Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Cobalt Layered Double Hydroxides Determined CoP/Co_2P Hybrids for Electrocatalytic Overall Water Splitting

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Contents

Experimental Section

Preparation of materials

Synthesis of Co-LDHs-1. In a typical synthetic procedure (*J. Mater. Chem. A*, **2018**, 6, 4636-4641), $Co(NO_3)_2\cdot 6H_2O$ (5 mmol，1455.2 mg) and 2-methylimidazole (10 mmol，821 mg) were added to methanol (15 mL) in a Teflon-lined autoclave (20 mL) and stirred for 10 min prior to thermal treatment at 80 ^oC for 4 h. The final product was collected and washed thrice with method before vacuum drying at 80 ^oC for 12 h.

Synthesis of Co-LDHs-2. For synthesis of Co-LDHs with a modified method (*Adv. Mater.*, **2017**, 1606793), $Co(NO_3)_2\cdot 6H_2O$ (1 mmol，291 mg) and hexadecyl trimethyl ammonium bromide (CTAB, 500 mg) were mixed in deionized water (25 mL) with stirring for 30 min. Afterwards, aqueous solution of $NaBH_4$ (100 mg in 15 mL H_2O) was added dropwise, and stirred for another 10 min. the final product was collected and alternatively washed with methanol and deionized water for three times before vacuum drying at 80 ^oC for 12 h.

Synthesis of ZIF-67. In a typical synthetic procedure (*J. Mater. Chem. A*, **2014**, 2, 12194–12200), $Co(NO_3)_2\cdot 6H_2O$ (4mmol，1164.2mg) and 2-methylimidazole (8 mmol，656.8 mg) were dissolved into methanol (50 mL) with sonication, respectively. The methanolic solution of 2-methylimidazole was slowly added to the methanolic solution of $Co(NO_3)_2$ with rigorously stirring. After that, the resulting solution was kept at room temperature for 24 h. The final product was collected and washed thrice with methanol before vacuum drying for 12 at 80 ^oC.

Transformation of Co-LDHs-1 into CoP/Co_2P-1. A porcelain boat containing Co-LDHs-1 (50 mg) placed at the downstream position and $NaH_2PO\cdot H_2O$ (1000 mg) loaded at the upstream side was put in a tubular furnace. The furnace was heated to 300 ^oC with a ramp rate of 5 ^oC min^{-1}, and kept the temperature for 2 h under N_2 atmosphere.

CoP/Co_2P-2 and CoP-3 were prepared by the same phosphorization procedure while Co-LDHs-2 and ZIF-67 were used to substitute for Co-LDHs-1, respectively.

Electrochemical measurements

Preparation of electrocatalyst inks: CoP/Co_2P-1, CoP/Co_2P-2, CoP-3 or RuO_2 (5 mg) were dispersed into the mixed solvent of water and 2-propanol with volume ratio of 1:1

(0.975 mL) before Nafion solution (0.025 mL, 5 *wt*%) was added, and was sonicated for 1 h in an ultrasonic bath to form a well-dispersed suspension.

Preparation of work electrodes: Glassy carbon (GC) electrodes (3 mm in diameter) were firstly polished with the mixture of alumina and deionized water on a Nylon plate. The polished GC electrodes were rinsed with deionized water before utilization. Carbon fiber papers (CFPs) were put into diluted HNO_3 (1 M) and sonicated for 30 min. The same treatment procedure was sequentially performed in deionized water, ethanol and acetone. Subsequently, a tape was used to define an area of 0.09 cm^2.

The as-made catalyst ink (5 μL) was drop-casted on the surface of a GC electrode or a CPF electrode with loading amount of ~0.36 mg cm^{-2} and dried at room temperature in air for 1 h before using. A conventional three-electrode setup was consisted of the working electrode of the loaded GC or CFP, the reference electrode of Ag/AgCl (3.5 M KCl) and the counter electrode of the polished Pt wire (oxygen evolution reaction, OER) and graphite rod (hydrogen evolution reaction, HER).

Electrochemical measurement: Linear-sweep voltammetry (LSV) tests were performed at a sweep rate of 5 mV s^{-1} in 1 M KOH and 0.5 M H_2SO_4 to evaluate HER performance, and in 1 M KOH to evaluate OER performance.

Cyclic voltammetry (CV) tests were carried out at variable sweep rate from 10 to 50 mV s^{-1} with an increment of 10 mV s^{-1} to measure the double-layer capacitance of electrocatalysts.

To further estimate HER performance, electrochemical impedance spectroscopy (EIS) was collected in 1 M KOH and 0.5 M H_2SO_4 at overpotential of 80 mV in the frequency range from 0.1 Hz to 100 kHz with oscillation potential amplitudes of 5 mV. To further estimate OER performance, EIS was collected in 1 M KOH at overpotential of 350 mV. The aforementioned electrochemical tests were performed while GC electrodes were used as the work electrode in a three-electrode cell.

To accomplish the overall water splitting, CoP/Co_2P load on CPF was used as anode and cathode. The polarization curve of two-electrode cell in 1 M KOH was collected at scan rate of 5 mV s^{-1}. Long-term stability of the two-electrode cell was investigated by chronoamperometry tests for 8 h in 1 M KOH solution. During the measurement process, the cell voltage was fixed at 1.65 V.

Materials and characterization methods

All chemical reagents were directly used without further purification. Chemicals and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd, China but Nafion solution (5 wt% in mixture of water and 2-propanol) was purchased from Sigma Aldrich.

The structure, morphology, phase and composite of materials were characterized by transmission electron microscopy (TEM, Tecnai F30 operated at 300 kV), scanning electron microscopy (SEM, HITACHI UHR FE-SEM SU8220), X-ray diffraction (XRD, Rigaku D/Max 2400 with Cu-Kα radiation, λ = 1.5418 Å), atomic force microscopy (AFM, Park Systems XE-70 with non-contact mode), X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi with Al- Kα radiation, $h\nu = 1486.6$ eV). Electrochemical measurements were carried on a CHI760E electrochemical workstation for LSV, CV, and chronoamperometry, and a ZAHNER ENNIUM electrochemical workstation for EIS.

