Supporting Information for

Self-supporting CoP-C nanosheet arrays derived from Metal-Organic Framework as synergistic catalysts for efficient water splitting

Min Wang[a,b], Yuanzhuo Li[a], Lingling Zhai[b], Xiang Zhang[a,*], Shuping Lau[b,*]

1. Experimental Procedures

1.1 Chemicals: $Co(NO_3)_2 \cdot 6H_2O$, 1,4-benzene dicarboxylic acid, polyvinyl pyrrolidone (Mw =58000), DMF, EtOH, KOH, KSCN, 20% Pt/C and RuO_2 were purchased from Sigma Aldrich. NaH_2PO_2 was used as the phosphorus source for phosphatization. Nickel foam (NF) with a thickness of 1.7 cm was purchased from Sigma Aldrich. 1 M KOH was purchased from Aladdin Ltd. (Shanghai, China). All chemicals were used as received without further purification. The ultra-pure water was purified through a Millipore system.

1.2 Synthesis Procedures

Synthesis of Ni_2P/NF

Commercial NF was washed with 3 M HCl and EtOH three times. The fresh NF in porcelain was placed at the middle of the furnace, and NaH_2PO_2 (0.5 g) in another porcelain boat was placed upstream of the furnace. The samples were heated at 300 ℃ for 1.5 h in the Ar atmosphere, with a ramping rate of 6 ℃ min^{-1}. After cooling down, a Ni_2P coating on the surface of NF (Ni_2P/NF) was obtained.

Synthesis of CoP-C/NF

The synthesized CoP-C/NiO/NF was further annealed for 1.5 h at 400 ℃ with a heat rate of 7 ℃ min^{-1} under 5 % H_2 and 95 % Ar mixed atmosphere, and the total flow was about 70 mL min^{-1}. After annealing, the NiO coating on the NF was converted into Ni (0), so a CoP-C nanosheet array supported by NF (CoP-C/NF) was obtained.

Synthesis of CoP-C/Ni-P/NF

The synthesized $Co_2(OH)_2(BDC)$ /NiO/NF was annealed for 1.5 h at 365 ℃ with a heat rate of 7 ℃ min^{-1} under 5 % H_2 and 95 % Ar mixed atmosphere total flow was about 70 mL min^{-1}. After annealing, the self-supporting complex was placed directly at the middle of a furnace, and NaH_2PO_2 (0.6 g) in another porcelain boat was placed upstream of the furnace. Subsequently, the samples were heated at 350 ℃ for 1.5 h in the Ar atmosphere, with a ramping rate of 6 ℃ min^{-1}. After phosphorization, the CoP-C nanosheet array supported by the Ni_2P-Ni_5P_4 coated NF (CoP-C/Ni-P/NF) was obtained.

2. Figures and tables

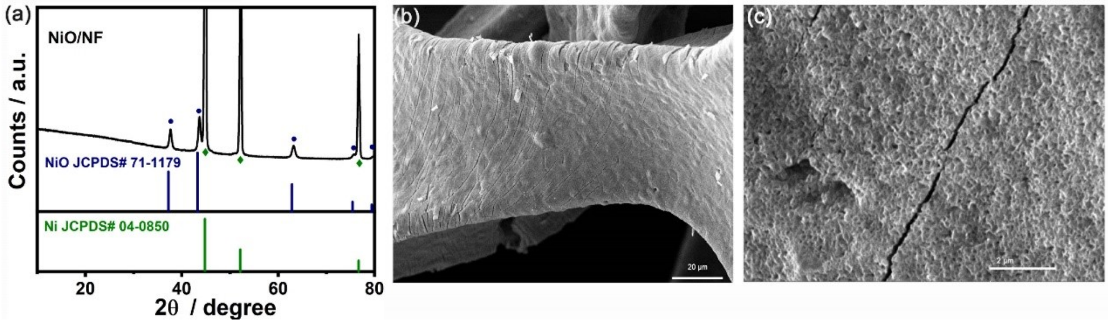

Fig. S1 XRD (a) SEM images under low magnification (b) and high magnification (c) of the pre-oxidized NF.

After oxidation, the surface of the NF becomes rough, although it seems smooth in a low magnification scanning electron microscopy (SEM) image. The X-ray diffraction (XRD) peaks at 37.4°, 43.3°, 61.8°, 75.4°, 79.3° correspond to NiO (JCPDS# 71-1179). Strong diffraction peaks at 44.5°, 51.8°, 76.3° index to the metallic nickel of NF (JCPDS# 04-0850). These results above hint towards the formation of NiO coating on the surface of NF (NiO/NF).

