# **Supporting information**

## Assembled cobalt phosphide nanoparticles on carbon nanofibers

## as a bifunctional catalyst for hydrogen evolution reaction and

### oxygen evolution reaction

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### 1. Supplementary Tables

Table S1. The activity comparison of CNF@CoP-CNTs with recently reported OER electrocatalysts in alkaline solution.

Catalyst	Electrolyte	E <sub>j10</sub> (mV)	Ref.
CNF@CoP-CNTs	1 M KOH	367(E <sub>j50</sub> )	This work
Co <sub>2</sub> P/Co <sub>2</sub> N@CNF-DNA(C)	1 M KOH	360	[1]
NiCoP/CNF	1 M KOH	268	[2]
CoP/NC	1 M KOH	290	[3]
Fe-CoP NSs	1 M KOH	312	[4]
CoP-TiO <sub>x</sub>	1 M KOH	337	[5]
CoP NFs	1 M KOH	323	[6]
<b>CoP / NCS-400</b>	1 M KOH	313	[7]
CoP / VGNHs	1 M KOH	300	[8]
O-CoP	1 M KOH	310	[9]
CoP@NPC	1 M KOH	300	[10]
N/MoeCoP@NPG	1 M KOH	201	[11]
CoP/CC	1 M KOH	176	[12]
Co3O4 CoP	1 M NaOH	320	[13]

Catalyst	Electrolyte	E <sub>j10</sub> (mV)	Ref.
CNF@CoP-CNTs	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	65	This work
CoP-CNTs hybrids	$0.5 \text{ M H}_2\text{SO}_4$	139	[14]
CoP nanosheets/MXene	$0.5 \text{ M H}_2 \text{SO}_4$	97	[15]
Nanoporous CoPS	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	107	[16]
CoP@P, N-C matrices	$0.5 \text{ M H}_2 \text{SO}_4$	87	[17]
Al, Fe-CoP/rGO	0.5 M H <sub>2</sub> SO <sub>4</sub>	138	[18]
Ni-CoP hollow polyhedrons	0.5 M H <sub>2</sub> SO <sub>4</sub>	144	[19]
CoP hollow Polyhedrons	0.5 M H <sub>2</sub> SO <sub>4</sub>	159	[20]
CoP NWs	0.5 M H <sub>2</sub> SO <sub>4</sub>	110	[21]
CoP NPs combined with WSe <sub>2</sub> nanosheets	0.5 M H <sub>2</sub> SO <sub>4</sub>	163	[22]
CoP/RGO	0.5 M H <sub>2</sub> SO <sub>4</sub>	105	[23]
Fe-CoP@CC	$0.5 \text{ M H}_2 \text{SO}_4$	80	[24]
Ni-CoP	1 M KOH	88	[25]

Table S2. The activity comparison of CNF@CoP-CNTs with recently reported HER electrocatalysts in acid solution.

2. Supplementary Figures 1 to S6



Figure S1. SAED patterns of (a) CNF

@CoP-5-CNTs , (b) CNF@CoP-10-CNTs , (c) CNF@CoP-12-CNTs , (d) CNF@CoP-15-CNTs , (e) CNF@CoP-18-CNTs , and (f) CNF@CoP-20-CNTs , respectively.



Figure S2. Energy dispersive X-ray spectroscopy (EDS) of CNF@CoP-15-CNTs.



Figure S3. XPS survey spectra of CNF@Co-CNTs.



Figure S4. XPS survey spectra of CNF@CoP-15-CNTs.

The existence of Co and P elements was proved by the XPS survey spectrum of CNF@CoP-15-CNTs.



**Figure S5.** CV curves of (a) CNF@CoP-5-CNTs, (b) CNF@CoP-10-CNTs, (c) CNF@CoP-12-CNTs, (d) CNF@CoP-15-CNTs, (e) CNF@CoP-18-CNTs, and (f) CNF@CoP-20-CNTs measured in 1.0 M KOH solution at scan rates from 10 to 50 mV s<sup>-1</sup>.



Figure S6. CV curves of (a) CNF@CoP-5-CNTs, (b) CNF@CoP-10-CNTs, (c) CNF@CoP-12-CNTs, (d) CNF@CoP-15-CNTs, (e) CNF@CoP-18-CNTs, and (f) CNF@CoP-20-CNTs measured in 0.5 M  $H_2SO_4$  solution at scan rates from 10 to 50 mV s<sup>-1</sup>.



Figure S7. SEM images of CNF@CoP-15-CNTs post electrochemical catalysis. (a) OER. (b) HER.

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