Supporting Information

Tailoring Unique Neural-Network-Type Carbon Nanofibers Inserted in CoP/NC Polyhedrons for Robust Hydrogen Evolution Reaction

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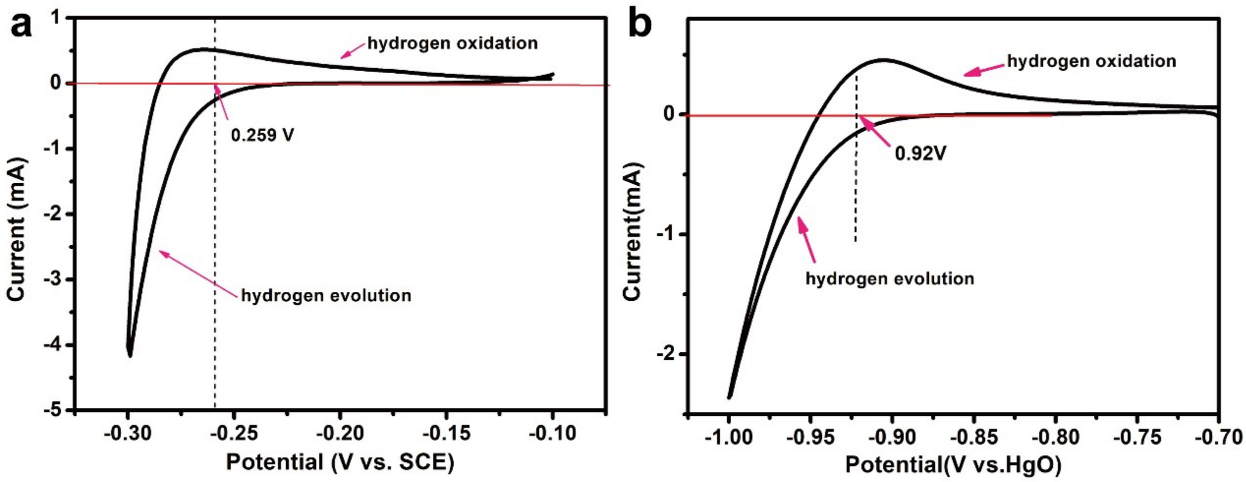
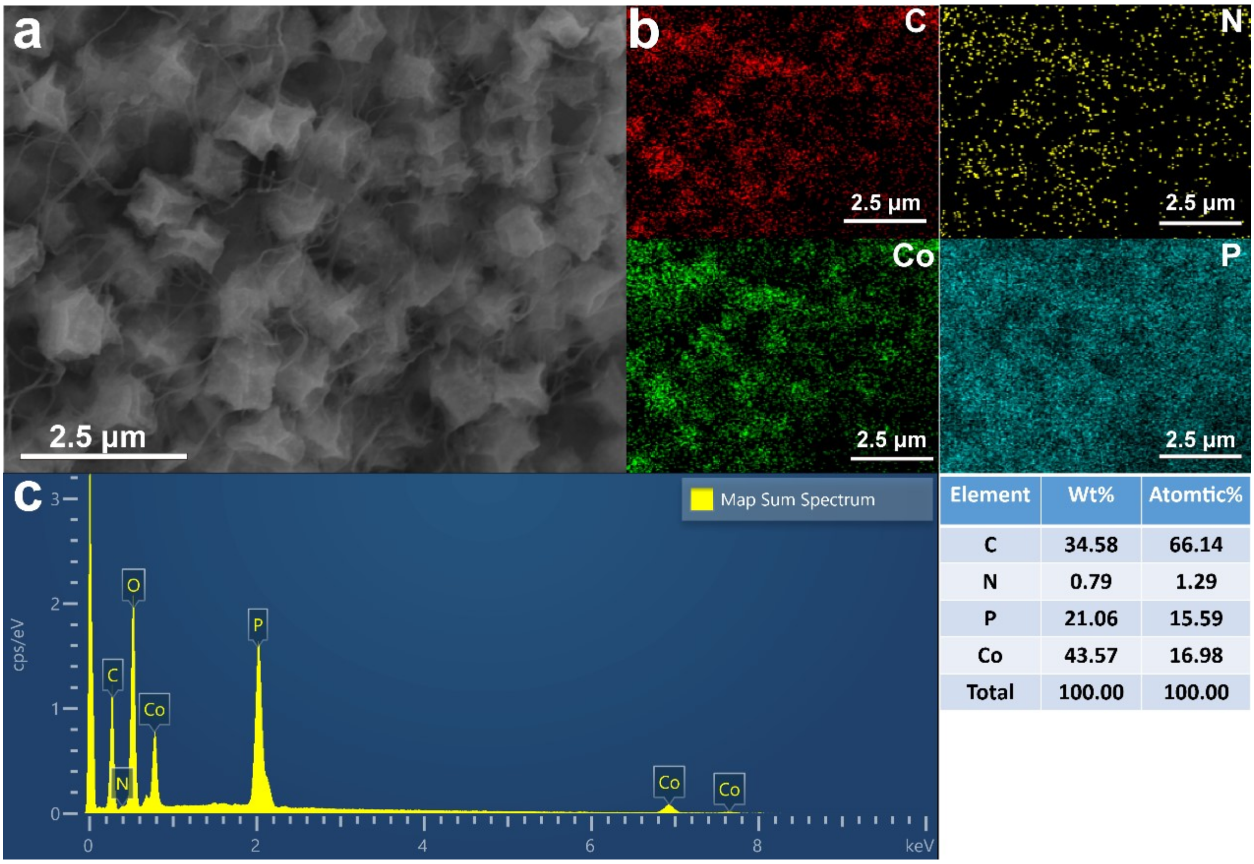