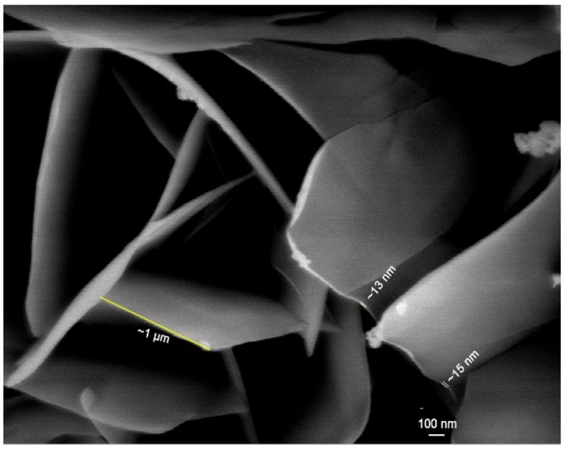

Fig. S2 The enlarged SEM image of $Co_2(OH)_2(BDC)$ nanosheet on the NiO/NF

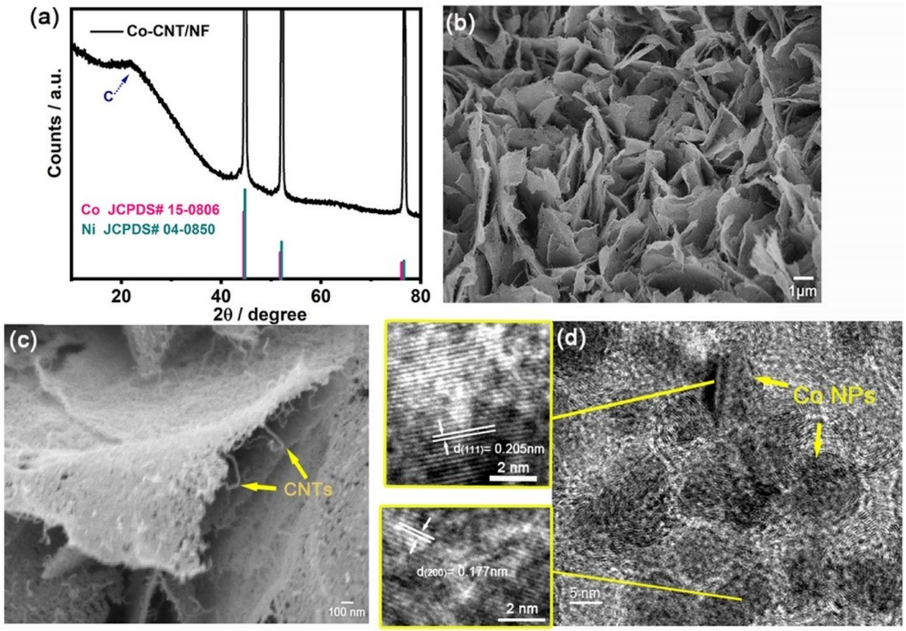

Fig. S3 Characterization of the Co-CNT/NF: (a) XRD spectrum, (b) and (c) SEM images in different magnifications, (d)TEM image of Co-CNT nanosheet. Inset: lattice fringes of Co nanoparticles.

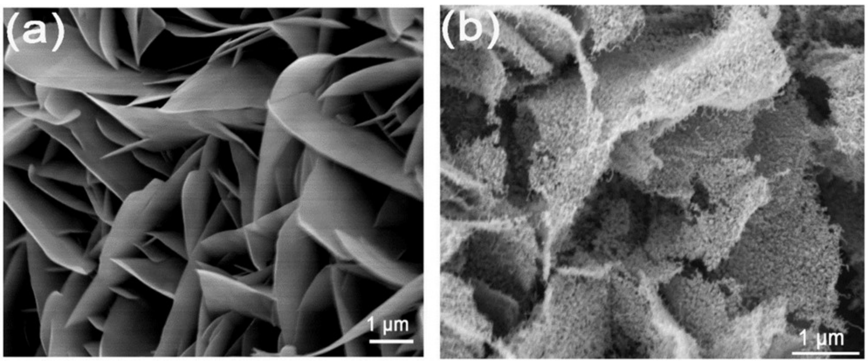

Fig. S4 SEM images of the $Co_2(OH)_2(BDC)/NiO/NF$ after calcination at 350 ℃ (a) and 450 ℃ (b) under 5% H_2-95% Ar mixed atmosphere for 1.5 h.

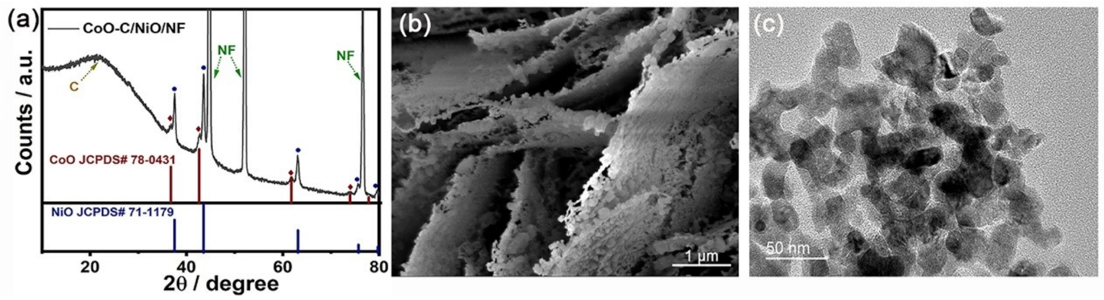

Fig. S5 XRD pattern (a), SEM image (b) and TEM image (b) of the $Co_2(OH)_2(BDC)$ nanosheet after calcination at 400 °C in pure Ar atmosphere.

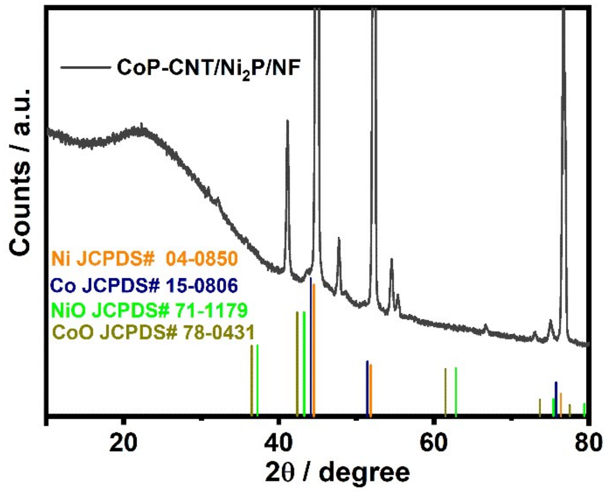

Fig. S6 The spectrum to contrast the XRD pattern of CoP-CNT/Ni_2P/NF and the standard card of metallic Co/Ni and CoO/NiO.