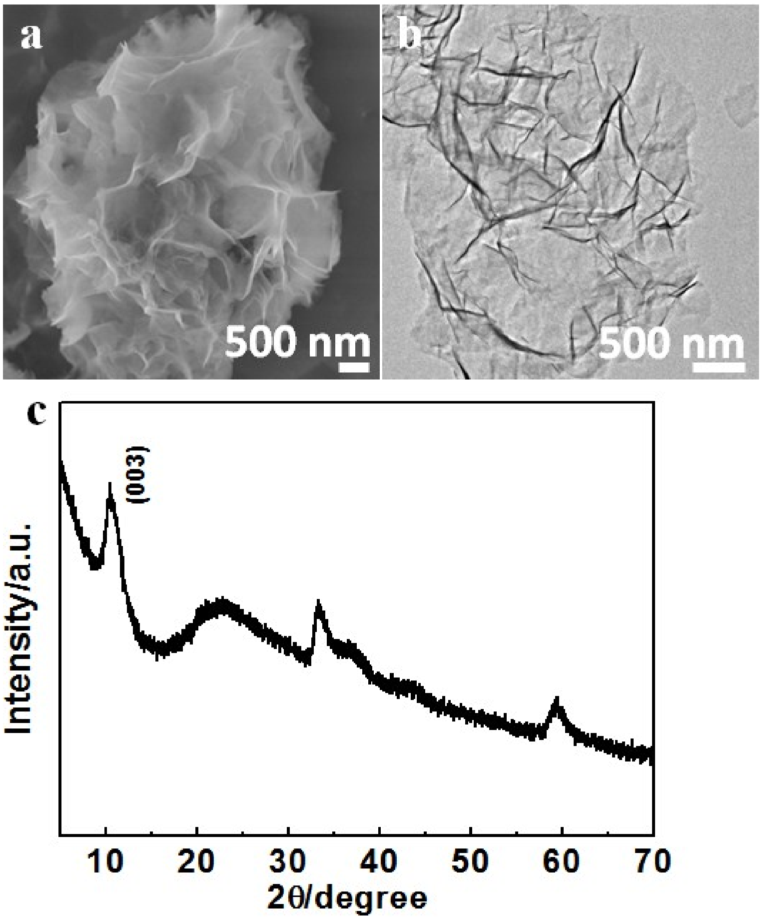

Figure S1. (a) SEM and (b) TEM images and XRD pattern of Co-LDHs_1.

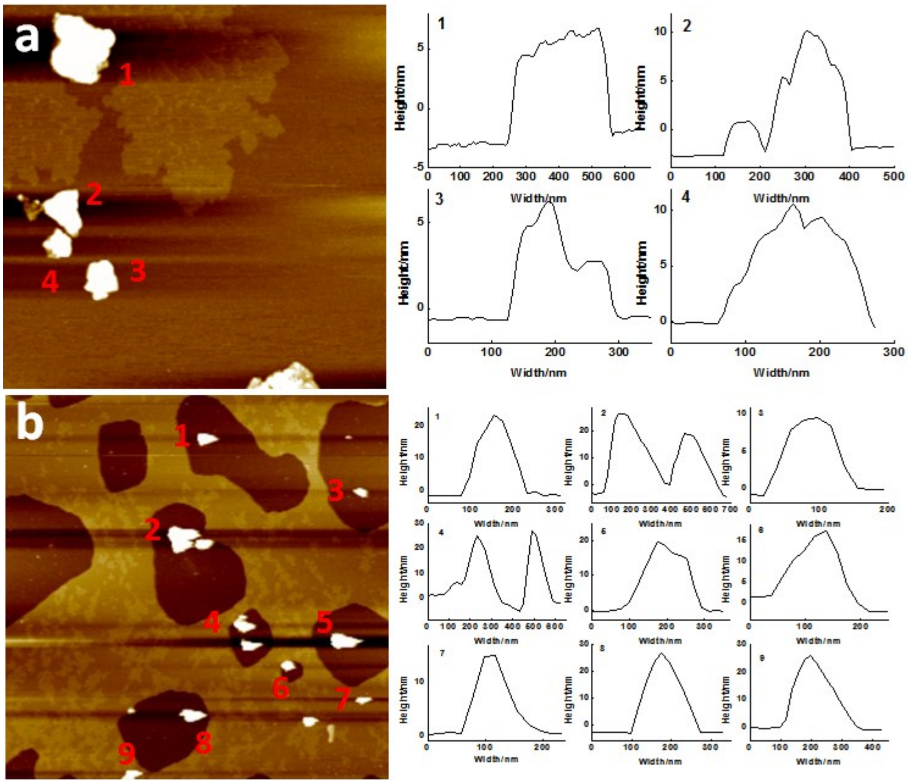

Figure S2. AFM images of (a) Co-LDHs_1 and (b) CoP/Co$_2$P_1. (Right) the thickness of corresponding nanosheets shown in the AFM images.

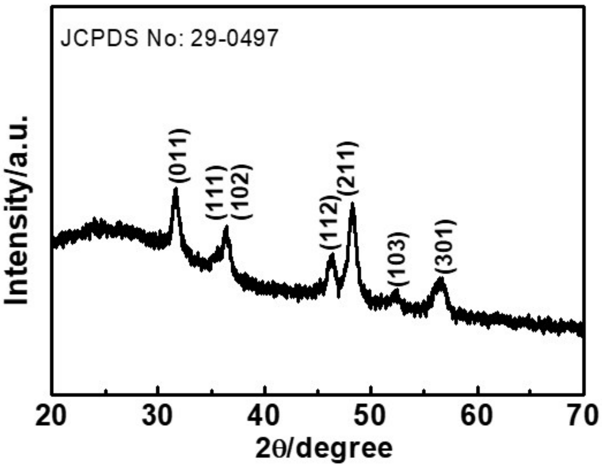

Figure S3. XRD pattern of CoP/Co_2P_1.

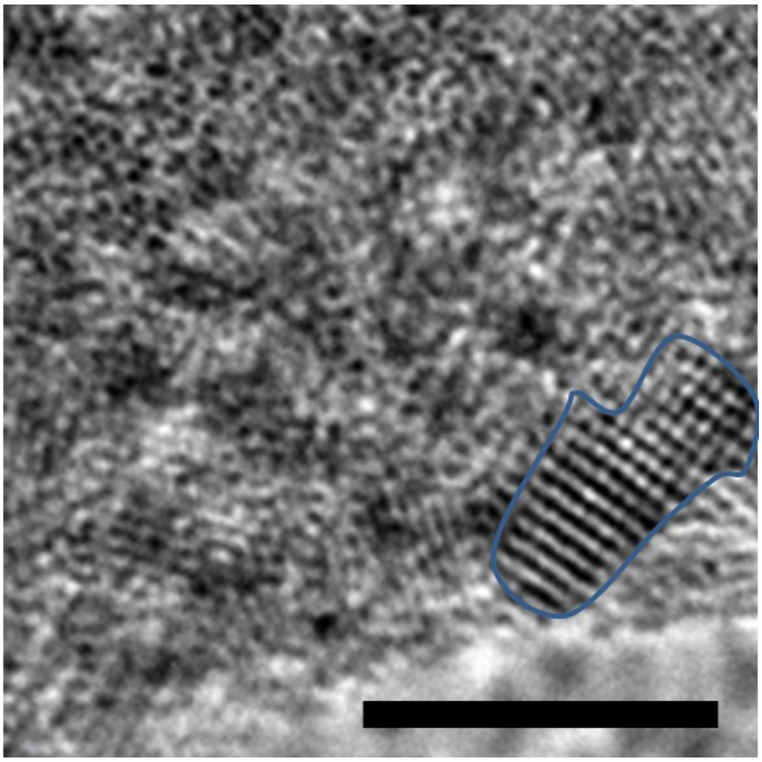

Figure S4. The HRTEM image of CoP/Co_2P_1, including high-crystalline region of CoP (highlighted by a curve) and low-crystalline region. The scale bar is 5 nm.