Figure S1. The reference electrodes of SCE and Hg/HgO were experimentally calibrated with respect to reversible hydrogen electrode (RHE) in 0.5 M H_2SO_4 and 1 M KOH respectively.



Element	Wt%	Atomtic%
C	34.58	66.14
N	0.79	1.29
P	21.06	15.59
Co	43.57	16.98
Total	100.00	100.00

Figure S2. (a) FESEM image, (b) EDS elemental mapping images of C, N, Co, P, (c)EDS spectrum and element content table of 3-D CNF@CoP/NC.

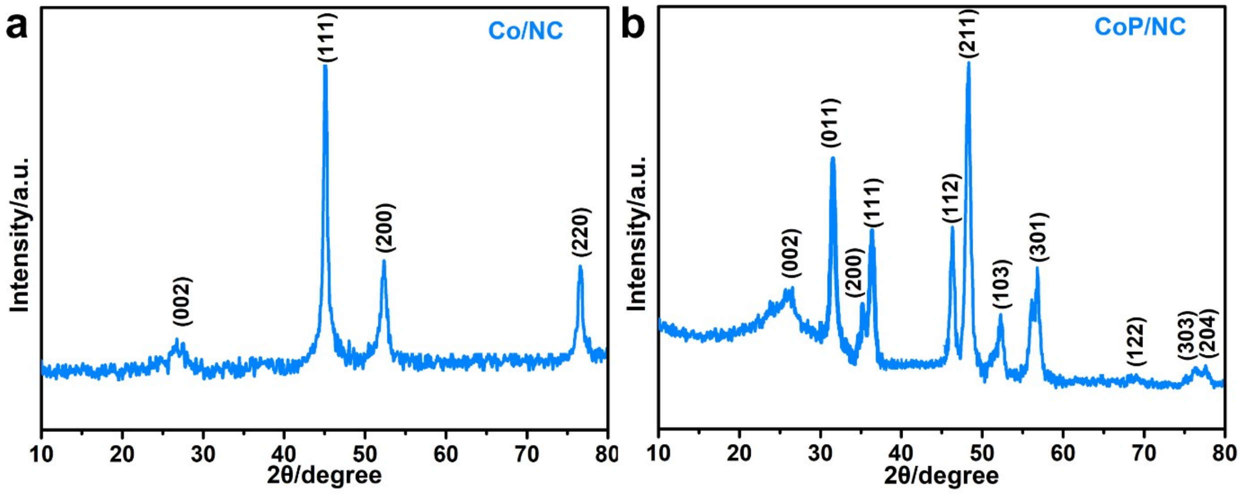


Figure S3. XRD patterns of Co/NC and CoP/NC.

