Supporting Information

Engineering Multinary Heterointerfaces in Two-Dimensional Cobalt Molybdenum Phosphide Hybrid Nanosheets for Efficient Electrocatalytic Water Splitting

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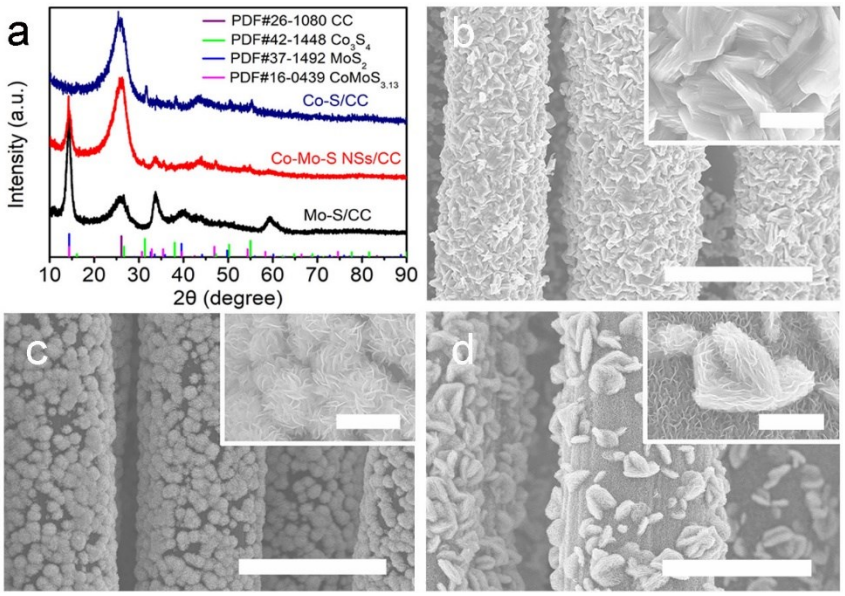

Figure S1 (a) XRD patterns and SEM images of (b) Co-S/CC, (c) Mo-S/CC and (d) Co-Mo-S/CC precursors. The scale bar is 10 μm. The inset represents its magnified images. The scale bar is 1 μm.

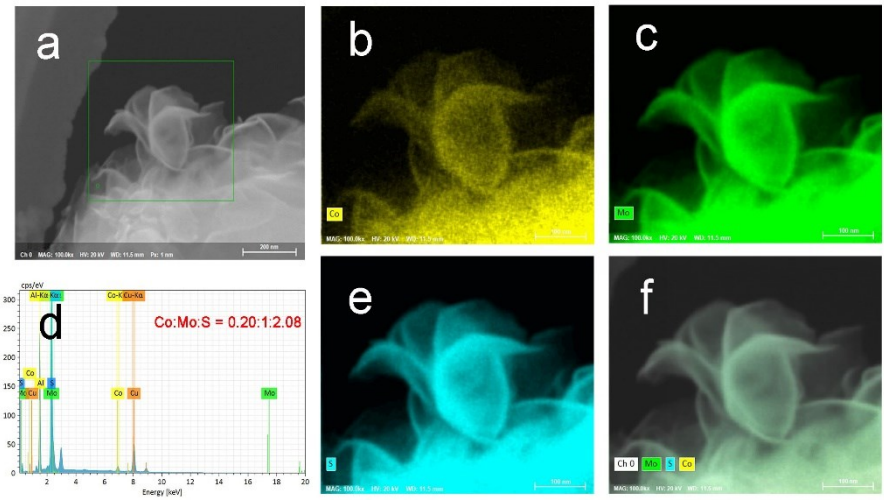

Figure S2 (a) SEM image and (d) energy dispersive spectroscopy (EDS) of the Co-Mo-S precursor and the elemental mapping images (b) Co, (c) Mo, (e) S and (f) overlayer. It shows the even distribution of Co, Mo and S elements onto the nanosheet. The scale bar is 100 nm.

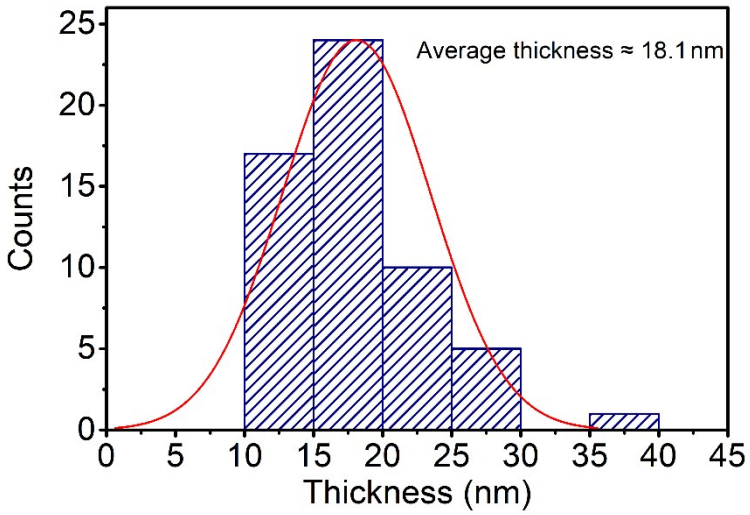

Figure S3 The thickness statistical chart of the Co-Mo-P NSs in Figure 1a.

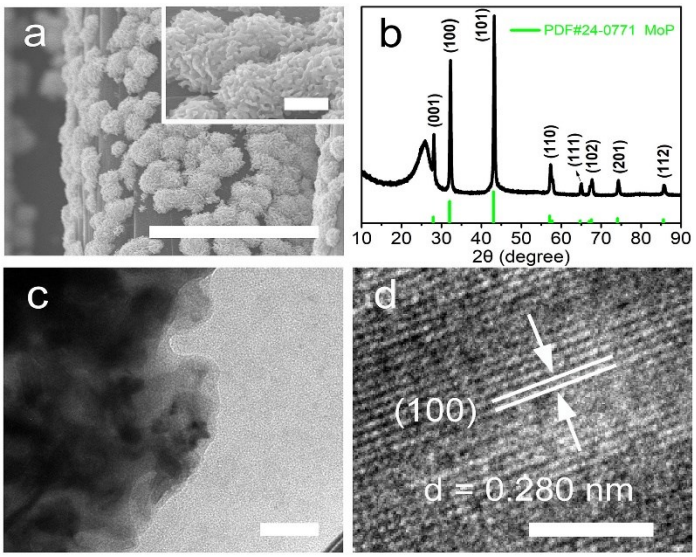

Figure S4 (a) SEM images and (b) XRD patterns of individual MoP/CC prepared without the Co salts. The scale bar is 5 μm and 500 nm, respectively. (c, d) TEM and High-resolution TEM images. The scale bar is 50 and 1 nm, respectively.