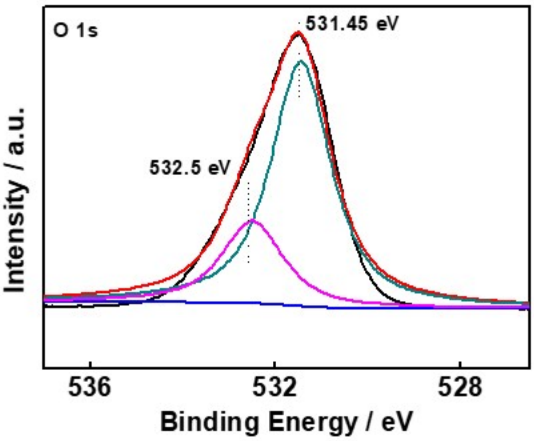

Figure S5. The O 1s XPS spectrum of CoP/Co_2P_1.

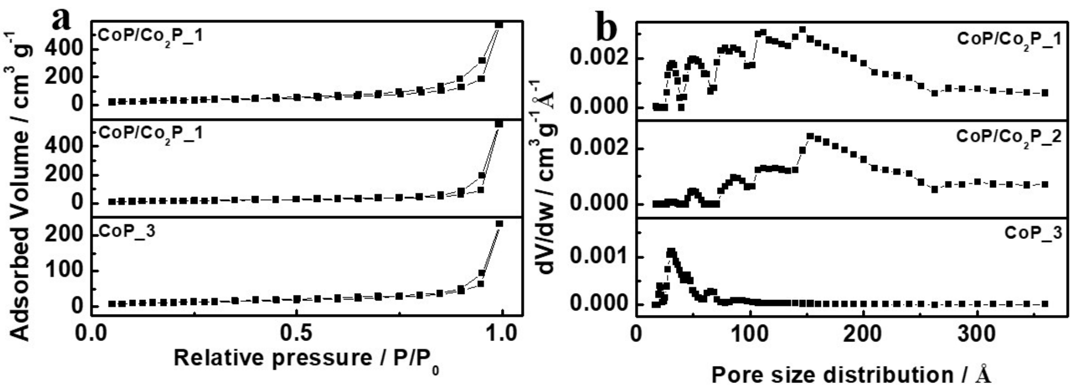

Figure S6. (a) N_2 sorption isotherms at 77 K of different cobalt-based phosphide samples; (b) corresponding pore size distribution curves.

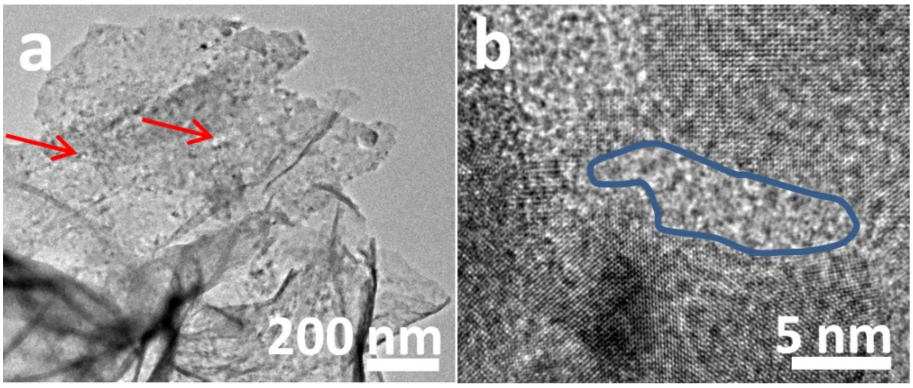

Figure S7. (a) TEM and (b) HRTEM images of CoP/Co_2P_1 to unveil the porous nanosheets.

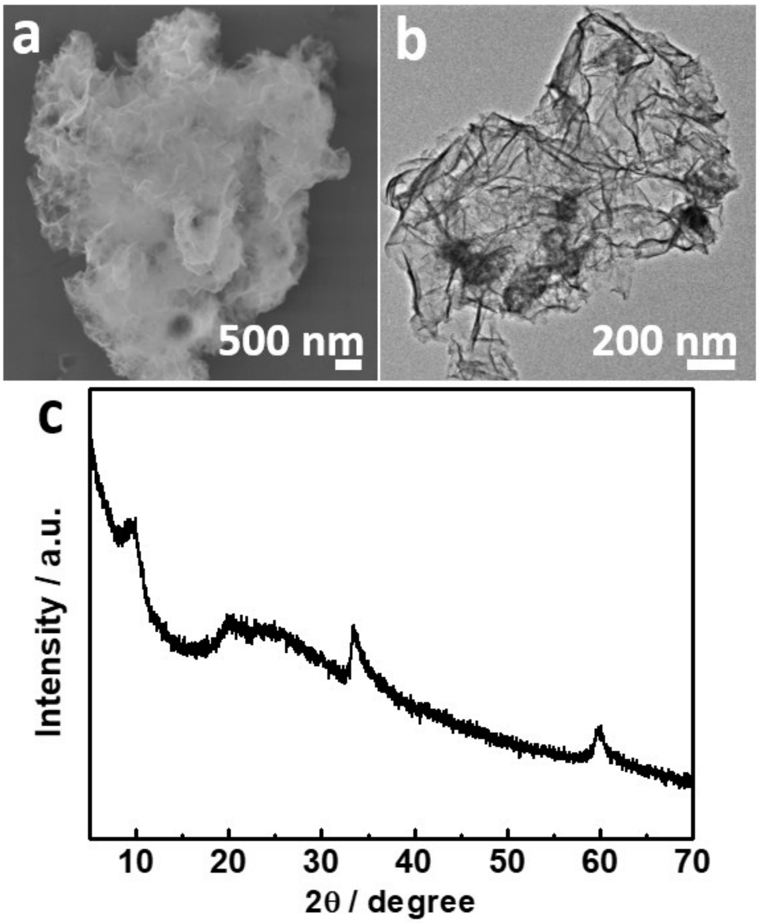

Figure S8. (a) SEM and (b) TEM images and (c) XRD pattern of Co-LDHs_2.

