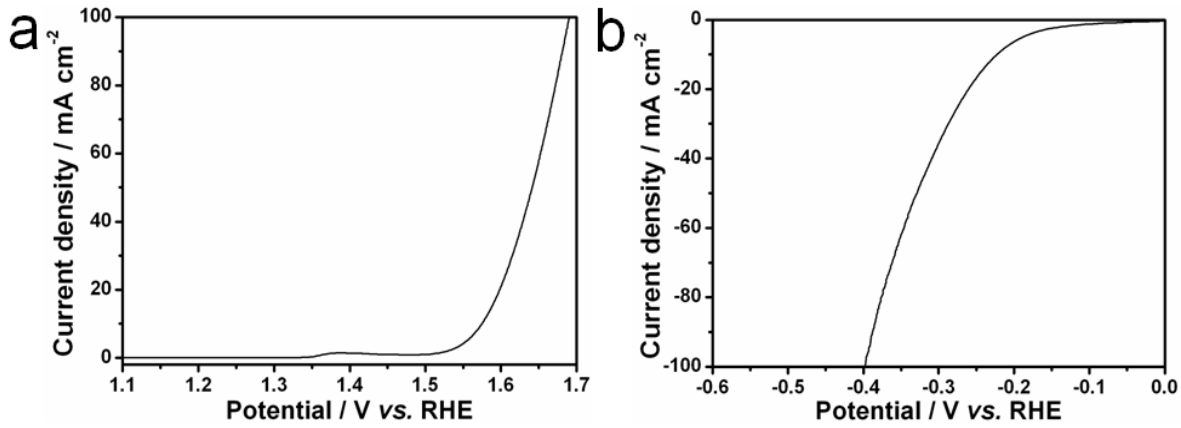


Fig. S9 Polarization curves of pristine Ni foam substrate for (a) OER and (b) HER.

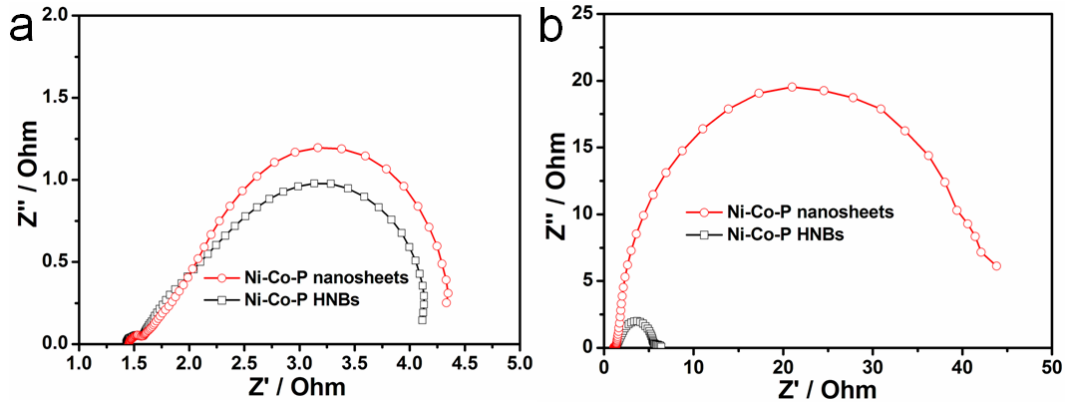


Fig. S10 Nyquist plots of the hierarchical Ni-Co-P HNBs and Ni-Co-P nanosheets for (a) OER and (b) HER.

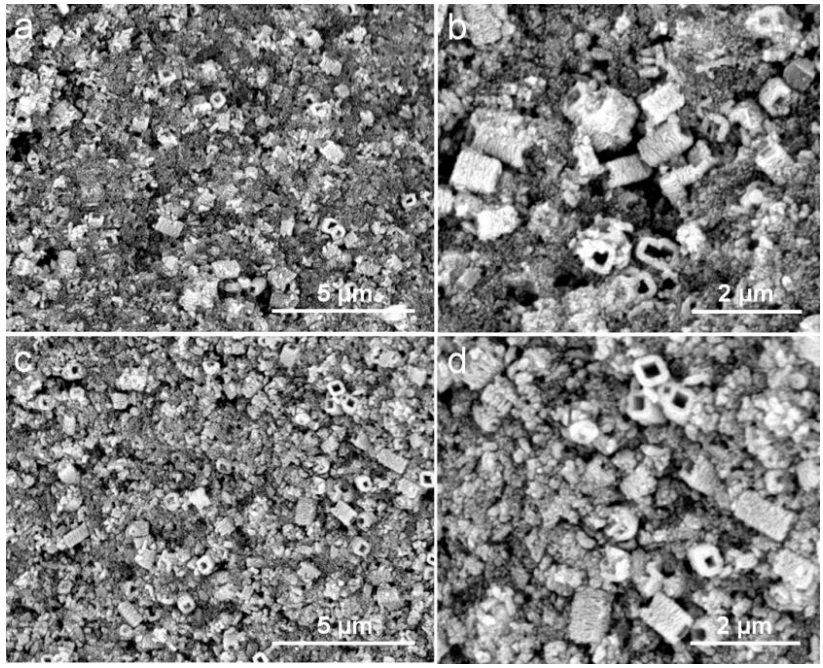


Fig. S11 FESEM images of Ni-Co-P HNBs after (a, b) OER and (c, d) HER durability tests.