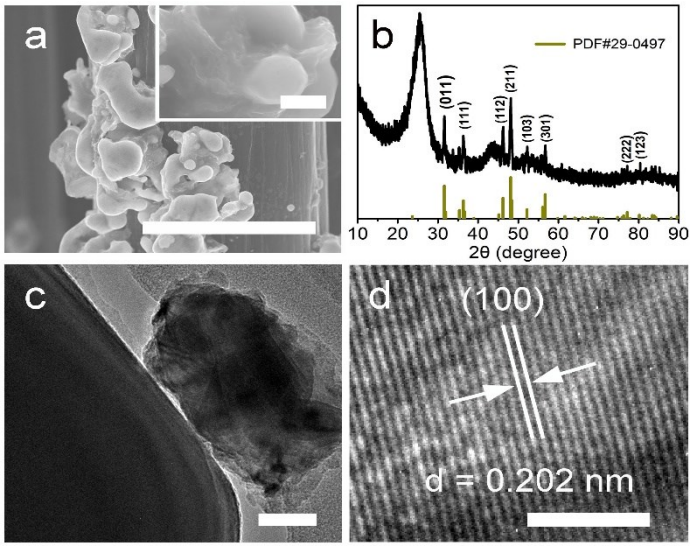

Figure S5 (a) SEM images and (b) XRD patterns of individual CoP/CC prepared without Mo salts. The scale bar is 5 μm and 500 nm, respectively. (c, d) TEM and HRTEM images. The scale bar is 50 and 1 nm, respectively.

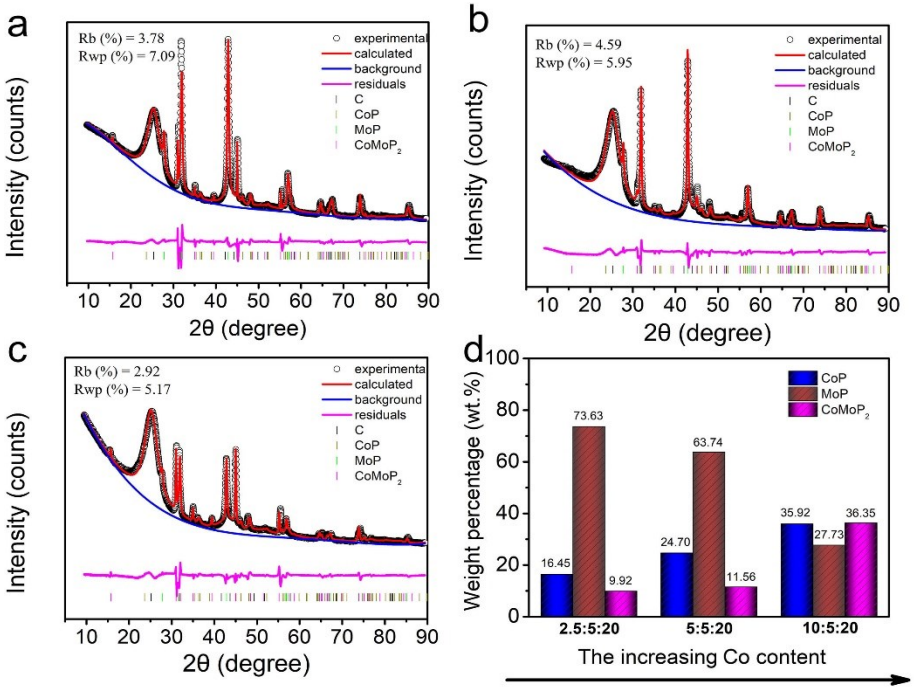

Figure S6 XRD refinement results of the Co-Mo-P NSs/CC samples with different molar mole ratio of (a) 2.5:5:20, (b) 5:5:20, (c) 10:5:20 and (d) the histogram of the CoP, MoP and $CoMoP_2$ content with the increasing of Co content. It confirms that this hybrid is consisted of CoP, MoP and $CoMoP_2$, and the proportion of heterogenous components are adjustable within a certain range.

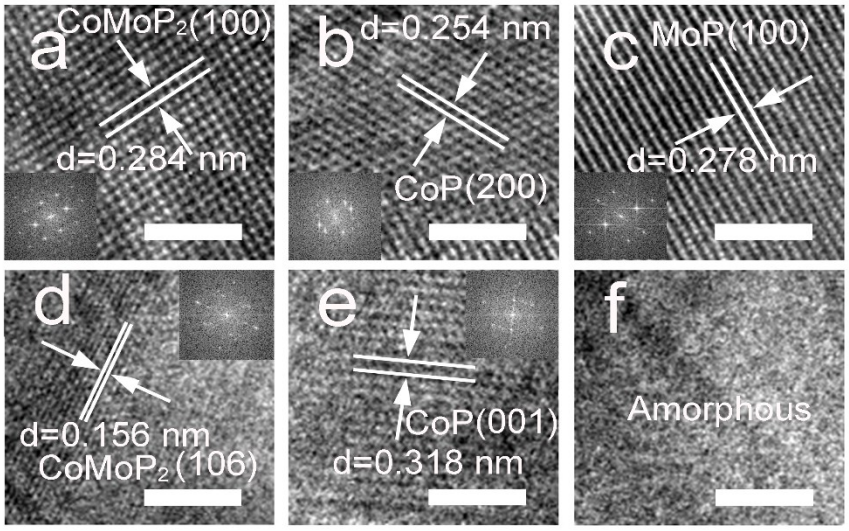

Figure S7 FTT images and the corresponding lattice spacing of the Co-Mo-P hybrid in Figure 1f: (a, d) represent the (100) and (106) planes and its lattice spacing of $CoMoP_2$, corresponding to the Ⅲ area in Figure 1f; (b, e) display the (200) and (001) planes of CoP, which is assigned to the Ⅰ area. (c) shows the (100) plane and corresponding lattice spacing of MoP, which corresponds to the Ⅱ area. (f) reflects the Ⅳ area in Figure 1f, which shows the amorphous component. All the scale bars are 2 nm.