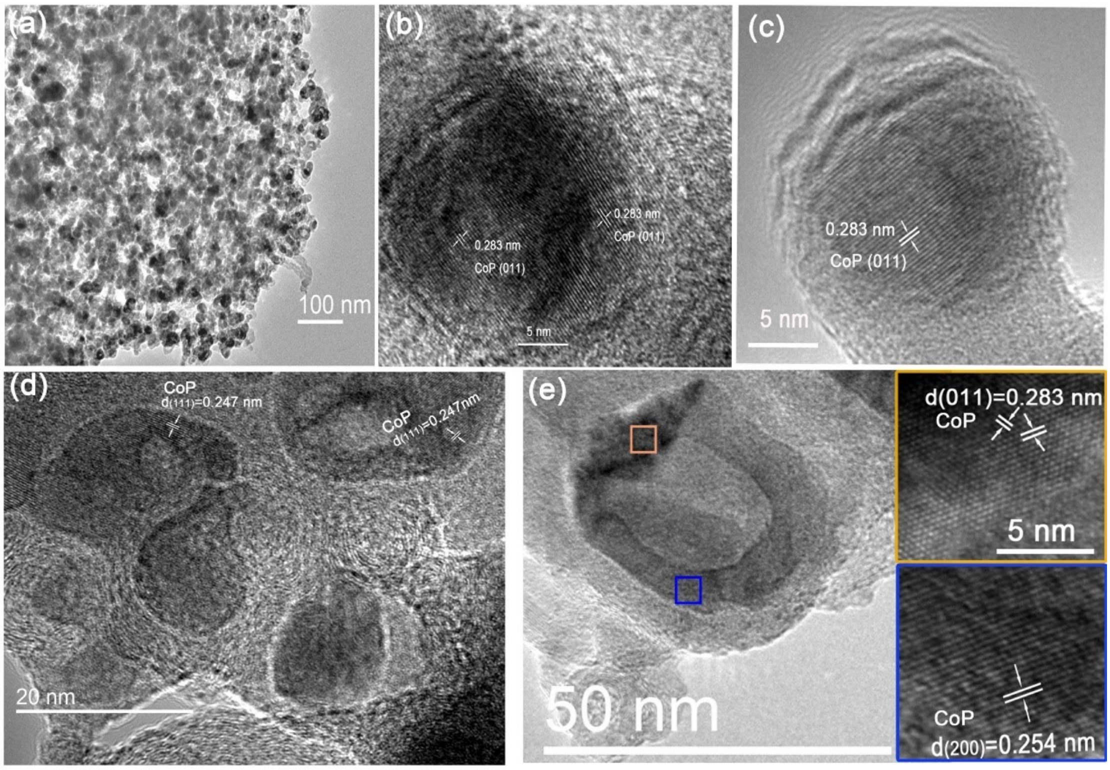

Fig. S7 TEM images of the CoP-CNT/Ni_2P/NF: (a) CoP-CNT nanosheet, (b) CoP NPs surrounded by CNTs in the nanosheet, (c) CoP NPs encapsulated by carbon layer. (d) and (e) some irregular hollow CoP NPs in the nanosheet.

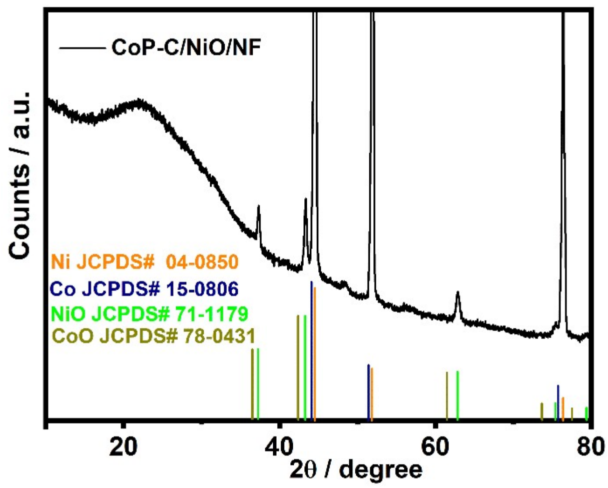

Fig. S8 The spectrum to contrast the XRD pattern of CoP-C/NiO/NF and the standard card of metallic Co/Ni and CoO/NiO.

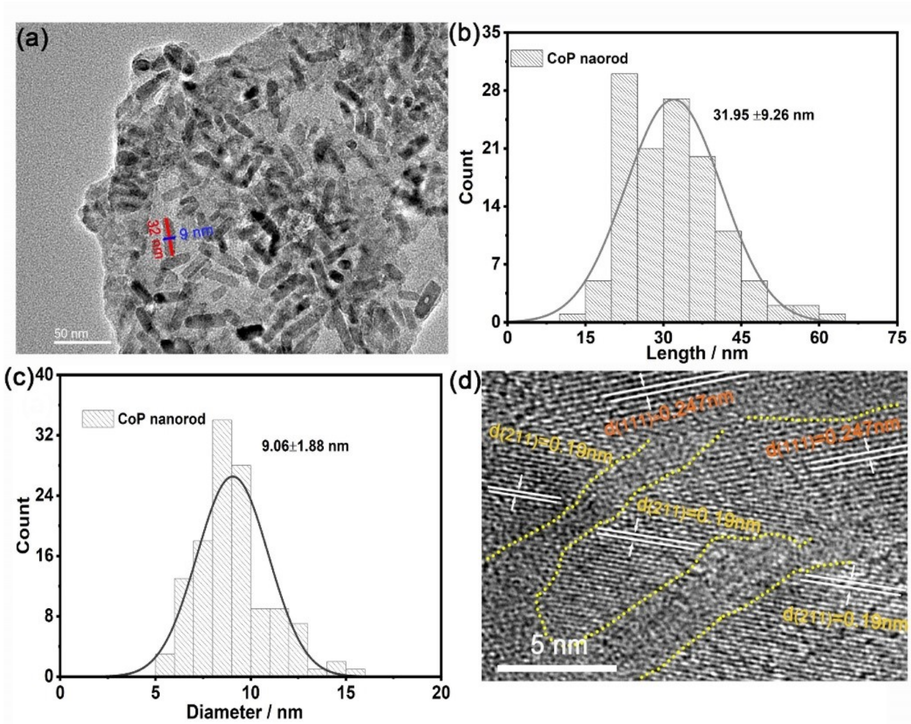

Fig. S9 (a)TEM image of the CoP-C nanosheet in the CoP-C/NiO/NF. (b) and (c) the size distribution of the CoP nanorod. (d) HRTEM image of the CoP-C nanosheet in the CoP-C/NiO/NF (edge site)

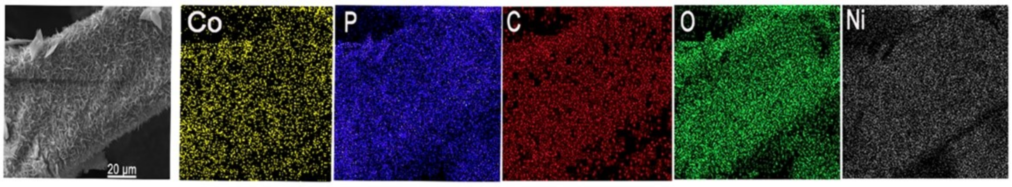

Fig. S10 The energy-dispersive X-ray spectroscopy elemental mapping images of CoP-C/NiO/NF.

Table S1 The corrsonding elements ratio in CoP-C/NiO/NF calculated by EDS.