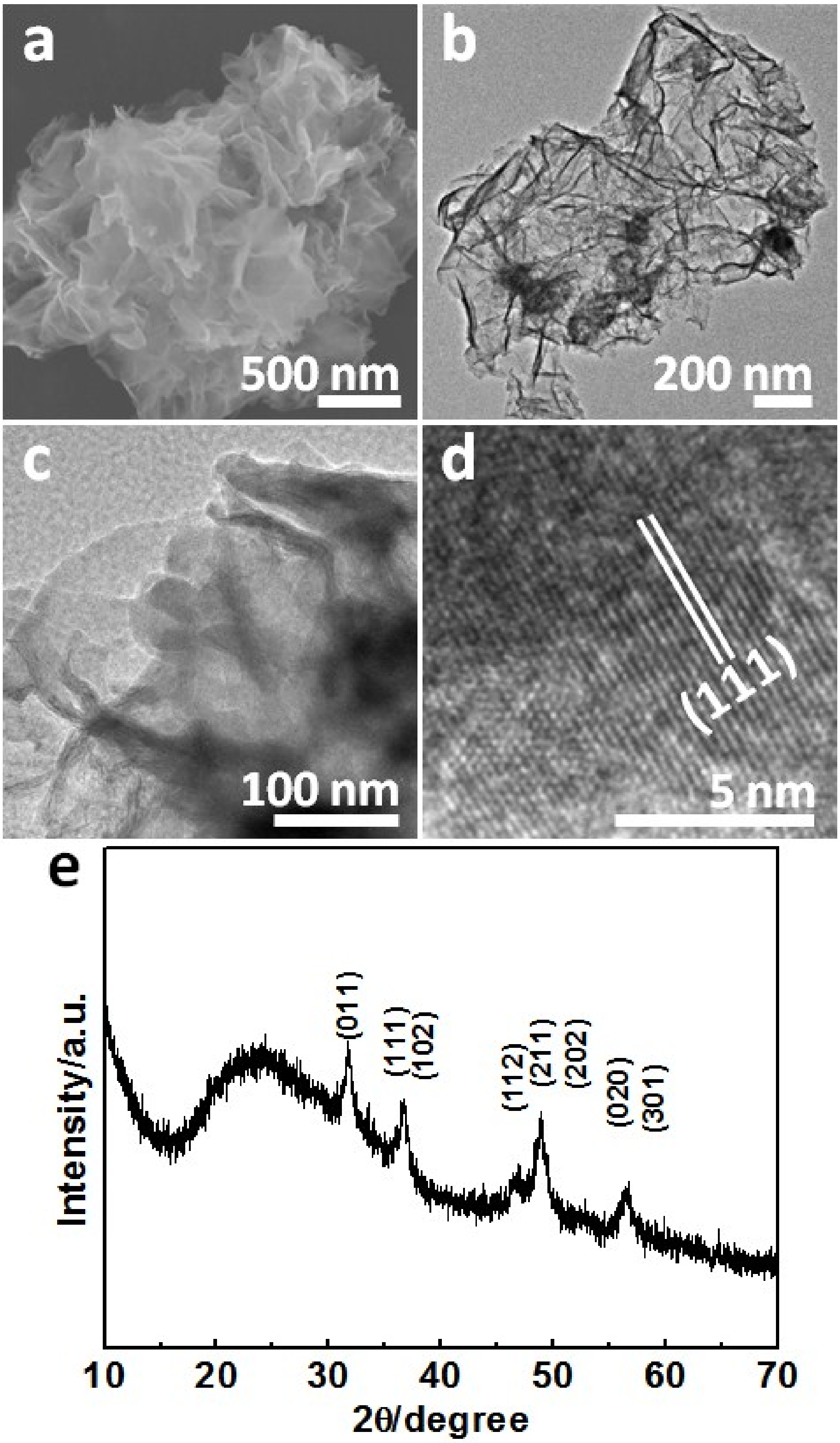

Figure S9. (a) SEM image, (b, c) TEM images with different magnifications, (d) HRTEM image and (e) XRD pattern of CoP/Co_2P_2.

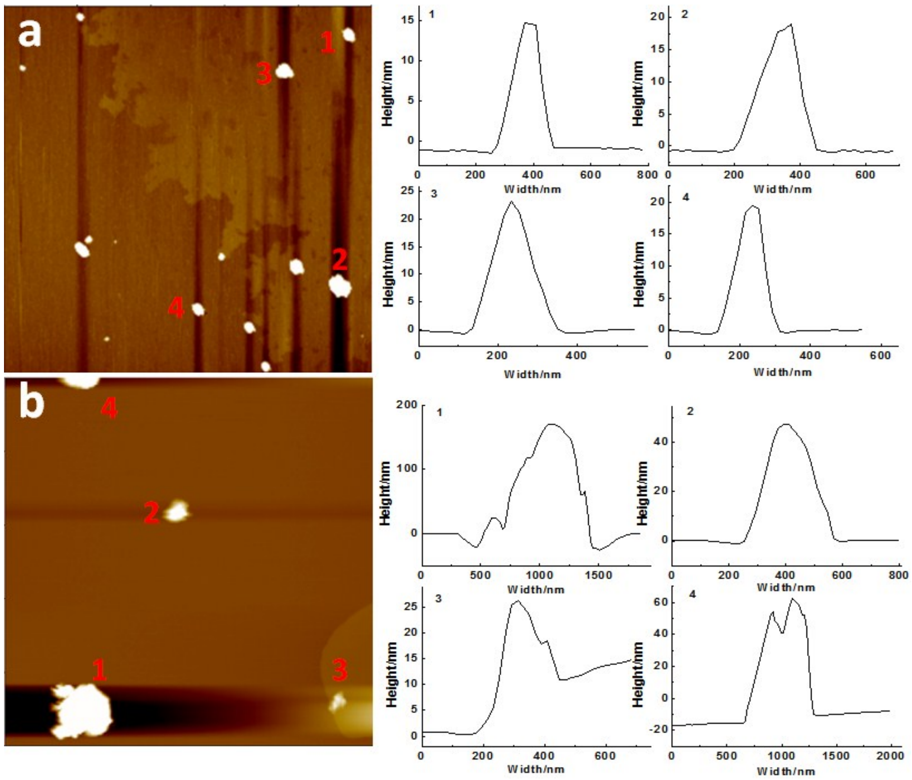

Figure S10. AFM images of (a) Co-LDHs_2 and (b) CoP/Co_2P_2. (Right) the thickness of corresponding nanosheets shown in the AFM images.

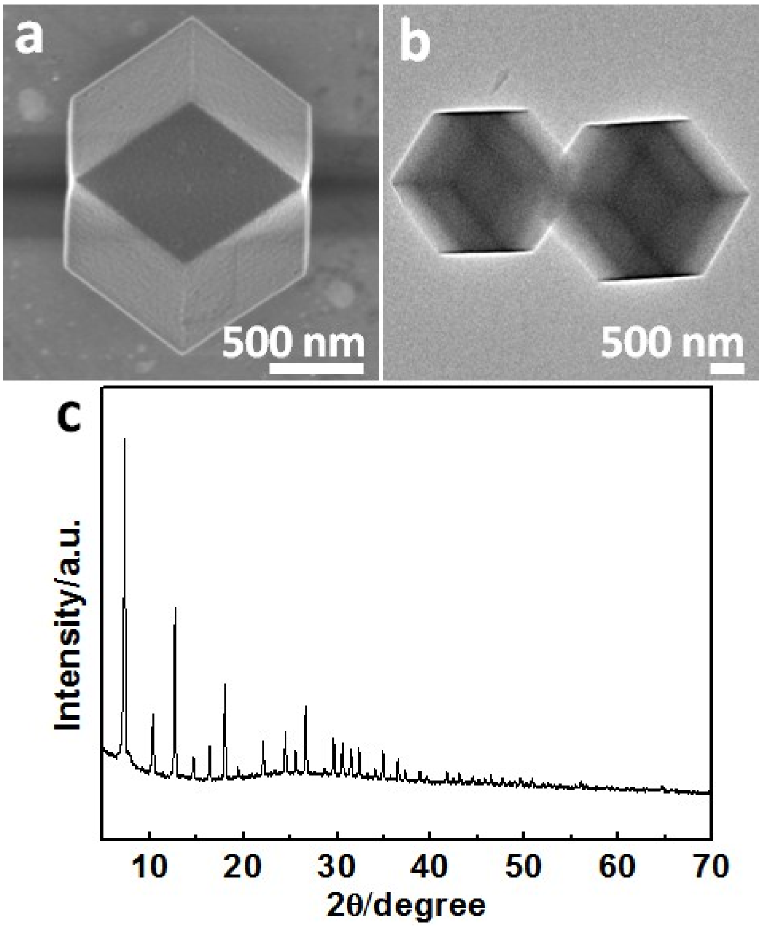

Figure S11. (a) SEM and (b) TEM images and XRD pattern of ZIF-67.