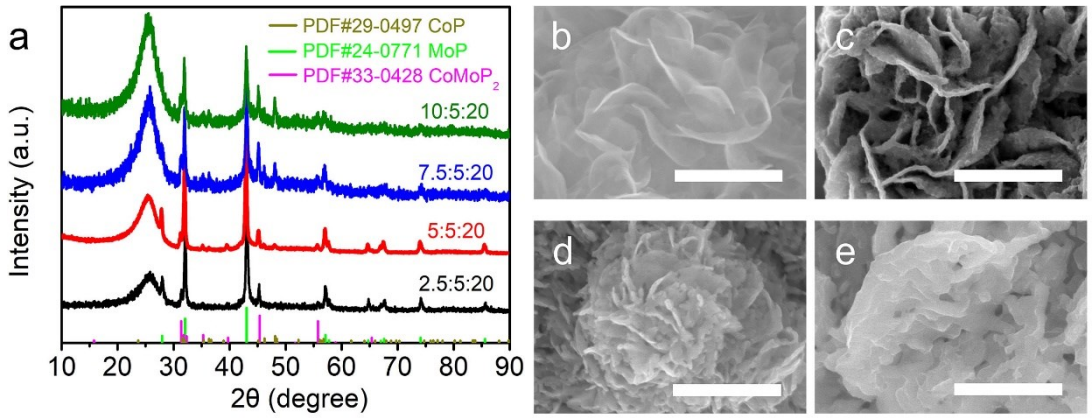

Figure S8 (a) XRD patterns of Co-Mo-P NSs/CC prepared by different raw molar ratio. SEM images of hybrid with different molar ratios: (b) 2.5:5:20, (c) 5:5:20, (d) 7.5:5:20 and (e) 10:5:20. The scale bar is 500 nm.

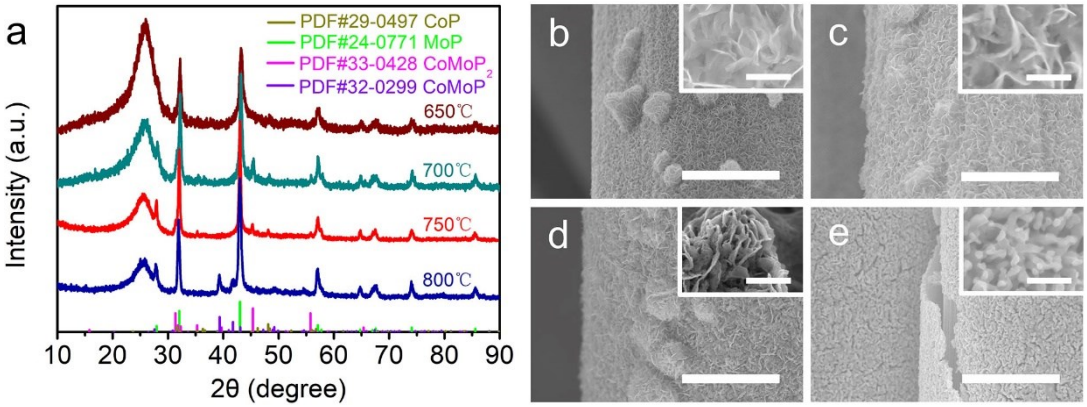

Figure S9 XRD pattern of Co-Mo-P NSs/CC prepared by different phosphorization temperatures. SEM images of Co-Mo-P NSs/CC prepared by the different phosphorization temperature: (a) 650 °C, (b) 700 °C, (c) 750 °C and (b) 800 °C. The inset are their related high-resolution SEM images. The scale bar is 3 μm and 300 nm, respectively.

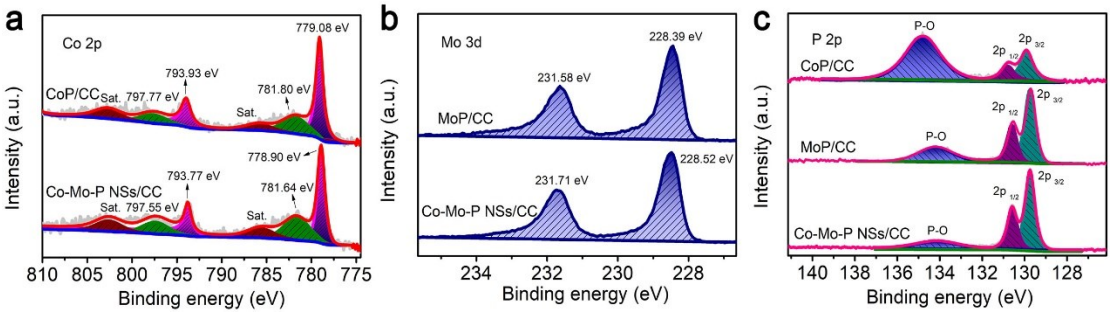

Figure S10 XPS spectra of the CoP/CC, MoP/CC and Co-Mo-P/CC: (a) Co 2p spectra for CoP/CC and Co-Mo-P/CC; (b) Mo 3d spectra for MoP/CC and Co-Mo-P/CC; (c) P 2p spectra of them.

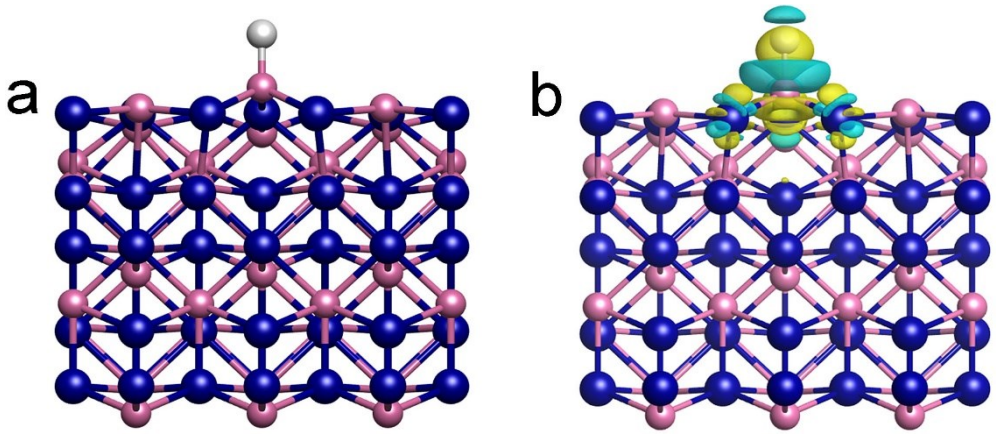

Figure S11 The structure model of the CoP (101) surface. (a) H atom is adsorbed on the P site. (b) The corresponding plots of charge density difference.