Co (atom%)	P (atom %)	C (atom %)	O (atom %)	Ni |(atom %)
5.96	14.11	23.49	30.94	25.50

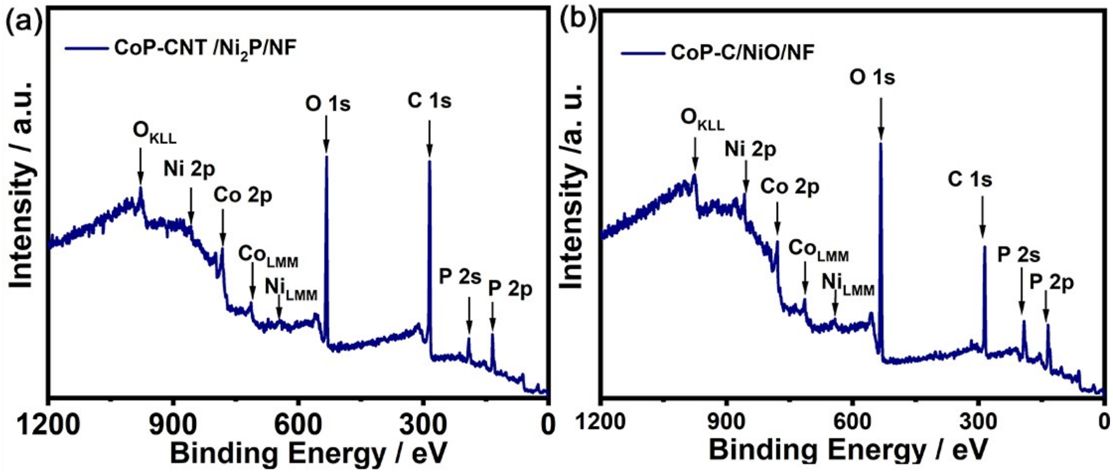

Fig. S11 XPS survey spectra of the CoP-CNT/Ni_2P/NF (a) and CoP-C/NiO/NF (b).

Fig. S11 shows characteristic peaks from outer electrons (s, p) and Auger electrons (LMM, KLL) of Ni, Co, O, C and P atoms in CoP-CNT/ Ni_2P/NF and CoP-C/NiO/NF.

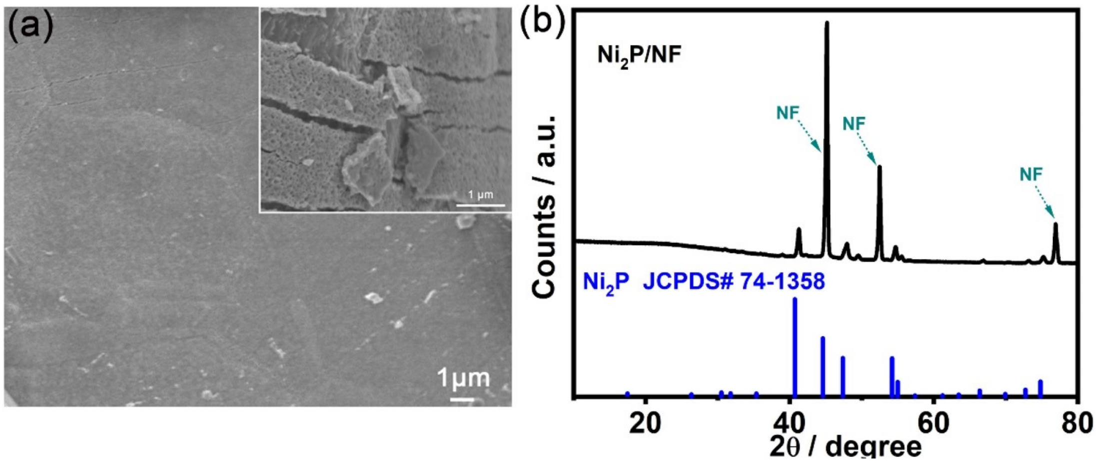

Fig. S12 (a) Low and high magnification (Inset) SEM image of Ni_2P/NF, (b) XRD pattern of Ni_2P/NF.

As shown in Fig. S12, the surface of NF seems smooth in the low magnification SEM image, while in the high magnification SEM image, a film of the Ni_2P on the NF could be observed. And XRD analysis proves the successful synthesis of Ni_2P on the surface of NF (Ni_2P/NF)

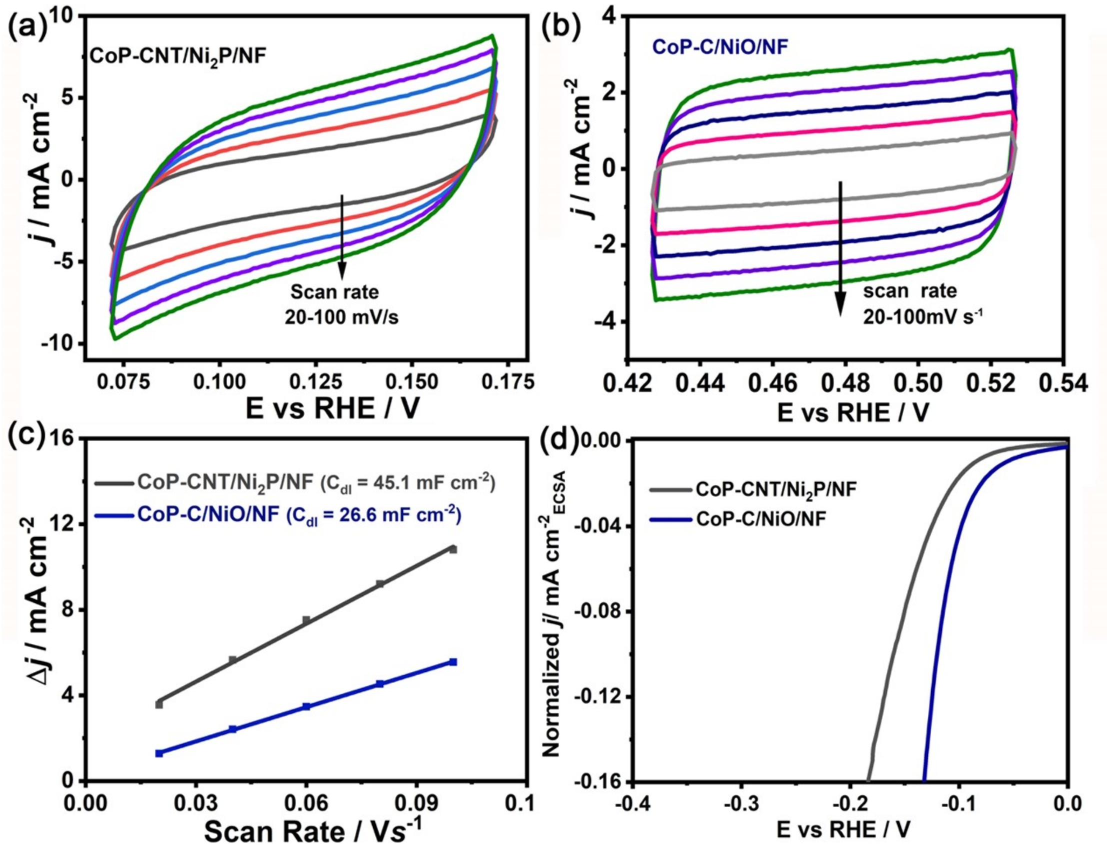

Fig. S13 Cyclic voltammetry curves of the CoP-CNT/Ni_2P/NF (a) and CoP-C/NiO/NF (b) at different scan rates from 20 mV s^{-1} to 100 mV s^{-1} in 1.0 M KOH solution. (c)The corresponding C_{dl} plots. (d) ECSA-normalized polarization curves of the CoP-CNT/Ni_2P/NF and CoP-C/NiO/NF.