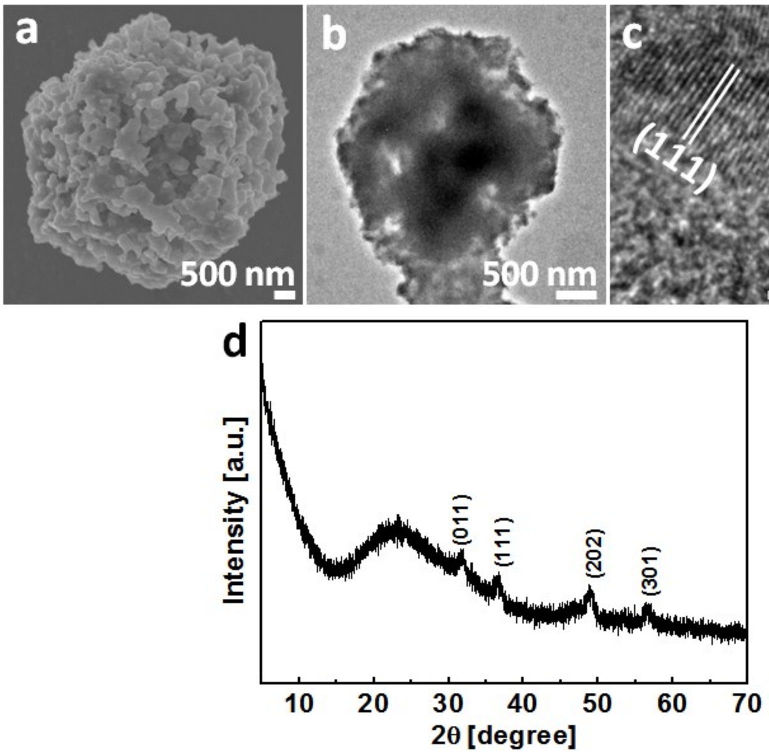

Figure S12. (a) SEM, (b) TEM and (c) HRTEM images and (d) XRD pattern of CoP_3.

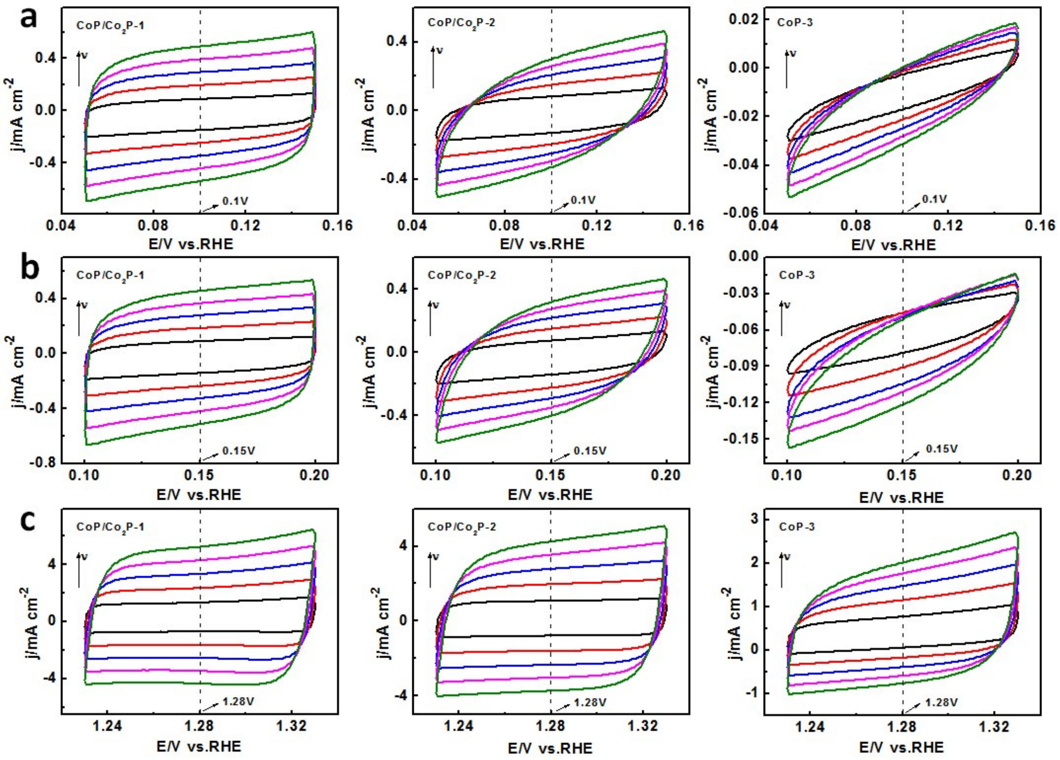

Figure S13. CV curves of various cobalt-based phosphides obtained with different scan rates of 10, 20, 30, 40, and 50 mV s^{-1} in (a) 0.5 M H_2SO_4 with a potential window of 0.05–0.15 V *vs*. RHE, (b) 1 M KOH with a potential of 0.1–0.2 V *vs*. RHE, and (c) 1 M KOH with a potential of 1.23–1.33 V *vs*. RHE.