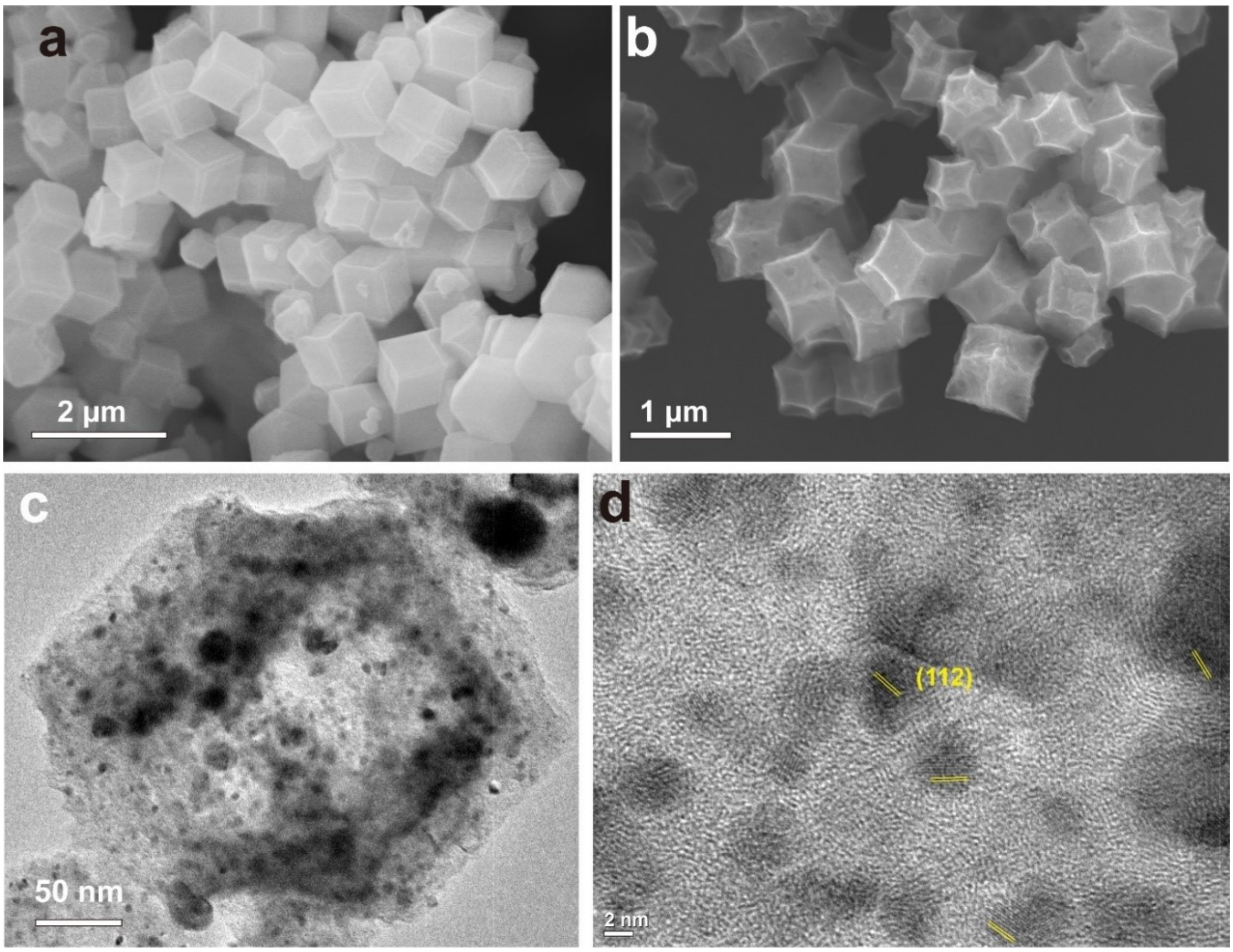


Figure S4. (a) FESEM image of ZIF-67, (b) FESEM image of CoP/ NC, (c) TEM image of CoP/NC, (d) HRTEM image of CoP/NC.

Table S1. Detailed comparison of the performance of 3-D CNF@CoP-in-NC in 0.5 M H_2SO_4 with those of representative non-noble-metal HER catalysts.

Catalyst	**η_{10} (mV)**	**Tafel slope (mV dec^{-1})**	**Ref.**
Mo_2C-N-CNFs	167	70	1
MoS_2/EEBP	126	68	2
CoP CPHs	133	51	3
CoP-OMC	112.18	56.67	4
Ni_2P/CNT	124	53	5
CoP-N-C	91	42	6
FeP GS	123	50	7
WP_2 nanorods	148	52	8
WP_2 submicroparticles	161	57	9
Bulk MoP	135	54	10
Ni_2P hollow NPs	117	46	11
FeP_2/C NPs	220	66	12
FeP NPs@NPC	130	67	13
CoP/CNT	122	54	14
3-D CNF@CoP/NC	64.5	48.6	This work

Table S2. Detailed comparison of the performance of 3-D CNF@CoP-in-NC in 1 M KOH with those of representative non-noble-metal HER catalysts.