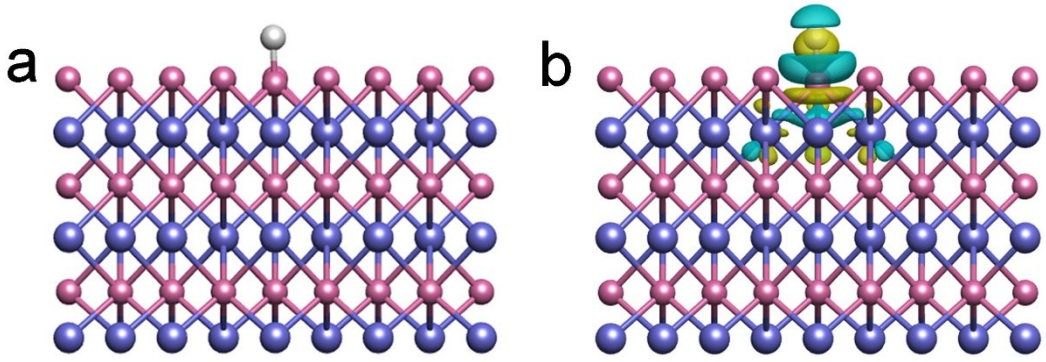

Figure S12 The structure model of the MoP (001) surface. (a) H atom is adsorbed on the P site and (b) the plots of charge density difference.

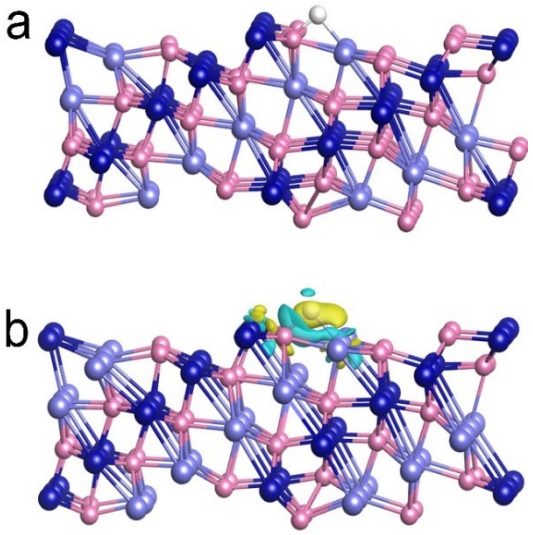

Figure S13 The structure model for the $CoMoP_2$ (106) surface. (a) H atom is adsorbed on the P site. (b) The corresponding charge density difference plots.

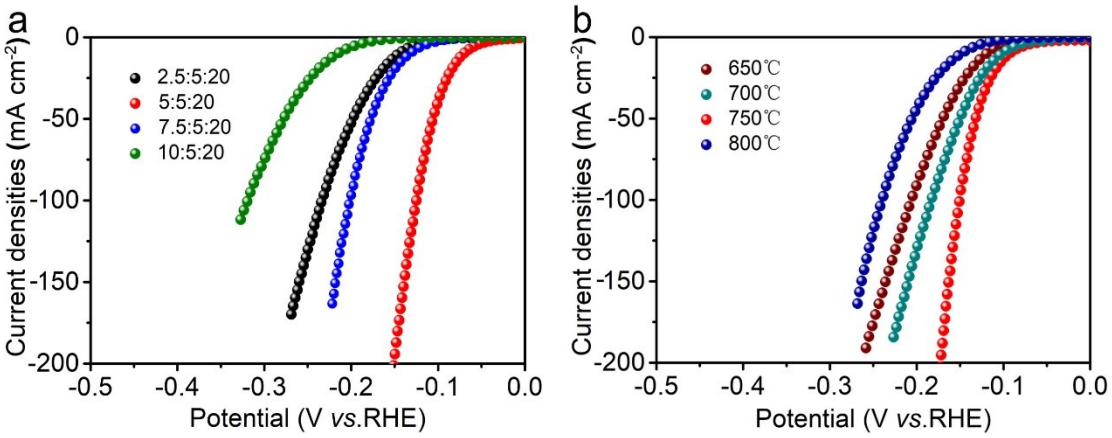

Figure S14 HER polarization curves for Co-Mo-P NSs/CC in 0.5 M H_2SO_4 electrolytes prepared by (a) different molar ratio of $CoCl_2 \cdot 6H_2O$, $Na_2MoO_4 \cdot 2H_2O$ and thiourea, and (b) different calcination temperatures.

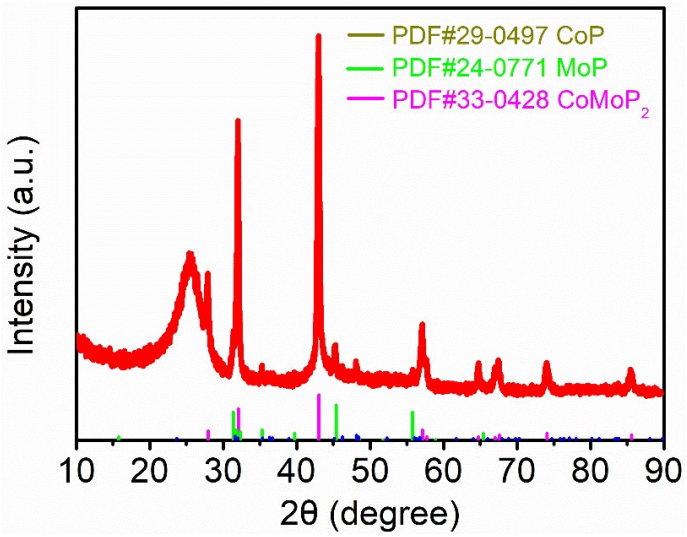

Figure S15 XRD patterns of the Co-Mo-P NSs after 20 h HER stability test. No other peaks of impurity were observed, indicating a superior structure stability.

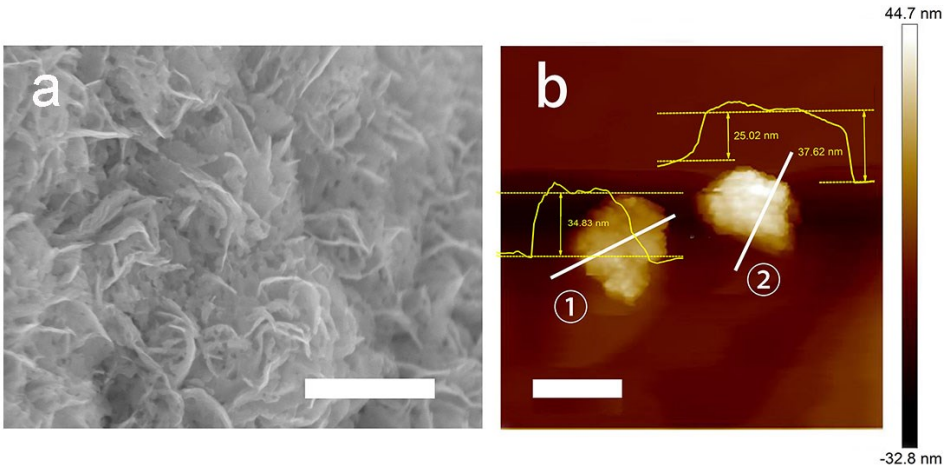

Figure S16 (a) SEM and (b) AFM images of the Co-Mo-P NSs after 20 h HER stability tests. The scale bar is 500 and 200 nm, respectively.