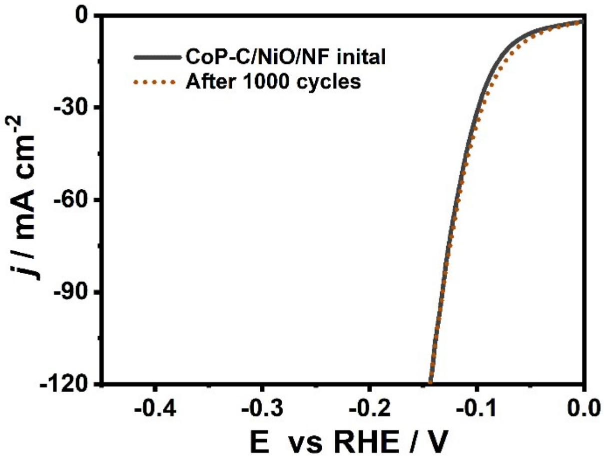

Fig. S14 The LSV curve of the CoP-C/NiO/NF toward HER in 1.0 M KOH solution before and after 1000 cycles.

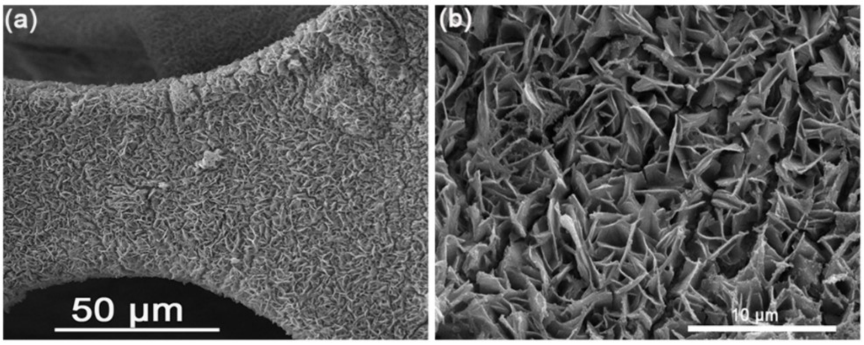

Fig. S15 The SEM images of the CoP-CNT/NiO/NF catalyst after long-time electrolysis towards HER for 20 h in 1.0 M KOH.

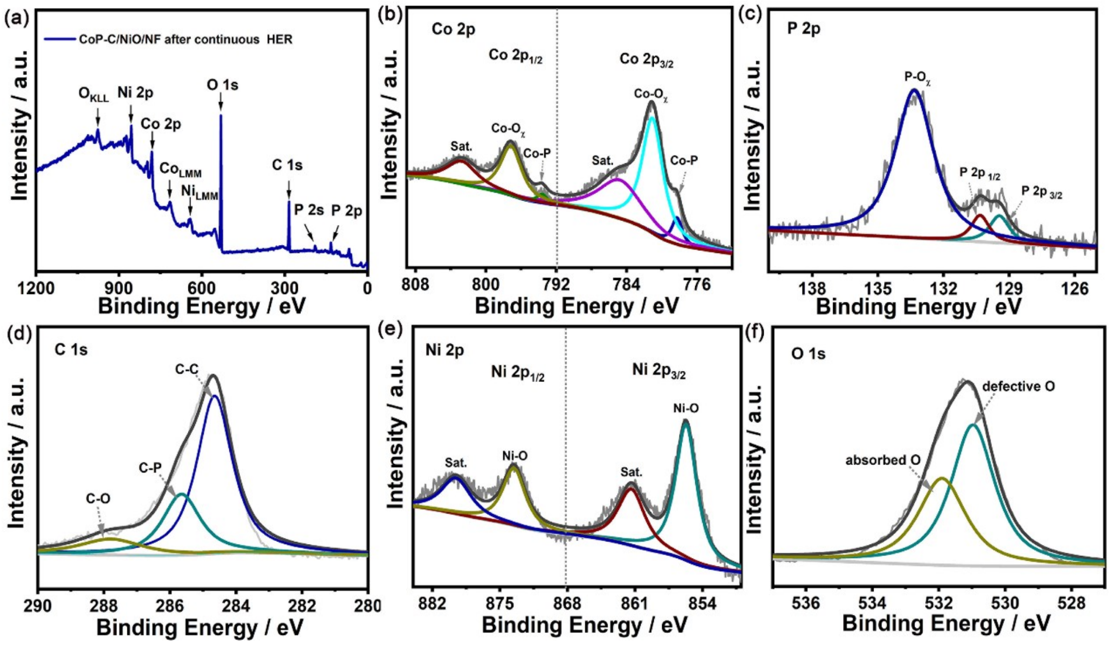

Fig. S16 The XPS spectrum of the CoP-C/NiO/NF catalyst after 20 h electrolysis toward HER in 1.0 M KOH solution: (a) survey -scan spectra (b) Co 2p (c) P 2p (d) C 1s (e) Ni 2p (f) O 1s.

Table S2 Comparison of HER and OER performance of self -supporting CoP-C nanosheet arrays with some previously reported CoP-based catalysts in 1.0 M KOH solution.