Catalyst	η_{10} (mV)	Tafel slope (mV dec^{-1})	Ref.
$Ni_{0.69}Co_{0.35}P$	167	47	15
$Ni_{12}P_5$/NF	170	106	16
Ni_3S_2/NF	220		17
CoP/Cu	94	42	18
NiCoP@NF	155	115	19
CoP/rGO-400	150	38	20
Porous Mo_2C	151	59	21
NiCoP/CNF900	130	83	22
FeP NAs/CC	218	146	23
FeP NTs/CC	120	59.5	24
CoP/CC	106	93	25
WP_2 nanorods	225	84	8
3-D CNF@CoP/NC	105.6	53.9	This work

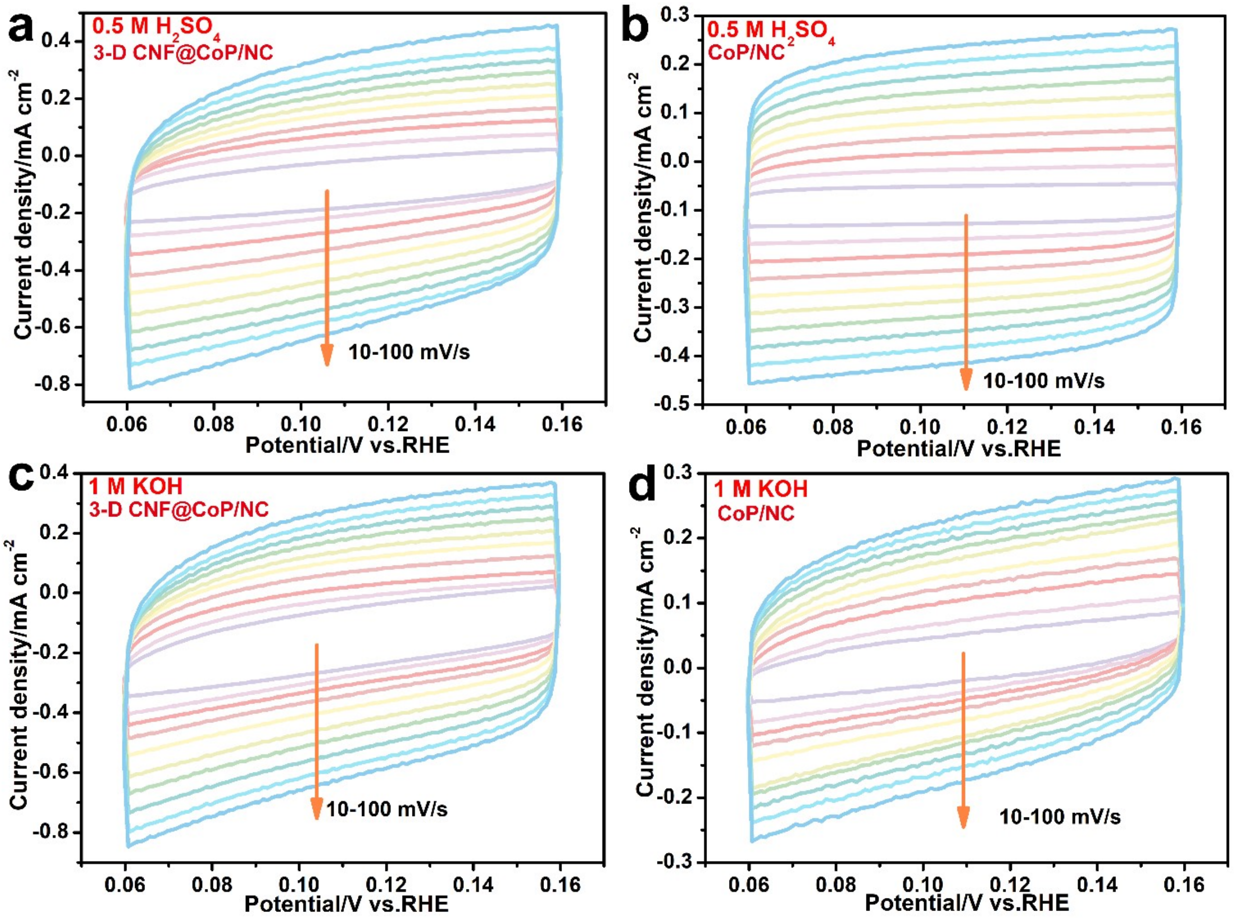


Figure S5. Scan rate dependence of the current densities in the CV curves of 3-D CNF@CoP/ NC (a) and CoP/NC (b) in 0.5 M H_2SO_4, 3-D CNF@CoP/NC (c) and CoP/NC (d) in 1M KOH with scan rates ranging from 10 mV s^{-1} to 100 mV s^{-1} at intervals of 10mV·s^{-1}.