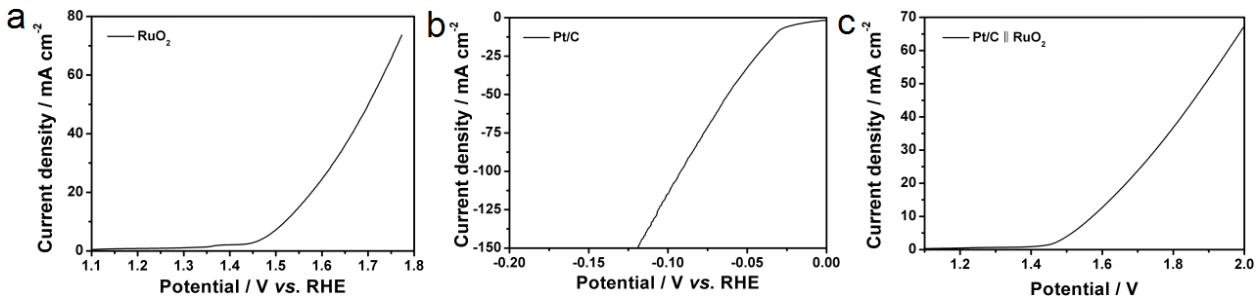


Fig. S12 Polarization curves of (a) RuO_2 for OER, (b) Pt/C (20 wt.% Pt) for HER, and (c) Pt/C||RuO_2 for overall water splitting. To reach the current density of 10 mA cm^{-2}, RuO_2 needs an overpotential of 290 mV for OER (a), while Pt/C needs an overpotential of 31 mV for HER (b). For the overall water splitting (c), RuO_2 electrode and Pt/C electrode were used as the anode and cathode, respectively. The cell voltage is 1.57 V at the current density of 10 mA cm^{-2}.

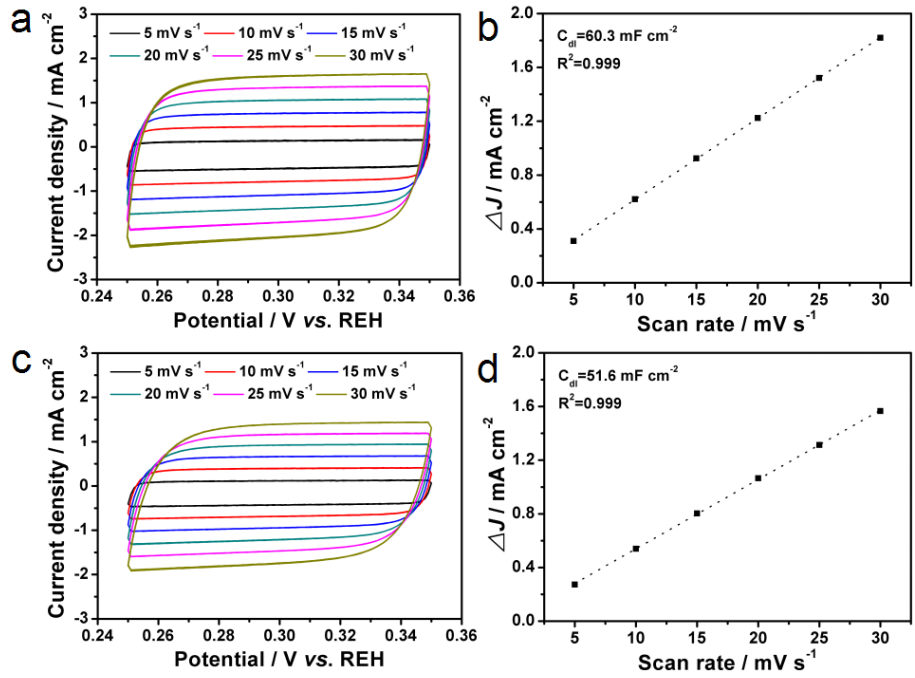


Fig. S13 CV curves of (a) Ni-Co-P HNBs and (c) Ni-Co-P nanosheets in the double layer region at scan rates of 5, 10, 15, 20, 25 and 30 mV s^{-1} in 1.0 M KOH; (b) and (d) current density as a function of scan rate derived from (a) and (c), respectively. As can be seen in this figure, the Ni-Co-P HNBs exhibit higher double-layer capacitance (C_{dl}) of 60.3 mF cm^{-2}, while it is only 51.6 mF cm^{-2} for Ni-Co-P nanosheets, indicating a higher electrochemical active surface area (ECSA) for the Ni-Co-P HNBs since the ECSA is generally proportional to the C_{dl} of the catalyst.