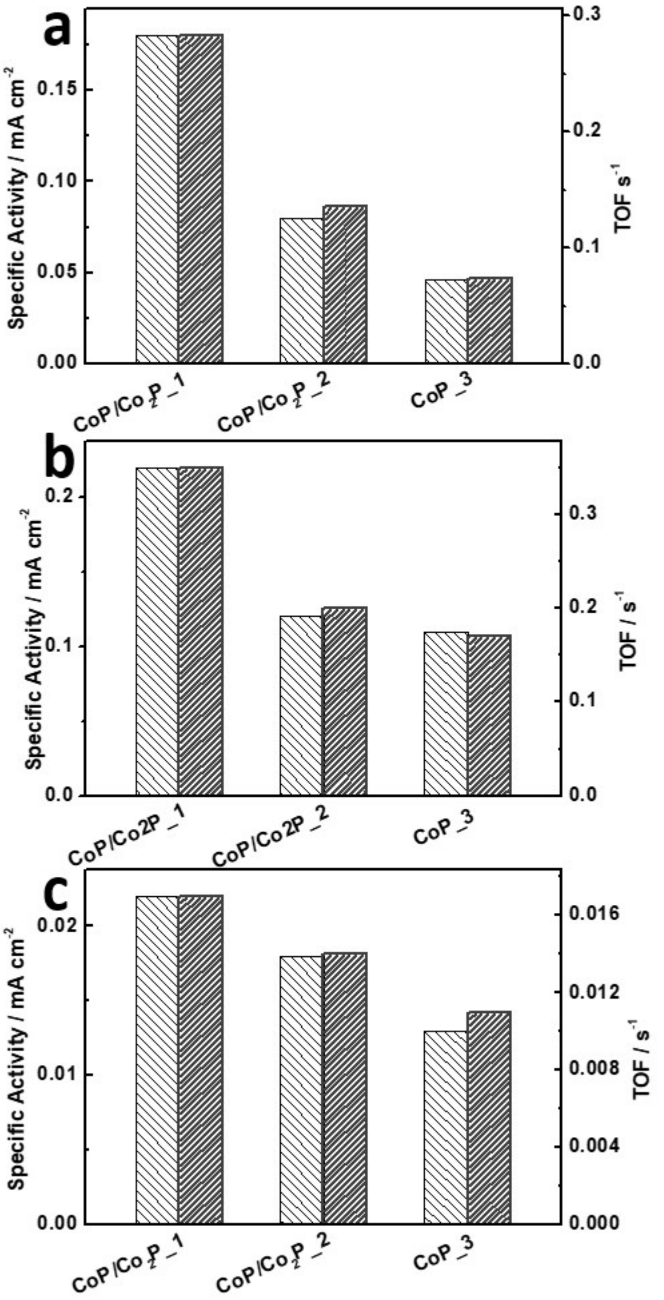

Figure S14. Specific activity and TOF of different electrocatalysts at potential of (a) 146 mV *vs* RHE for HER in 0.5 M H_2SO_4, (b) 155 mV *vs* RHE for HER in 1 M KOH, and (c) 1.539 V *vs* RHE for OER in 1 M KOH

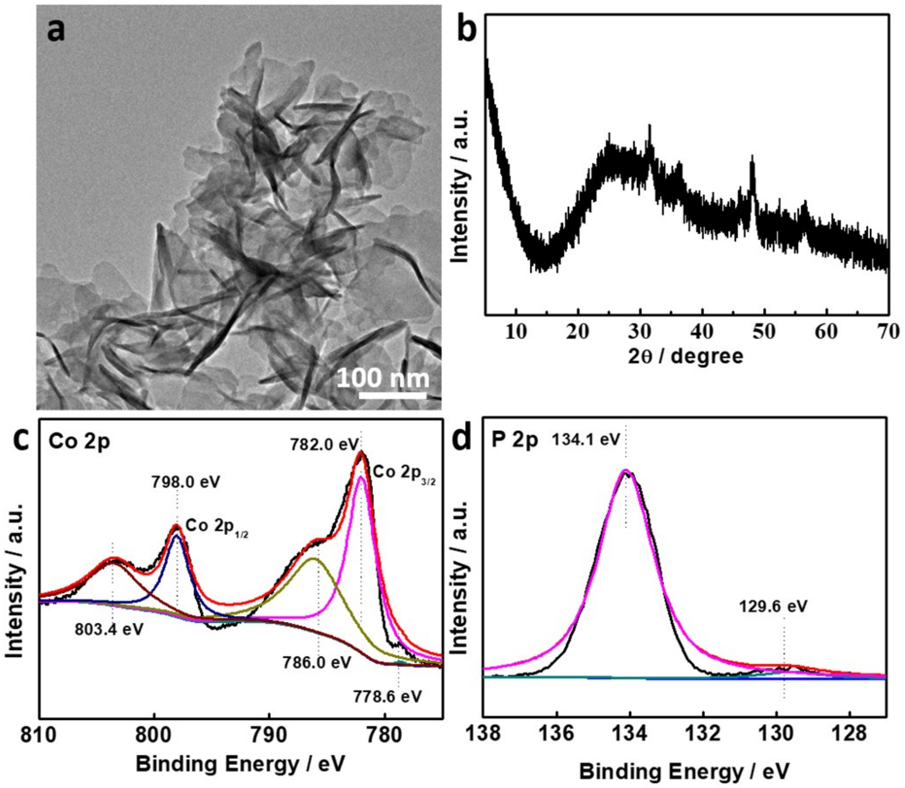

Figure S15. (a) TEM image, (b) XRD pattern, and XPS spectra of (c) Co 2p and (d) P 2p of CoP/Co_2P_1 as anode for electrocatalytic OER after stability measurement.

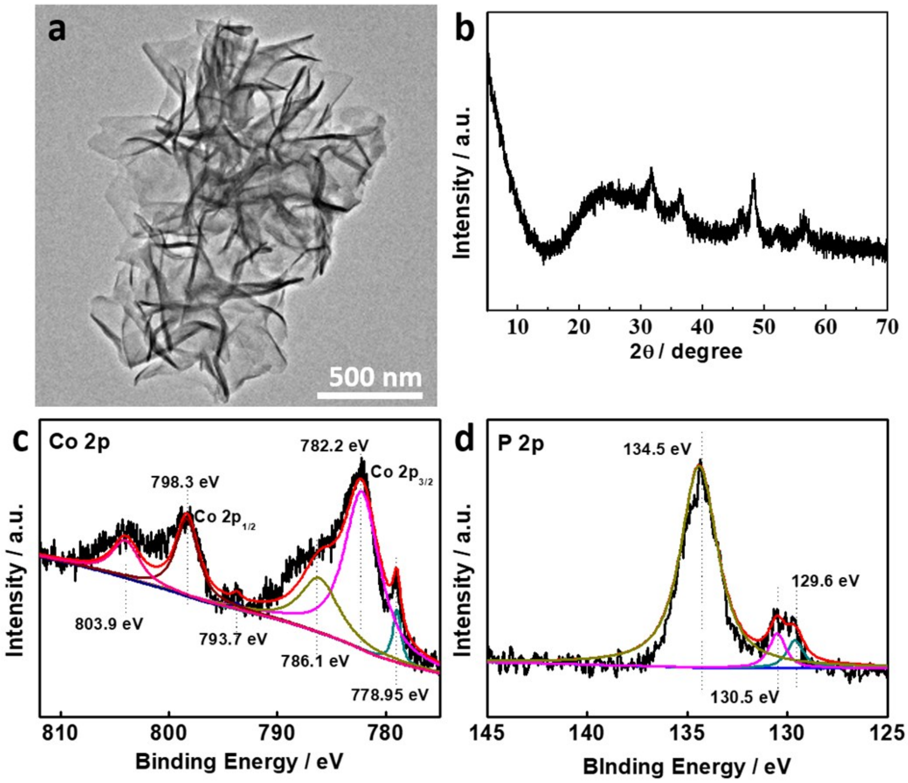

Figure S16. (a) TEM image, (b) XRD pattern, and XPS spectra of (c) Co 2p and (d) P 2p of CoP/Co_2P_1 as cathode for electrocatalytic HER after stability measurement.

Table S1. ECSA of CoP/Co_2P_1 and _2 and CoP_3.

Electrode (0.07 cm^{-2})	ECSA (in 0.5 M H_2SO_4 for HER)	ECSA (in 1 M KOH for HER)	ECSA (in 1 M KOH for OER)
CoP/Co_2P_1	19.8 cm^{-2}	16.1 cm^{-2}	165.2 cm^{-2}
CoP/Co_2P_2	10.4 cm^{-2}	11 cm^{-2}	134.05 cm^{-2}
CoP _3	0.42 cm^{-2}	0.82 cm^{-2}	45.33 cm^{-2}

Table S2. Comparison of electrocatalytic activity of various transition metal phosphides towards HER based on η_{10} and Tafel slope.