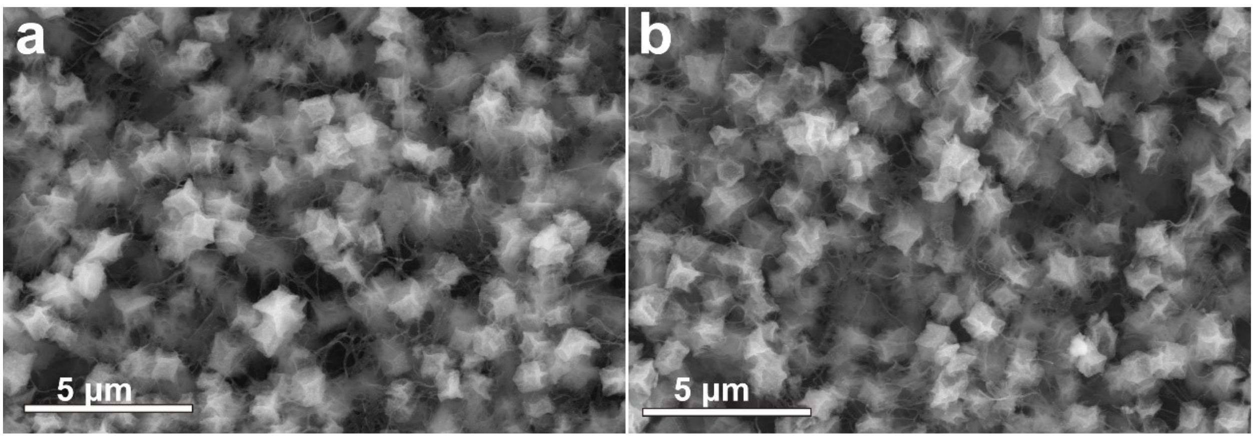


Figure S6. FESEM images of 3-D CNF@CoP/NC after chronoamperometric test in 0.5 M H_2SO_4 (a) and 1 M KOH (b).