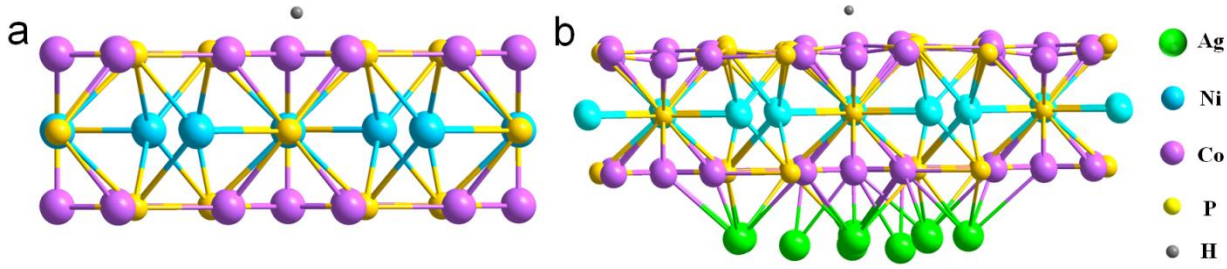


Fig. S14 The crystal structure of (a) Ni-Co-P and (b) Ag-incorporated Ni-Co-P material for the calculation of the HER Gibbs free-energy change.

Table S1. OER performances of representative electrocatalysts in alkaline electrolyte.

Catalysts	Overpotential (mV) at 10 mA cm^{-2}	Reference
Ni_2P nanoparticles	290	*Energy Environ. Sci.* **2015**, *8*, 2347
np-$(Co_{0.52}Fe_{0.48})_2P$	270	*Energy Environ. Sci.* **2016**, *9*, *2257*
MnCoP nanoparticles	330	*J. Am. Chem. Soc.* **2016**, *138*, 4006
Co_4N/CC	257	*Angew. Chem. Int. Ed.* **2015**, *54*, 14710
Co-P film	340	*Angew. Chem. Int. Ed.* **2015**, *54*, 6251
CoP MNA	290	*Adv. Funct. Mater.* **2015**, *25*, 7337
NiCoP@NF	280	*Nano Lett*. **2016**, *16*, 7718
CoP/rGO hybrids	340	*Chem. Sci.* **2016**, *7*, 1690.
FeP	288	*Chem. Eur. J*. **2015**, 21, 18062.
NiCoP nanoparticle	310	*Adv. Mater. Interfaces* **2016**, 3, 1500454.
hierarchical Ni-Co-P HNBs	270	This work

Table S2. HER performances of representative electrocatalysts in alkaline electrolyte.

Catalysts	Overpotential (mV) at 10 mA cm^{-2}	Reference
CoP/Ti	128	*Adv. Mater.* **2017**, *29*, 1602441
Ni_2P particles	~220	*Energy Environ. Sci.* **2015**, *8*, 2347
NiFe LDH/NF	210	*Science* **2014**, *345*, 1593
CoOx@CN	232	*J. Am. Chem. Soc.* **2015**, *137*, 2688
Ni_3FeN-NPs	158	*Adv. Energy Mater*. **2016**, *6*, 1502585
CoNiP@NF	155	*J. Mater. Chem. A* **2016**, *4*, 10195
NiCoP-2.5-300 hollow polyhedrons	124	*ACS Appl. Mater. Interfaces* **2017**, *9, 5982*
$Ni_{0.23}Co_{0.77}P$ films	128	*Adv. Funct. Mater*. **2016**, *26*, 7644
$NiFeO_x$	88	*Nat. Commun.* **2015**, *6*, 7261
hierarchical Ni-Co-P HNBs	107	This work

Table S3. Overall water splitting performances of our sample compared with recently reported representative electrocatalysts in alkaline electrolytes.

Catalysts	Potential (V) at 10 mA cm^{-2}	Reference
$NiFeO_x$	1.51	*Nat. Commun.* **2015**, *6*, 7261
Ni_5P_4 films	1.69	*Angew. Chem. Int. Ed.* **2015**, *127*, 12538
Co-P films	1.65	*Angew. Chem. Int. Ed.* **2015**, *54*, 6251
Co_xPO_4/CoP	1.91	*Adv. Mater*. **2015**, *27*, 3175
$NiCo_2O_4$	1.65	*Angew. Chem. Int. Ed.* **2016**, *55*, 6290
Ni_2P	1.63	*Energy Environ. Sci.* **2015**, *8*, 2347
CoP/GO-400	1.70	*Chem. Sci*. **2016**, *7*, 1690
CoSe film	1.65	*Chem. Commun.* **2015**, *51*, 16683
NiCoP nanoparticle	1.64	*Adv. Mater. Interfaces* **2016**, *3*, 1500454
hierarchical Ni-Co-P HNBs	1.62	This work