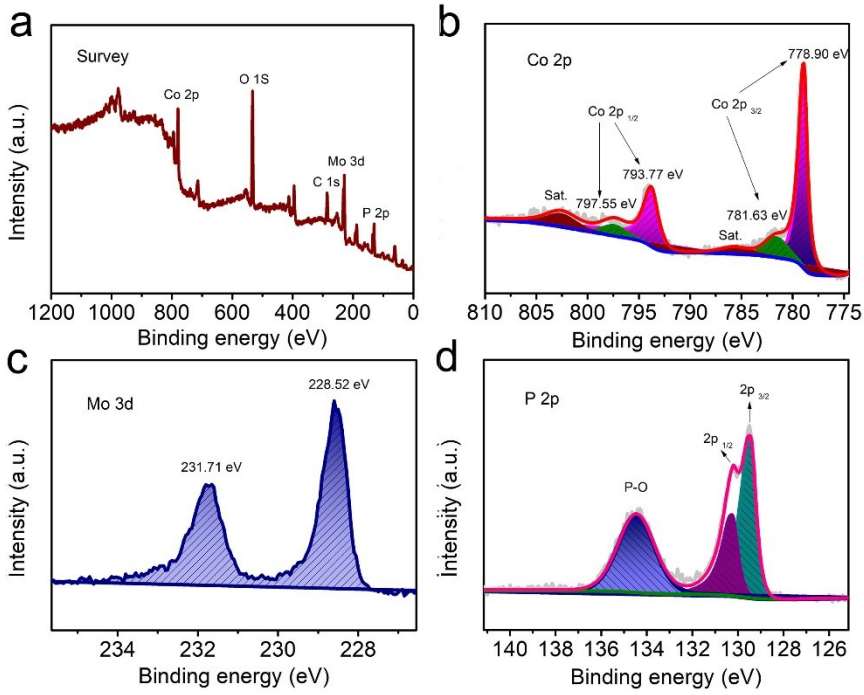

Figure S17 XPS spectrum of Co-Mo-P NSs: (a) the survey spectrum, (b) Co 2p, (c) Mo 3d and (d) P 2p region after long-term HER stability.

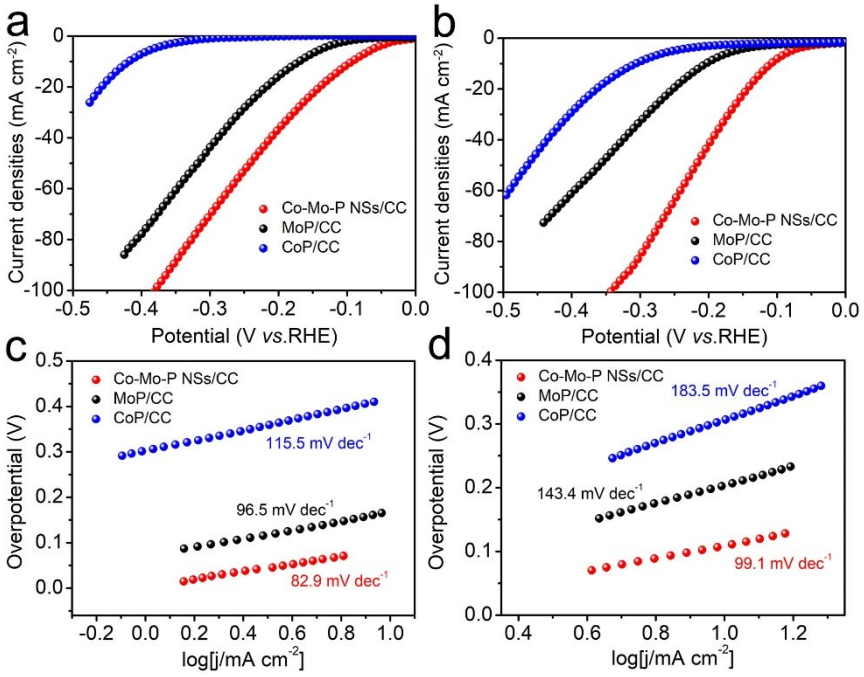

Figure S18 HER polarization curves and the corresponding Tafel plots for Co-Mo-P NSs/CC (a, c) in 1.0 M PBS and (b, d) in 1.0 M KOH with 2 mV s^{-1}, respectively.

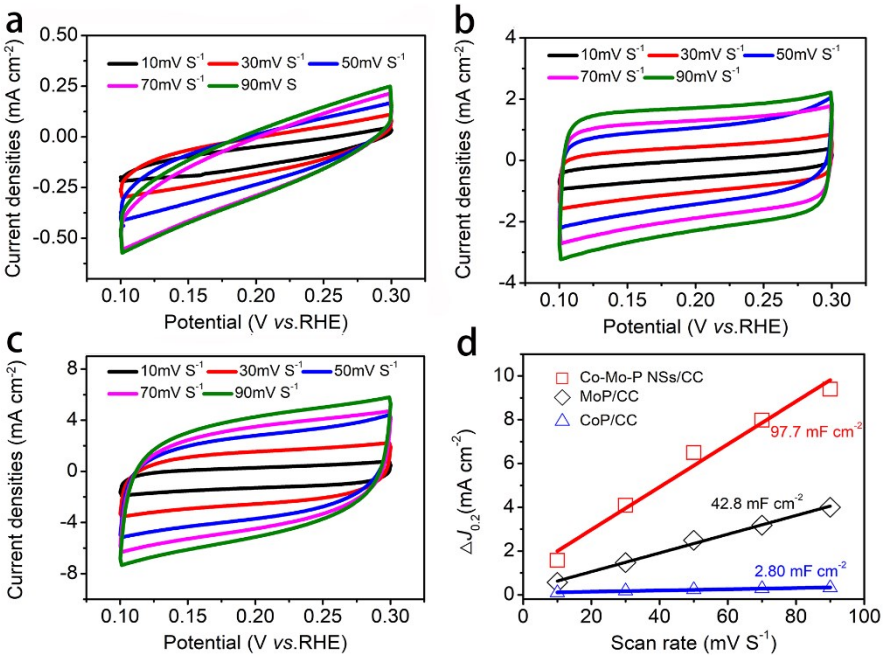

Figure S19 Cyclic voltammograms in the non-faradaic region of 0.1-0.3 V *vs.* RHE at various scan rates of (a) CoP/CC, (b) MoP/CC, (c) Co-Mo-P NSs/CC and (d) the capacitive currents densities at 0.2 V *vs.* RHE as a function of scan rates in 0.5 M H_2SO_4, which illustrate the Co-Mo-P NSs/CC holds large ECSA value than that of the individual ones.