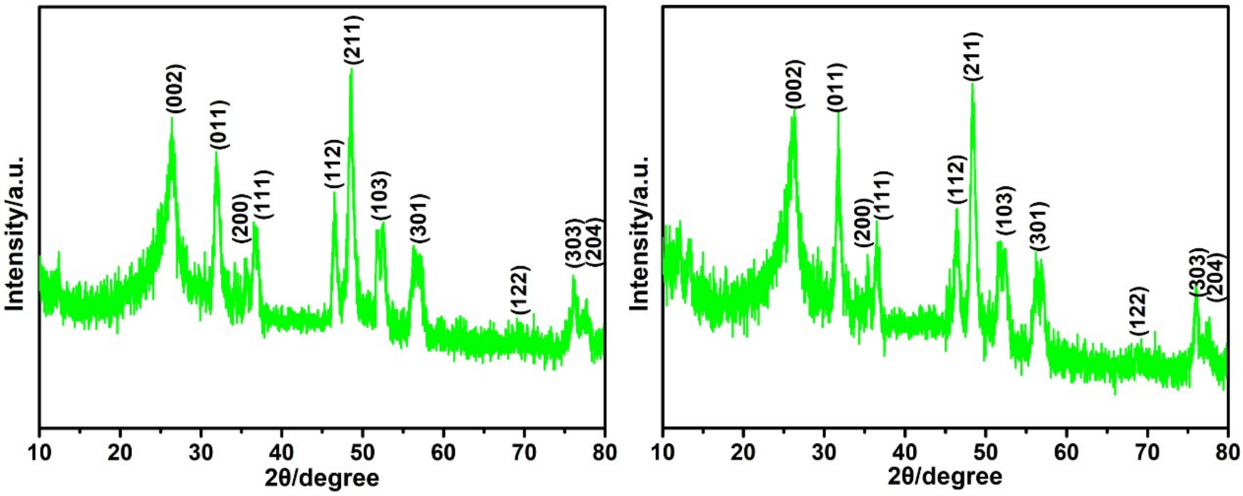
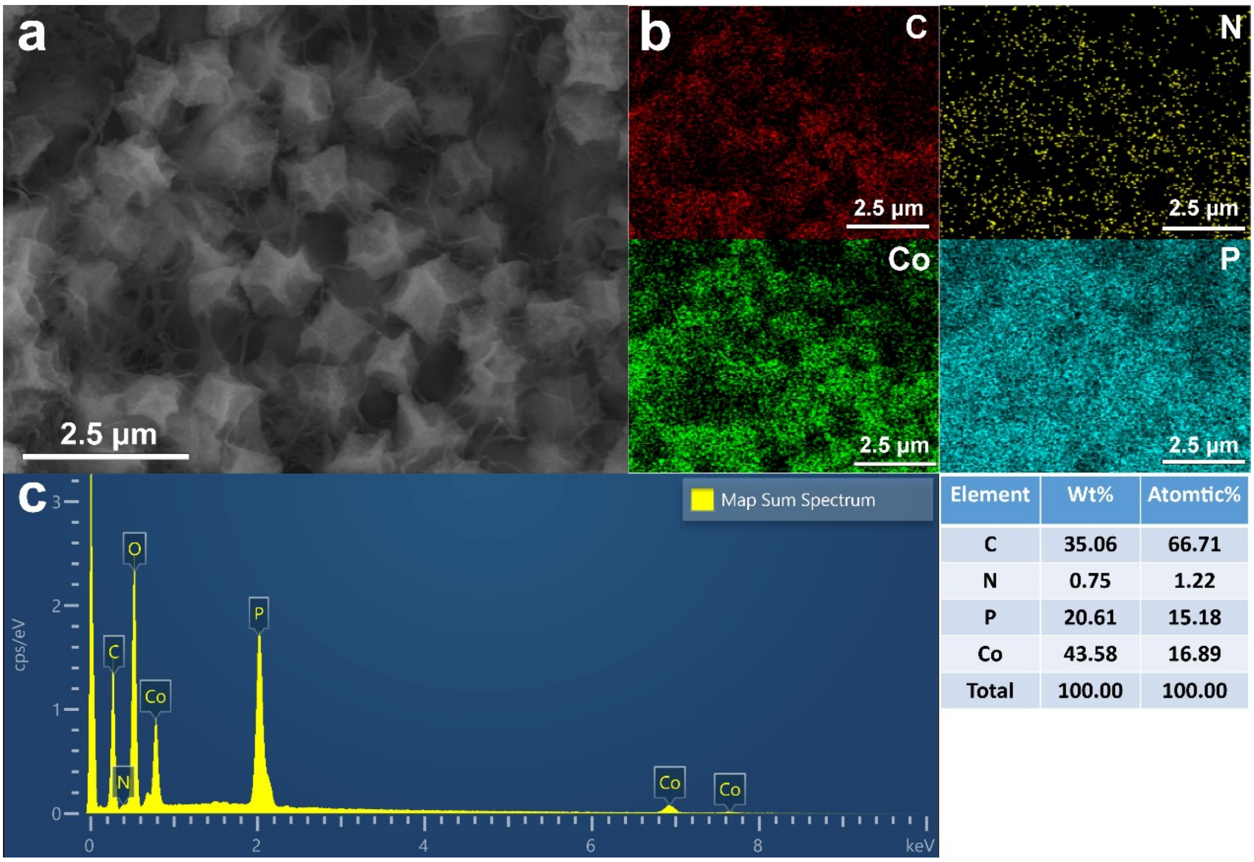
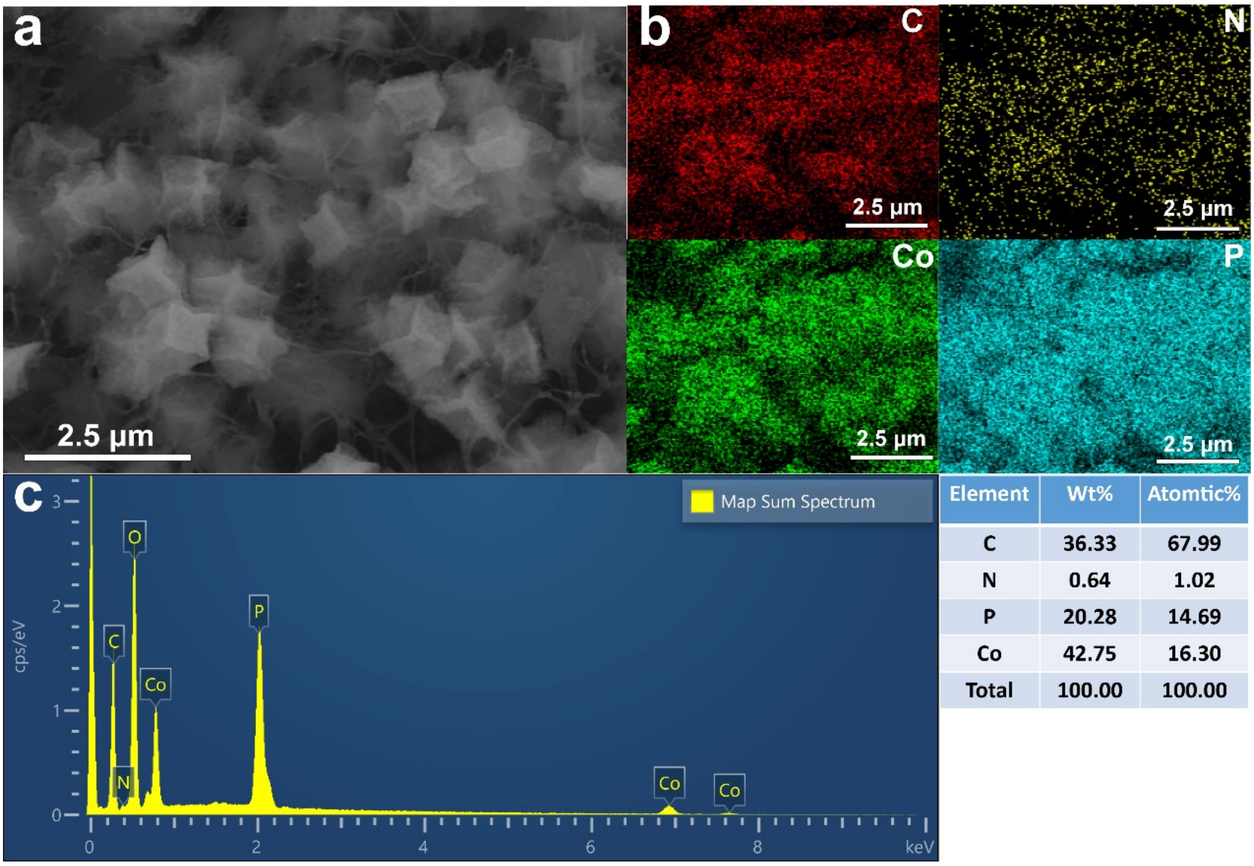