Catalyst	**HER**		**OER**		**Reference**
	η10 (mV	**Tafel Slope (mV dec-1)**	**η10 (mV**	**Tafel Slope (mV dec-1)**	
CoP-C/NiO/NF	72	51	265	65	This work
CoP-CNT/ Ni_2P/NF	82	62	253	58	This work
2D CoP@NC	127	58	300	---	*ACS Catal.* **2017**, *7*, 3824.
CoP@BCN	215	52	---	---	*Adv. Energy Mater.* **2017***, 7,* 1601671.
NiO@NiCoP	112	56	---	---	*Electrochim. Acta* **2018**, *292*, 88.
CoP/NPC/TF	80	50	---	---	*Adv. Energy Mater*. **2019**, *9*, 1803970.
CoP/Co-MOF/CF	34	43	---	---	*Angew. Chem., Int. Ed.* **2019***, 58*, 4679.
W-CoP NAs/CC	94	63	---	--	*Small* **2019**, *15*, 1902613.
CoP/Co_2P@NC/Ti	49	51	--	--	*I Sci*. **2020**, 101264.
CoP-Ni_2P	105	64	320	69	*ACS Appl. Mater. Interfaces* ***2017****, 9,* 23222.
CoP/NCNHP	115	66	310	70	*J. Am. Chem. Soc.* **2018**, 1*40*, 2610.
Holey Ni-Co-P nanosheet	58	57	280	---	*J. Am. Chem. Soc.* **2018**, *140*, 5241.
CoP(MoP)-$CoMoO_3$@CN	198	95	296	105	*ACS Appl. Mater. Interfaces* **2019***, 11,* 6890.
Co_xP@NC	187	58.5	380	79.5	*Carbon* **2019**, *145*, 694.
CoP@NPCP nanoplate	150	20	421	115	*Carbon* **2019**. *150*. 446.
C-CoP nanocages	173	63.1	333	71.1	*Nanoscale* **2019**, *11*, 17084.
Ni_2P@G	103	56.5	275 (20)	56.2	*J. Mater. Chem. A* **2019***, 7,* 13455.
(FeNiP)/P-doped graphene	173	50.3	229	49.7	*J. Mater. Chem. A* **2019**, *7*, 14526.
CoP/CN@MoS_2	149	88	289	69	*ACS Appl. Mater. Interfaces* **2019**, *11*, 36649.
Ce-CoP	144	70	270	63	*ACS Sustain. Chem. Eng.* **2020***, 8,* 10009.

CoP -InNC@CNT	159	56	270	84	*Adv. Sci.* **2020**, *7*, 1903195.
Co-P@PC	76	---	280	53	*Small* **2020**, *16*, 1900550.
hcp-Co@NC	90	90.7	290	71.2	*Appl.Catal.-B: Environ.* **2020***, 266,* 118621.
C@ Ni_8P_3/NF	110	46	267	51	*ACS Appl. Mater. Interfaces* **2016**, *8,* 27850.
Co_2P/Co foil	159	59	319	79	*J. Mater. Chem. A* **2017**, *5*, 10561.
CoO@CoNC @ NF	190	98	309	53	*Chem* **2017**, *2*, 791.
NiFe LDH@NiCoP/NF	120	88.2	220	48.6	*Adv. Funct. Mater.* **2018***, 28,* 1706847.
CoP NS/CC	90	53.5	310	53.9	*J. Mater. Chem. A* ***20****18, 6,* 24277.
WCoP @ (S, N)-C/CC	67	66	280	---	*ACS Energy Lett.* **2018***, 3, 1434.*
2%Mo-Ni_2P/CoP/NF	118 (50)	45.4	319 (50)	46.1	*Appl. Catal.-B: Environ.* **2020***, 272,* 118951.
NiCoP/C nanobox	---	---	330	96	*Angew. Chem. Int. Ed.* **2017**, *56*, 3897.
CoPi-HSNPC-800	--	--	320	85	*ACS Sustain. Chem. Eng.* **2019***, 7*, 13559.
CoP-NC-CNT	---	----	251	82.1	*Carbon* **2019**, *141,* 643.
NiCoP-O/NC nanosheets	--	--	300	94	*Nano Energy* **2020***, 9,* 104453.
CoP/D-Co-Cu MOF	---	---	290	65	*J. Mater. Chem. A* **2020**, *8*, 14099.
Co_3O_4@CoP /Ni foil	---	---	238	51.4	*Adv. Energy Mater.* **2017***, 7,* 1602643.
Co_3O_4@Ni_2P-CoP /NF	---	---	290 (50)	75	*Electrochim. Acta* **2019**, *298*, 525.
CoS_2@NGC@NF	--	--	243	71	*J. Mater. Chem. A* **2020***, 8,* 6795.

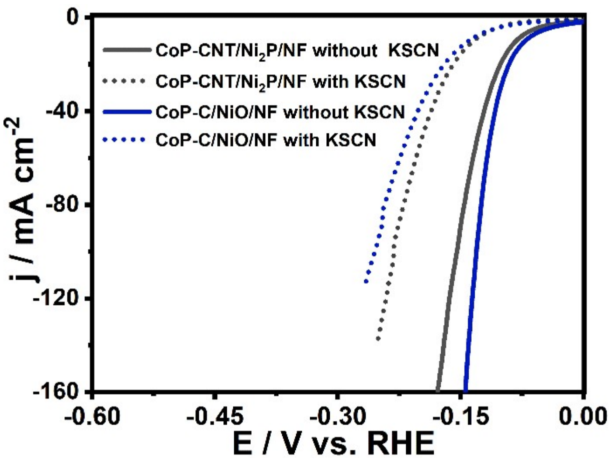

Fig. S17 Polarization curves of the CoP-CNT/Ni_2P/NF and CoP-C/NiO/NF with and without the addition of 10 mmol KSCN toward HER in 1.0 M KOH.

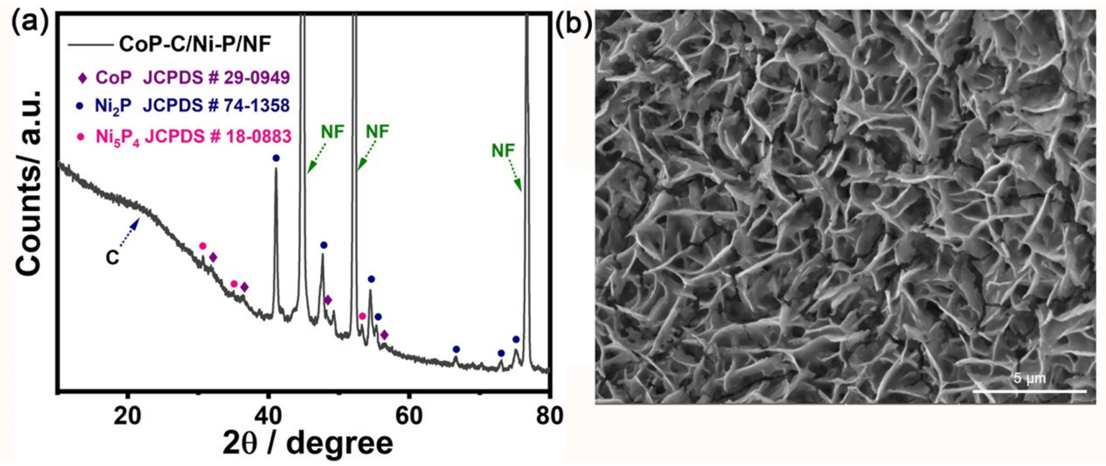

Fig. S18 XRD pattern (a) and SEM image (b) of the CoP-C/Ni-P/NF.