Electrocatalyst	Overpotential (η_{10}/mV)	Tafel slope (mV dec^{-1})	Electrolyte	Reference
Ni_2P@NPCNFs	108	62	1 M KOH	ChemSusChem, 2017, 10, 4544–4551
Co_2P–C	96	68	0.5 M H_2SO_4	J. Am. Chem. Soc., 2017, 139, 11248–11253
CoP	100	48	0.5 M H_2SO_4	J. Mater. Chem. A, 2015, 3, 5420–5425
CoP hollow polyhedron	159	59	0.5 M H_2SO_4	ACS Appl. Mater. Interfaces, 2016, 8, 2158–2165
$Co_{0.68}Fe_{0.32}P$	116	64	1 M KOH	Small, 2017, 13, 1701167
Ni_2P–CoP	105	64	0.5 M H_2SO_4	ACS Appl. Mater. Interfaces, 2017, 9, 23222–23229
MoP	125	54	0.5 M H_2SO_4	Adv. Mater., 2014, 26, 5702–5707
O-Co_2P	160	61.1	1 M KOH	Adv. Mater., 2017, 1606980
Co_2P	134	71	0.5 M H_2SO_4	Nano Energy, 2014, 9, 373–382
Co_2P/Ti	75±2	45	0.5 M H_2SO_4	Chem. Mater., 2015, 27, 3769–3774
Co_2P; Co_2P/NCNTs	154; 171 (η_{20})	101; 62	0.5 M H_2SO_4	J. Mater. Chem. A, 2016, 4, 4745–4754
Co_2P@CP	120; 70	64.9; 59.7	0.5 M H_2SO_4; 1 M KOH	ACS Energy Lett., 2018, 3, 1360–1365
Ni_5P_4–Ni_2P-NS	120	64.7	0.5 M H_2SO_4	Angew. Chem. Int. Ed., 2015, 54, 8188–8192
MoP@PC	153	66	0.5 M H_2SO_4	ngew. Chem. Int. Ed., 2016, 55,12854–12858
CoP/Co_2P	99; 103	51.4; 61.2	0.5 M H_2SO_4; 1 M KOH	This work

Table S3. Comparison of electrocatalytic performance of various transition metal-based electrodes for overall water splitting according to potential at 10 mA cm^{-2}.

Electrolyzer	Potential (V, j_{10})	Electrolyte /substrate	Reference
CoP/rGO-400	1.7	1 M KOH/CFP	Chem. Sci., 2016, 7, 1690–1695
Ni_3S_2/NF	1.73 (13)	1 M KOH/Ni foam	J. Am. Chem. Soc., 2015, 137, 14023–14026
NiO@NF‖Ni_2P@NF	1.65	1 M KOH/Ni foam	Nanoscale, 2017, 9, 4409–4418
Ni_5P_4	1.7	1 M KOH/Ni foil	Angew. Chem. Int. Ed., 2015, 54, 12361–12365
a-CoSe/Ti	1.65	1 M KOH/Ti foil	Chem. Commun., 2015, 51, 16683–16686
NiS/Ni foam	1.64	1 M KOH/Ni foam	Chem. Commun., 2016, 52, 1486–1489
$NiCo_2O_4$	1.65	1 M KOH/Ni foam	Angew. Chem. Int. Ed., 2016, 55, 6290–6294
EG/H−$Co_{0.85}$Se|P	1.64	1 M KOH/Graphene	Adv. Mater., 2017, 1701589
$NiCo_2O_4$‖$Ni_{0.33}Co_{0.67}S_2$	1.65 (5)[a]	1 M KOH/Ti foil	Adv. Energy Mater., 2015, 5, 1402031
CP/CTs/Co-S	1.743	1 M KOH/CP	ACS Nano, 2016, 10, 2342–2348
Co_2P	1.44	1 M KOH/Ni foam	Green Chem., 2016, 18, 1459–1464
Co_2P-CNT	1.53	1 M KOH/CP	Nano Energy, 2016, 30, 303–311
CoP/Co_2P	1.65	1 M KOH/CFP	This work

[a] potential at current density of 5 mA cm^{-2}.

Electrochemically active surface area (ECSA) calculation

ECSA was calculated from double layer capacitance (C_{dl}) by the equation
$ECSA = C_{dl} \cdot S/C_s$ (1),
where C_s is the specific capacitance of the catalyst and S is the surface area of the electrode (GC electrode: 0.07 cm^{-2}). C_{dl} can be achieved by calculating the linear slope of capacitive current densities ($\Delta j = j_a - j_c$, where j_a and j_c represent anodic and cathodic current density, respectively) in non-Faradaic regime of CV as a function of scan rates (v). Thus, C_{dl} was calculated by the equation
$C_{dl} = \Delta j/v$ (2).
C_s is determined by electrode materials and electrolyte solutions. The average specific capacitance of CoP were roughly estimated to be 40 μF cm^{-2} in alkaline solution, and 35 μF cm^{-2} in acid solution. Owing to small amount of Co_2P in the hybrids, the ECSA of CoP/Co_2P was estimated from CoP.

(1) Electrochemical measurements for HER in 0.5 M H_2SO_4.

CoP/Co_2P_1:

$$ECSA = \frac{9.9\ MF\ cm^{-2} \times 0.07\ cm^2}{35\ \mu F\ cm^{-2}} = 19.8\ cm^2;$$

CoP/Co_2P_2:

$$ECSA = \frac{5.2\ MF\ cm^{-2} \times 0.07\ cm^2}{35\ \mu F\ cm^{-2}} = 10.4\ cm^2;$$

CoP_3:

$$ECSA = \frac{0.21\ MF\ cm^{-2} \times 0.07\ cm^2}{35\ \mu F\ cm^{-2}} = 0.42\ cm^2.$$

(2) Electrochemical measurements for OER in 0.5 M H_2SO_4.

CoP/Co_2P_1:

$$ECSA = \frac{94.4\ MF\ cm^{-2} \times 0.07\ cm^2}{40\ \mu F\ cm^{-2}} = 165.2\ cm^2;$$

CoP/Co_2P_2:

$$ECSA = \frac{76.6\ MF\ cm^{-2} \times 0.07\ cm^2}{40\ \mu F\ cm^{-2}} = 134.05\ cm^2;$$

CoP_3:

$$ECSA = \frac{25.9\ MF\ cm^{-2} \times 0.07\ cm^2}{40\ \mu F\ cm^{-2}} = 45.33\ cm^2.$$

(3) Electrochemical measurements for HER in 1 M KOH.