Figure S7. XRD patterns of 3-D CNF@CoP/NC after long-term test in 0.5 M H_2SO_4 (a) and 1M KOH (b).



Element	Wt%	Atomtic%
C	35.06	66.71
N	0.75	1.22
P	20.61	15.18
Co	43.58	16.89
Total	100.00	100.00

Figure S8. (a) FESEM image, (b) EDS elemental mapping images of C, N, Co, P, (c) EDS spectrum and element content table of 3-D CNF@CoP/NC after a long-term test in 0.5 M H_2SO_4.



Element	Wt%	Atomtic%
C	36.33	67.99
N	0.64	1.02
P	20.28	14.69
Co	42.75	16.30
Total	100.00	100.00

Figure S9. (a) FESEM image, (b) EDS elemental mapping images of C, N, Co, P, (c) EDS spectrum and element content table of 3-D CNF@CoP/NC after a long-term test in 1 M KOH.

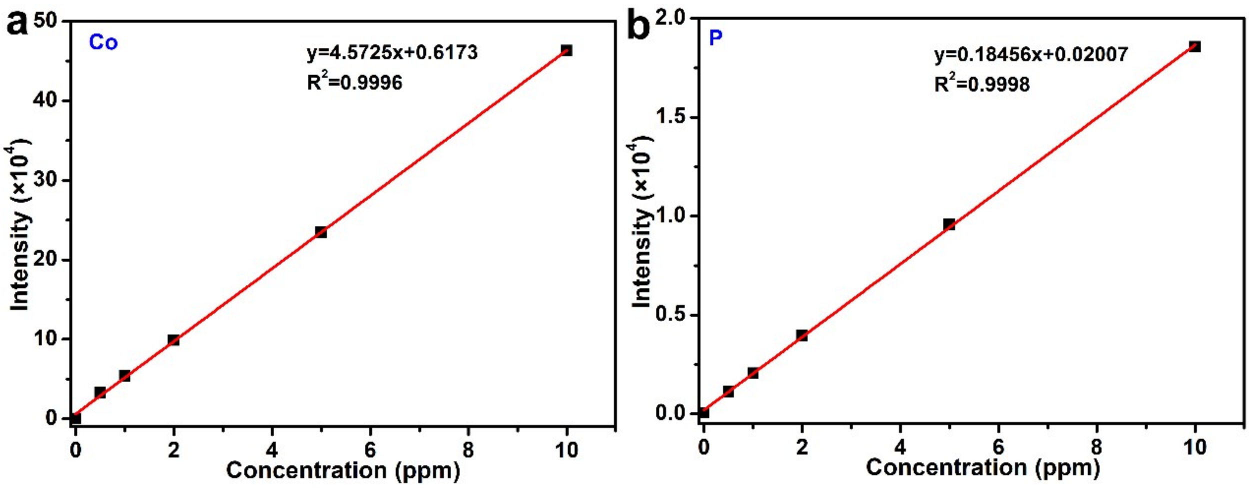


Figure S10. The working curve of Co (a) and P (b) by ICP-OES.