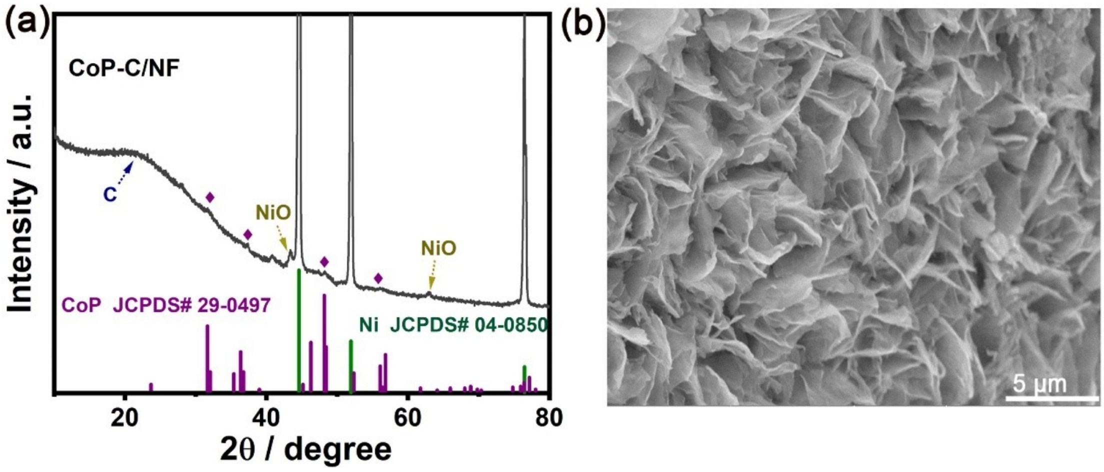

Fig. S19 XRD pattern (a) and SEM image (b) CoP-C/NF.

As shown by the XRD pattern in Fig. S19, less NiO was resting on the surface of NF in CoP-C/NF.

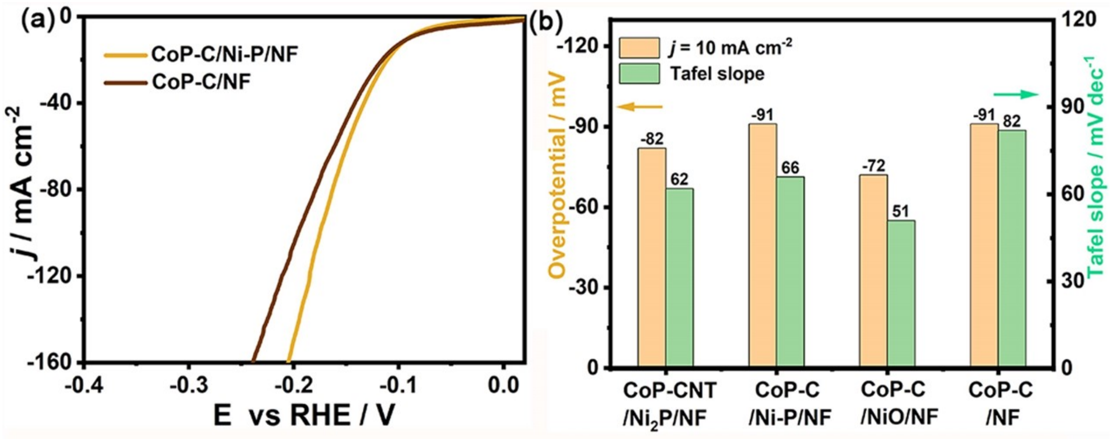

Fig. S20 (a) polarization curves of the CoP-C/Ni-P/NF and CoP-C/NF toward HER in 1.0 M KOH solution at a scan rate of 5 mV s^{-1}. (b) The histogram of the overpotential at j = 10 mA cm^{-2} and corresponding Tafel slope for the synthesized Co-based catalysts toward HER in 1.0 M KOH solution.

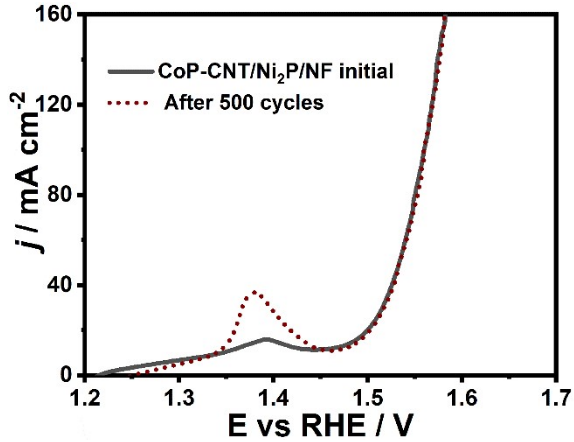

Fig. S21 The LSV curve of the CoP-CNT/Ni_2P/NF towards OER in 1.0 M KOH before and after 500 cycles.

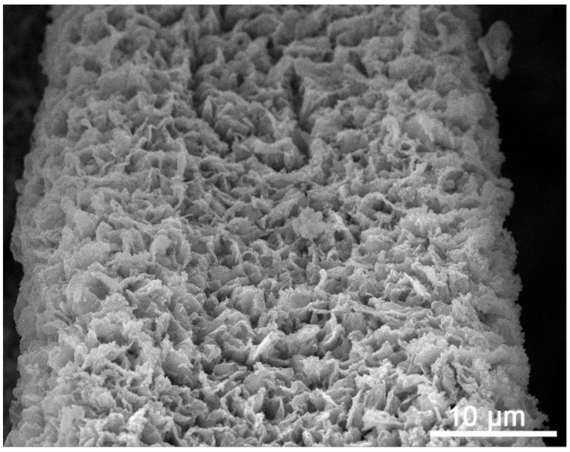

Fig. S22 SEM image of the CoP-CNT/Ni_2P/NF catalyst after long-time electrolysis toward OER in 1.0 M KOH.