CoP/Co_2P_1:

$$ECSA = \frac{9.2\ MF\ cm^{-2} \times 0.07\ cm^2}{40\ \mu F\ cm^{-2}} = 16.1\ cm^2;$$

CoP/Co_2P_2:

$$ECSA = \frac{6.3\ MF\ cm^{-2} \times 0.07\ cm^2}{40\ \mu F\ cm^{-2}} = 11.0\ cm^2$$

CoP_3:

$$ECSA = \frac{0.47\ MF\ cm^{-2} \times 0.07\ cm^2}{40\ \mu F\ cm^{-2}} = 0.82\ cm^2$$

Specific activity estimation

The active sites (Ni) per surface area.

$$\left(\frac{number\ of\ atoms/unit\ cell}{volume\Big/_{unit\ cell}}\right)^{\frac{2}{3}}$$

Number of Ni:

$$= \left(\frac{8}{5.077 \times 3.281 \times 5.587}\right)^{\frac{2}{3}} = 1.9477 \times 10^{15}\ cm^{-2}$$

The specific activity of electrocatalysts was estimated by normalizing current to electrochemically active surface area (ECSA) of catalysts according to an equation of j_s = i/ECSA

At potential of 146 mV *vs* RHE for HER (0.5 M H_2SO_4)

CoP/Co_2P_1:

$$j_{s(H_2)} = \frac{50\ mA\ cm^{-2} \times 0.07\ cm^{-2}}{19.8\ cm^{-2}} = 0.177\ mA\ cm^{-2}$$

CoP/Co_2P_2:

$$j_{s(H_2)} = \frac{12.9\ mA\ cm^{-2} \times 0.07\ cm^{-2}}{10.4\ cm^{-2}} = 0.087\ mA\ cm^{-2}$$

CoP_3:

$$j_{s(H_2)} = \frac{0.278\ mA\ cm^{-2} \times 0.07\ cm^{-2}}{0.42\ cm^{-2}} = 0.046\ mA\ cm^{-2}$$

At potential of 155 mV *vs* RHE for HER (1 M KOH)

CoP/Co_2P_1:

$$j_{s(H_2)} = \frac{50\ mA\ cm^{-2} \times 0.07\ cm^{-2}}{16.1\ cm^{-2}} = 0.22\ mA\ cm^{-2}$$

CoP/Co_2P_2:

$$j_{s(H_2)} = \frac{19.4\ mA\ cm^{-2} \times 0.07\ cm^{-2}}{11.0\ cm^{-2}} = 0.12\ mA\ cm^{-2}$$

CoP_3:

$$j_{s(H_2)} = \frac{1.28\ mA\ cm^{-2} \times 0.07\ cm^{-2}}{0.82\ cm^{-2}} = 0.11\ mA\ cm^{-2}$$

At potential of 1.539 V *vs* RHE for OER (1 M KOH)

CoP/Co_2P_1:

$$j_{s(O_2)} = \frac{50\ mA\ cm^{-2} \times 0.07\ cm^{-2}}{165.2\ cm^{-2}} = 0.022\ mA\ cm^{-2}$$

CoP/Co_2P_2:

$$j_{s(O_2)} = \frac{33.8\ mA\ cm^{-2} \times 0.07\ cm^{-2}}{134.05\ cm^{-2}} = 0.018\ mA\ cm^{-2}$$

CoP_3:

$$j_{s(O_2)} = \frac{8.7\ mA\ cm^{-2} \times 0.07\ cm^{-2}}{45.33\ cm^{-2}} = 0.013\ mA\ cm^{-2}$$

TOF calculation

The total number of hydrogen (oxygen) turnovers.

Hydrogen:
$$\frac{1\,mol\,H_2}{2\,mol\,e^-} \times j \times \frac{1\,mol}{96485\,C} \times \frac{6.022\times10^{23}\,e^-}{1\,mol} = 3.12\times10^{18} j\,C^{-1} = 3.12\times10^{15} j\,mA^{-1}\,s^{-1}$$

Oxygen:
$$\frac{1\,mol\,O_2}{4\,mol\,e^-} \times j \times \frac{1\,mol}{96485\,C} \times \frac{6.022\times10^{23}\,e^-}{1\,mol} = 3.12\times10^{18} j\,C^{-1} = 1.56\times10^{15} j\,mA^{-1}\,s^{-1}$$

At potential of 146 mV vs RHE for HER (0.5 M H_2SO_4)

CoP/Co_2P_1:

$$TOF_{H_2} = \frac{3.12\times10^{15}\times 50\,mA\,cm^{-2}\times\frac{0.07\,cm^{-2}}{19.8\,cm^{-2}} mA^{-1}\,s^{-1}}{1.9477\times10^{15}\,cm^{-2}} = 0.28\,s^{-1}$$

CoP/Co_2P_2:

$$TOF_{H_2} = \frac{3.12\times10^{15}\times 12.9\,mA\,cm^{-2}\times\frac{0.07\,cm^{-2}}{10.4\,cm^{-2}} mA^{-1}\,s^{-1}}{1.9477\times10^{15}\,cm^{-2}} = 0.14\,s^{-1}$$

CoP_3:

$$TOF_{H_2} = \frac{3.12\times10^{15}\times 0.278\,mA\,cm^{-2}\times\frac{0.07\,cm^{-2}}{0.42\,cm^{-2}} mA^{-1}\,s^{-1}}{1.9477\times10^{15}\,cm^{-2}} = 0.074\,s^{-1}$$

At potential of 155mV vs RHE for HER (1 M KOH)

CoP/Co_2P_1:

$$TOF_{H_2} = \frac{3.12\times10^{15}\times 50\,mA\,cm^{-2}\times\frac{0.07\,cm^{-2}}{16.1\,cm^{-2}} mA^{-1}\,s^{-1}}{1.9477\times10^{15}\,cm^{-2}} = 0.35\,s^{-1}$$

CoP/Co_2P_2:

$$TOF_{H_2} = \frac{3.12\times10^{15}\times 19.4\,mA\,cm^{-2}\times\frac{0.07\,cm^{-2}}{11.03\,cm^{-2}} mA^{-1}\,s^{-1}}{1.9477\times10^{15}\,cm^{-2}} = 0.20\,s^{-1}$$

CoP_3:

$$TOF_{H_2} = \frac{3.12\times10^{15}\times 1.28\,mA\,cm^{-2}\times\frac{0.07\,cm^{-2}}{0.82\,cm^{-2}} mA^{-1}\,s^{-1}}{1.9477\times10^{15}\,cm^{-2}} = 0.17\,s^{-1}$$

At potential of 1.539 V vs RHE for OER (1 M KOH)

CoP/Co_2P_1:

$$TOF_{O_2} = \frac{1.56 \times 10^{15} \times 50\ mA\ cm^{-2} \times \frac{0.07\ cm^{-2}}{165.2\ cm^{-2}} mA^{-1}\ s^{-1}}{1.9477 \times 10^{15}\ cm^{-2}} = 0.017\ s^{-1}$$

CoP/Co_2P_2:

$$TOF_{O_2} = \frac{1.56 \times 10^{15} \times 33.8\ mA\ cm^{-2} \times \frac{0.07\ cm^{-2}}{134.05\ cm^{-2}} mA^{-1}\ s^{-1}}{1.9477 \times 10^{15}\ cm^{-2}} = 0.014\ s^{-1}$$

CoP_3:

$$TOF_{O_2} = \frac{1.56 \times 10^{15} \times 8.7\ mA\ cm^{-2} \times \frac{0.07\ cm^{-2}}{45.33\ cm^{-2}} mA^{-1}\ s^{-1}}{1.9477 \times 10^{15}\ cm^{-2}} = 0.011\ s^{-1}$$