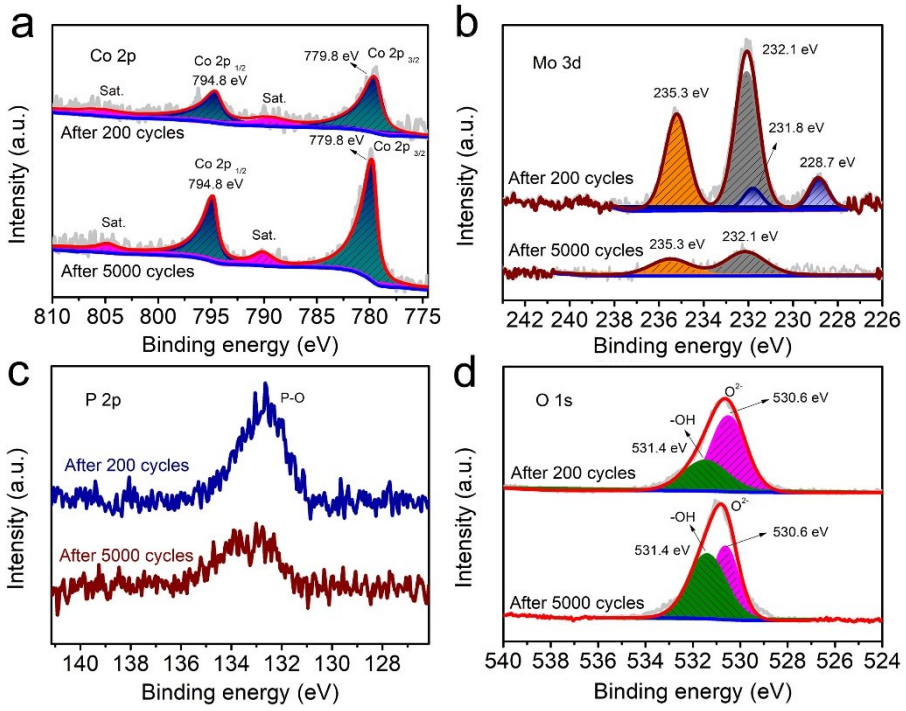

Figure S20 XPS spectra of Co-Mo-P NSs/CC after 200 and 5000 cycles: (a) Co 2p, (b) Mo 3d, (c) P 2p and (d) O 1s region. The peaks in the P 2p spectra at ≈133.5 eV can be assigned to the phosphate (PO_x) or P-O signals.

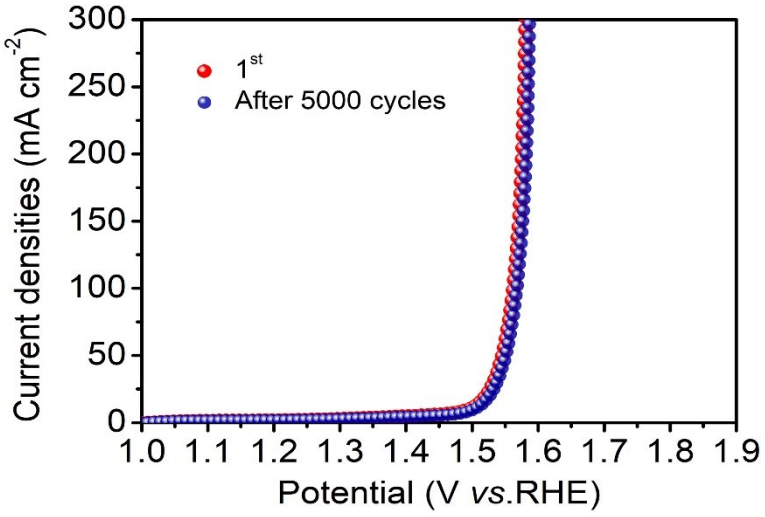

Figure S21 LSV curves of the hybrid for OER before and after 5000 CV cycles in 1.0 M KOH solution.

Table S1. Chemical composition of the Co-Mo-S/CC precursors and Co-Mo-P NSs/CC samples with different Co contents by ICP-AES analysis.

Catalysts (The molar ratio of $CoCl_2·6H_2O$, $Na_2MoO_4·2H_2O$ and thiourea)	**Co (at.%)**	**Mo (at.%)**	**S (at.%)**	**P (at.%)**	**The atom ratio of Co:Mo**
Co-Mo-S/CC (2.5:5:20)	5.97	58.01	36.02	-	0.10:1
Co-Mo-S/CC (5:5:20)	15.17	52.76	32.07	-	0.28:1
Co-Mo-S/CC (7.5:5:20)	30.44	38.54	31.02	-	0.79:1
Co-Mo-S/CC (10:5:20)	42.77	26.09	31.14	-	1.64:1
Co-Mo-P NSs/CC (2.5:5:20)	6.77	72.08	-	21.15	0.09:1
Co-Mo-P NSs/CC (5:5:20)	8.94	71.95	-	19.11	0.12:1
Co-Mo-P NSs/CC (7.5:5:20)	23.71	58.37	-	17.93	0.41:1
Co-Mo-P NSs/CC (10:5:20)	58.26	14.04	-	27.70	4.15:1

ICP-AES results evaluated the chemical composition of Co-Mo-S/CC and Co-Mo-P NSs/CC prepared by different molar ratio of $CoCl_2·6H_2O$, $Na_2MoO_4·2H_2O$ and thiourea. The atomic percent content of Co among precursors is from 5.97 to 42.77% with the increasing of Co salts. After phosphating treatment, the atomic percent content of Co is from 6.77 to 58.26%, and the atomic ratio of Co:Mo is between 0.09:1 and 4.15:1 with the increase of Co salts.

Table S2. Density of states at Fermi level of the various materials or heterointerface.

Materials	Density of states at Fermi level/eV
CoP	0.0729
MoP	0.1275
$CoMoP_2$	0.1070
CoP-$CoMoP_2$	0.1072
CoP-MoP	0.1106
MoP-$CoMoP_2$	0.1080

Table S3. Comparison of HER performance in acid electrolytes for the electrocatalysts in the literatures and this work.