Table S3. ICP result of different samples.

Sample	wt.%	
	Co	P
3-D CNF@CoP/NC before a long-term test	35.7	18.8
3-D CNF@CoP/NC after a long-term test in 0.5 M H_2SO_4	35.2	18.3
3-D CNF@CoP/NC after a long-term test in 1 M KOH	34.9	18.4

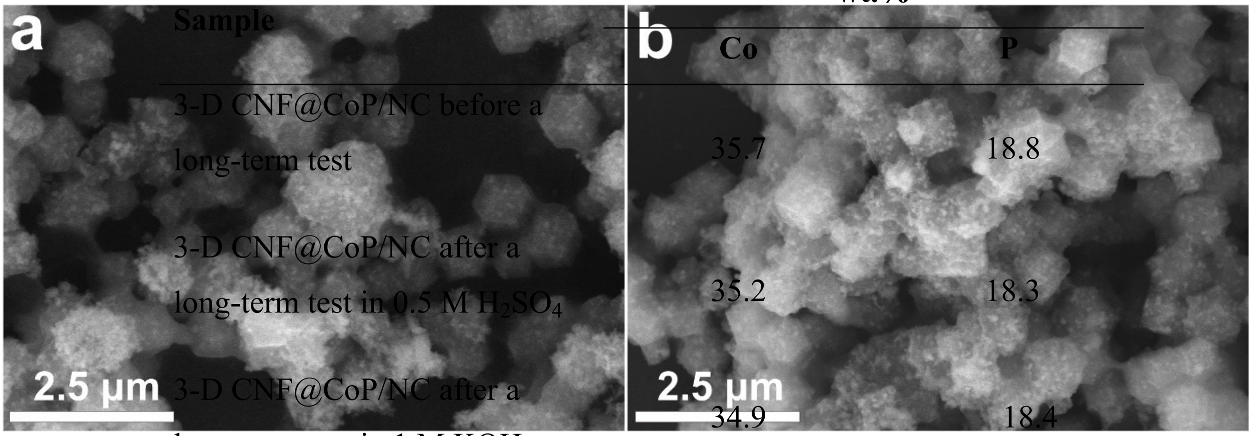


Figure S11. FESEM images of 3-D 3-D CNF@CoP/NC after chronoamperometric test in 0.5 M H_2SO_4 (a) and 1 M KOH (b).

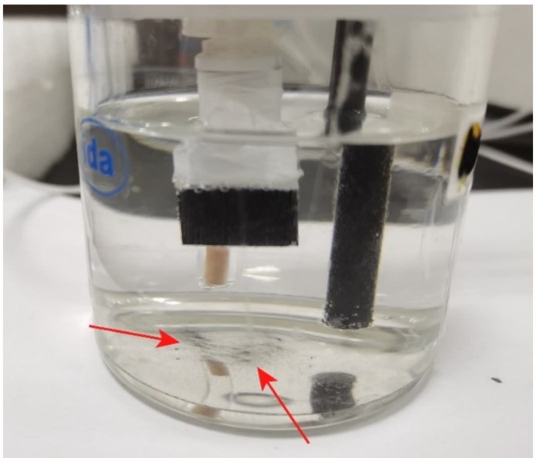


Figure S12. Photograph of electrolytic cell during electrolysis.

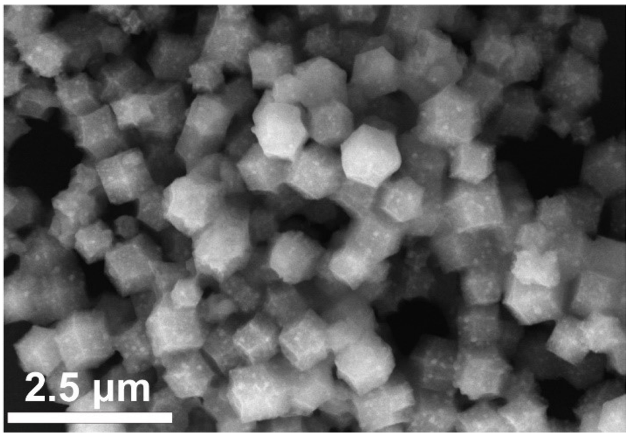


Figure S13. FESEM image of 3-D 3-D CNF@CoP/NC before chronoamperometric test.

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