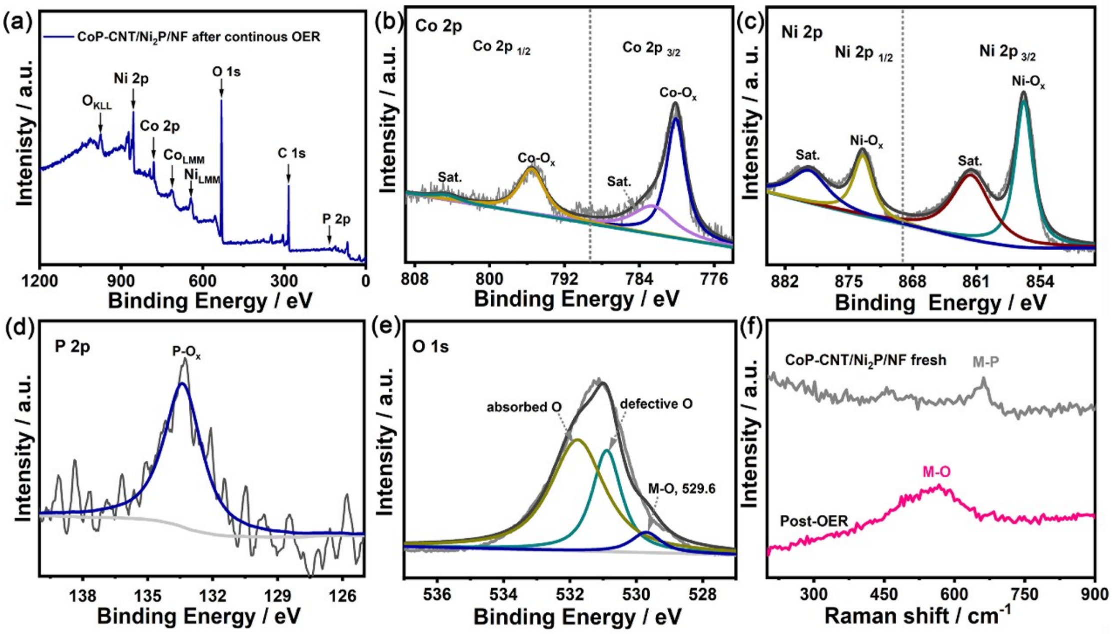

Fig. S23 (a-e) The XPS spectrum of the CoP-CNT/Ni_2P/NF catalyst after long-time electrolysis towards OER in 1.0 M KOH. (f) Raman spectra of the CoP-CNT/Ni_2P /NF before and post OER.

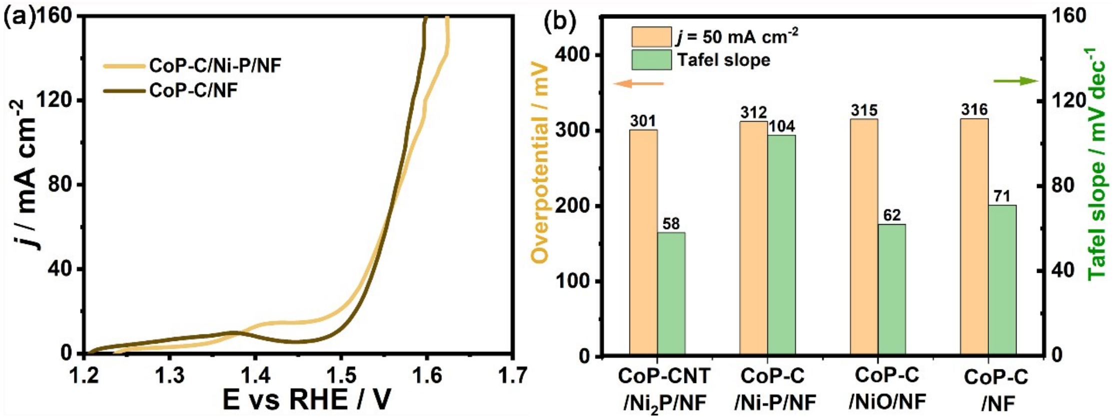

Fig. S24 (a) Polarization curves of the CoP-C/Ni-P and CoP-C/NF towards OER in 1.0 M KOH at a scan rate of 1mV s^{-1}. (b) The histogram of the overpotential at 50 mA cm^{-2} and corresponding Tafel slope for the synthesized Co-based catalysts towards OER in 1.0 M KOH.

Table S3 Comparison of overall water splitting performance of self -supporting CoP-C nanosheet arrays with some previously reported Co/Ni-based catalysts in 1.0 M KOH solution.

Catalyst	Cell voltage (j =10 mA cm^{-2}, η_{10})	Reference
CoP-C/NiO/NF || CoP-CNT/NiO/NF	1.57 V	This work
CoP/NCNHP	1.64 V	*J. Am. Chem. Soc.* **2018**, *140*, 2610.
Co/CoP-HNP	1.68 V	*Mater. Horiz.* **2018**, *5*, 108.
Ni_2P-NPCMS	1.62 V	*Electrochim. Acta* **2019**, *297*, 755
Co-P@PC	1.60 V	*Small* **2020**, *16*, 1900550.
CoP@a-CoOx	1.66 V	*Adv. Sci.* **2018**, *5*, 1800514
$Co_2P/Mo_2C/Mo_3$-Co_3C@C	1.74 V	*J. Mater. Chem. A* **2018**, *6*, 5789.
NiCoP@NiFe	1.57 V	*Adv. Funct. Mater.* **2018**, *28,* 1706847.
Ni_2P/CoN-PCP	1.58 V	*Chem. Commun.* **2018**, *54,* 12101.
CoP-InNC@CNT	1.58 V	*Adv. Sci.* **2020**, *7*, 1903195.
Ni-Co-P/NF	1.58 V	*Nano Lett.* **2016**, *16,* 7718.
2D Fe-doped CoP arrays	1.60 V	*Nano Energy* **2017**, *41*, 583.
NiO/NF || Ni_2P/NF	1.70 V	*Nanoscale* **2017**, *9*, 4409.
Ni-Co-P-HNBs /NF	1.62 V	*Energy Environ. Sci.* **2018**, *11*, 872.
NiCoP/NF@NC	1.57V	*ACS Appl. Mater. Interfaces* **2018**, *10*, 41237.
WCoP @ (S, N)-C/CC	1.65 V	*ACS Energy Lett.* **2018**, *3*, 1434.
CoNiP@CN/NF	1.59 (η_{30})	*Appl. Catal.-B: Environ.* **2019**, *259*, 118053.
N-Co-Ni-P/NF || Fe-Co-OOH/NF	1.51 V	*ACS Sustain. Chem. Eng.* **2020**, *8*, 8949.
NiCoP@NiMn/NF	1.51 V	*ACS Appl. Mater. Interfaces* **2020**, *12,* 4385.
2%Mo-Ni_2P/CoP/NF	1.57V	*Appl. Catal.-B: Environ.* **2020**, *272*, 118951.
Co-NCNTFS/NF	1.62 V	*ACS Appl. Mater. Interfaces* **2020**, *12*, 3592.