Catalysts (the substrate)	Tafel slope (mV dec^{-1})	Current density (j, mA cm^{-2})	η (mV) at the j	TOF (s^{-1})	Ref.
Co-Mo-P NSs/CC	52.6	10/100	69.6/124.4	0.33	This work
CoP/CC	71.2	10/100	156.7/268.3	0.11	This work
MoP/CC	59.0	10/100	134.4/219.8	0.06	This work
MoP@NPCS (GCE)	83	10	113	-	*Appl. Catal. B: Environ.* 2020, 263, 118352.
MoP@C (CC)	54	10	49	-	*Adv. Energy Mater.* 2018, 8, 1801258.
m-CoP-NiCoP/CC	57.2	10	75	-	*J. Mater. Sci.* 2021, 56, 3375.
FLNPC@MoP-NC/MoP-C/CC	50	10	74	1.0	*Adv. Funct. Mater.* 2018, 28, 801527.
$Co_{0.85}Se$ NSs@Co	54	10	121	-	*Nano Res.* 2020, 13, 2950
N-MoP@C (GCE)	62	10	150	-	*Chem. Commun.* 2018, 54, 2502.
α-MoC_{1-x}-MoP/C (GCE)	57	10	173	~0.325	*Electrochim. Acta* 2020, 334, 135624.
$NiMoP_2$/CC	56	100	199	0.15	*J. Mater. Chem. A* 2017, 5, 7191.
Carbon-coated Co-Mo-P/CC	52.9	10	96	-	*Int. J. Hydrogen Energy*, 2020, 45, 544.
SnO_2 nanotubes (GCE)	104	10	147	-	*J. Alloy. Compd*. 2021, 865, 158597
MoP-RGO (GCE)	62	10	117	-	*Electrochim. Acta* 2017, 232, 254.
Ru@Co/N-CNTs (GCE)	33	10	92	-	*ACS Sustainable Chem. Eng*. 2020, 8, 9136.
HiHo-NiCoP (GCE)	52	10	103	-	*Chem. Commun.* 2020, 56, 90.
MoP@PC (GCE)	59.3	10	258	-	*ACS Appl. Mater. Interfaces* 2018, 10, 17140.
Fe_3S_4(52.1wt%)/ MIL-53 (GCE)	60	10	92	-	*Chem. Commun.* 2019, 55, 4570
N-MoP (GCE)	68	10	175	-	*Electrochim. Acta* 2020, 342, 136059.
$FeMoS_{(mw)}$ (GDE)	57	10	140	-	*ACS Catal*. 2020, 10, 14336.
Mo_2N-Mo_2C (GCE)	55	10	157	0.086	*Adv. Mater.* 2018, 30, 1704156.
CoP@PCM (Cu wire)	75.4	10	155	-	*ChemCatChem* 2020, 12, 3929.
$RuTe_2$/Gr (GCE)	33	10	72	-	*Chem Asian J.* 2020, 15, 2886
Mo_xC (GCE)	-	10	239	~0.03	*J. Catal.* 2019, 371, 325.

Table S4. Comparison of HER performance in neutral or near-neutral medium for electrocatalysts in the literatures and this work.

Catalysts (the substrate)	**Tafel slope (mV dec^{-1})**	**Current density (j, mA cm^{-2})**	**η (mV) at the j**	**Loading mass (mg·cm^{-2})**	**Ref.**
Co-Mo-P NSs/CC	82.9	10	91.2	2.5	This work
CoP/CC	115.5	10	418.0	2.5	This work
MoP/CC	96.5	10	169.4	2.5	This work
MoP/MoS_2/CC	48	10	96	0.029	*ACS Appl. Mater. Interfaces*, 2019, 11, 25986.
Ti-CoSP (Ni-foam)	118	10	132	-	*Chem. Mater.* 2020, 32, 9591
Ni-Co-Fe-P/NF	121.7	10	104	-	*Int J Hydrogen Energy* 2020, 45, 2504.
MoP700 (GCE)	79	10	196	-	*ACS Catal.* 2019, 9, 8712-8718.
W-Mo_xC/C (GCE)	54.3	10	178	-	*Electrochim. Acta*, 2021 370, 137796
v-NiFe LDH (Ni foam)	46.3	10	87	-	*ACS Energy Lett.* 2019, 4, 1412.
CoO/Co_4N/NF	80	10	145	-	*J. Mater. Chem. A* 2018, 6, 24767
CN-Ru-RuO_2/C_3N_4 (GCE)	92	10	342	-	*Nano Energy*, 2020, 76, 105079
$Ni(OH)_2$/Ni:Pi (Ni foam)	175	10	340	-	*Inorg. Chem. Front.* 2019, 6, 3093.
Co, Mo_2C-CNF	92.8	10	206	-	*Chem. Eur. J*, 2020, 397, 125481
Fe-NiS/$Ni(OH)_2$ (FTO glass)	118	10	196	-	*Appl. Catal. A: Gen,* 2019, 586, 117226.
NiCu@C (Graphite plate)	80	10	164	0.38	*Adv. Energy Mater.* 2018, 8, 1701759.
Co-HNP/CC	38	10	87	1.0	*Angew. Chem. Int. Ed.* 2016, 55, 6725.
Cu-PDA CPs (GCE)	83	10	290	-	*Catal. Sci. Technol.,* 2019, 9, 4347.
Ru-S-Sb/antimonene (Carbon paper)	118	10	153	-	*Chem. Commun.* 2019, 55, 10884
Fe@N-CNT/IF	199.6	10	130	-	*Adv. Sci.* 2019, 6, 1901458.
Mn-Ni-S/NF	65	10	84	-	*J. Mater. Chem. A*, 2019, 7, 25628.
PdP_2@CB (GCE)	72.3	10	84.6	0.285	*Angew. Chem. Int. Ed.* 2018, 57, 14862.
$Ni_{0.1}Co_{0.9}P$ (CFP)	103	10	125	0.58	*Angew. Chem. Int. Ed.* 2018, 57, 15671.
Co-Fe-P (GCE)	138	10	138	0.285	*Nano Energy* 2019, 56, 225.

Table S5. Comparison of HER performance in alkaline electrolytes for electrocatalysts in the literatures and this work.

Catalysts (the substrate)	**Tafel slope ($mV\ dec^{-1}$)**	**Current density (j, $mA\ cm^{-2}$)**	**η (mV) at the j**	**loading mass ($mg \cdot cm^{-2}$)**	**Ref.**
Co-Mo-P NSs/CC	99.1	10	108.9	2.5	This work
CoP/CC	183.5	10	306.0	2.5	This work
MoP/CC	143.4	10	204.4	2.5	This work
CoP/Ni_2P@HP NCP (GCE)	65.5	10	294	-	*Nanoscale* 2020, 12, 23851.
NiP_2 (Graphite)	85.5	10	178	-	*Electrochim. Acta* 2020, 344, 136116
$NiWO_4/Ni_3S_2$ (Nickel foam)	112	10	136	-	*Appl. Catal. B: Environ.* 2020, 274, 119120.
c-$CoSe_2$/CC	85	10	190	-	*Adv. Mater.* 2016, 28, 7527.
Co-BDC/MoS_2 (GCE)	86	10	248	-	*Small* 2019, 15, 1805511.
Co_3O_4-CuO (GCE)	65	10	288	-	*Int J Hydrogen Energy* 2019, 44, 26148.
N-doped Ni_3S_2/NF	113	10	155	0.59	*Adv. Energy Mater.* 2018, 8, 1703538.
MoP/CD (GCE)	77.49	10	70	-	*Nano Energy* 2020, 72, 104730
CoB@MoS_2 (GCE)	80.9	10	146	-	*Nanoscale,* 2020, 12, 10158.
MoS_x@NiO (GCE)	43	10	406	-	*Adv. Funct. Mater.* 2019, 29, 1807562.
Fe-CoP/Ti	75	10	78	1.03	*Adv. Mater.* 2017, 29, 1602441.
CoP NWs/CC	42.8	10	65	-	*Adv. Mater.* 2018, 30, 1703322.
CoMoOS (Copper foam)	86	10	130	-	*Nanoscale*, 2019, 11, 3500.
10% Ni-WSe_2 (GCE)	109	10	215	-	*J. Mater. Chem. A* 2020, 8, 403.
Co doped ReS_2 (GCE)	61.0	10	240	-	*Chem. Commun.* 2020, 56, 8472-8475
MoS_2/CoS_2 (GCE)	86.2	10	75	-	*J. Mater. Chem. A*, 2020, 8, 11435
$MoSe_2/SnS_2$ (GCE)	109	10	285	-	*Nano energy* 2019, 64, 103918.
Ni-Co-P HNBs (Ni foam)	88	10	107	2.0	*Energy Environ. Sci.* 2018, 11, 872.
MoP/NF	54.6	10	114	-	*Small Methods* 2018, 2, 1700369.

Table S6. Comparison of OER performance in alkaline electrolytes for electrocatalysts in the literatures and this work.

Catalysts (the substrate)	**Tafel slope (mV dec^{-1})**	**Current density (j, mA cm^{-2})**	**η (mV) at the j**	**TOF (s^{-1})**	**Ref.**
Co-Mo-P NSs/CC	67.6	10/100	261.9/331.0	1.14	This work
CoP/CC	116.7	10/100	390.5/586.1	0.022	This work
MoP/CC	101.0	10/100	345.9/468.0	0.038	This work
Ni_3C/C (Carbon fiber)	46.0	10/100	316/390	0.099	*Adv. Mater.* 2016, 28, 3326.
FeNiCoP	38.0	10	281	-	*Electrochim. Acta* 2021, 368, 137618.
$Co_xFe_{1-x}P$ (GCE)	37.0	10	277	0.0107	*ChemSusChem* 2019, 12, 4461.
Co/CoP (GCE)	79.5	10	340	-	*Adv. Energy Mater.* 2017, 7, 1602355.
$Co_2Mo_3O_8$@ NC-800 (GCE)	87.5	10/40	331/422	-	*Angew. Chem. Int. Ed.* 2020, 59, 11948.
CoMnP (GCE)	61.0	10	330	-	*J. Am. Chem. Soc.* 2016, 138, 4006.
MoS_2/CoB-Se/CC	86	10	270	-	*Sustain. Energy. Fuel* 2020, 4, 5036.
$Ni_{2(1-x)}Mo_{2x}P$ MWs/NF	-	50/100	323/346	0.452	*Nano Energy* 2018, 53, 492.
Ag@$Co(OH)_x$/CC	76.0	10	250	-	*Angew. Chem. Int. Ed.* 2020, 59, 7245.
CdP_2-CDs-CoP (Ni foam)	82.94	10	285	-	*ACS Sustainable Chem. Eng.* 2021, 9, 1297-1303
P-Co_3O_4 (Ti mesh)	51.6	10	280	0.0158	*Energy Environ. Sci.* 2017, 10, 2563.
PA-PPy/CC	54.9	10	340	-	*Angew.Chem.Int. Ed.* 2019, 58, 4318.
$SrIrO_3$ (GC/CC)	42	10	300	-	*Chem. Mater.* 2020, 32, 11, 4509.
$SrCo_{0.85}Fe_{0.1}P_{0.05}O_{3-\delta}$ (NF)	52.4	10	280	-	*Appl. Catal. B: Environ.* 2020, 272, 119046
$Co(OH)_2$-TCNQ/CF	101.0	25/50	296/315	0.97	*Adv. Mater.* 2018, 30, 1705366.
P/Mo-Co_3O_4@C C	59.4	10	265	-	*Adv. Sci.* 2020, 7, 1902830.
Co-Ni_3N (CC)	57.0	10	307	0.0134	*Adv. Mater.* 2018, 30, 1705516.
$FeNi_3$@NC (GCE)	77.0	10	277	-	*Appl. Catal. B: Environ.* 2020, 268, 118729

Table S7. Comparison of overall water splitting perfromance in alkaline electrolytes for electrocatalysts in the literatures and this work.

Catalysts (the substrate)	**Current density (j, mA cm^{-2})**	**η (mV) at the j**	**Ref.**
Co-Mo-P NSs/CC	10	1.56	This work
Ni-Co-P HNBs (Ni foam)	10	1.62	*Energy Environ. Sci.* 2018, 11, 872.
$NiCo_2O_4$ (Ni foam)	10	1.65	*Angew. Chem. Int. Ed.* 2016, 55, 6290.
Co-NC@Mo_2C (GCE)	10	1.685	*Nano Energy* 2019, 57, 746.
CdS@Co_9S_8/Ni_3S_2 (Co/Ni alloy)	10	1.56	*J. Mater. Chem. A* 2020, 8, 3083
$Co_{0.75}Ni_{0.25}(OH)_2$ (Carbon fiber paper)	10	1.56	*Small* 2019, 15, 1804832.
V-CoP@ a-CeO (CC)	10	1.56	*Adv. Funct. Mater.* 2020, 30, 1909618
Co_6W_6C@NC (CC)	10	1.585	*Small* 2020, 16, 1907556
IrNi-$FeNi_3$/NF	10	1.47	*Appl. Catal. B: Environ.* 2021, 286, 119881
$Co_2Mo_3O_8$@NC-800 (GCE)	10	1.67	*Angew. Chem. Int. Ed.* 2020, 59, 11948.
MoS_2/CoB-Se/CC	10	1.58	*Sustain. Energy. Fuel* 2020, 4, 5036.
Pt/C/NF‖RuO_2/NF	10	1.53	*Chem. Commun.* 2016, 52, 1486.
Co-Mo-P-O (Ni foam)	10	1.57	*ACS Sustainable Chem. Eng.* 2020, *8*, 2835.
CuSe (NF/FTO)	10	1.68	*ChemSusChem* 2020, 13, 3222.