Electronic Supplementary Information

Phosphorus doped $NiCo_2S_4$ nanocrystals grown on electrospun carbon nanofibers as ultra-efficient electrocatalysts for hydrogen evolution reaction

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Experimental details

1. Materials

Polyacrylonitrile (PAN, Mw = 150000 g mol^{-1}) was purchased from Sigma-Aldrich. Multi-walled carbon nanotubes with a diameter of 30-50 nm were obtained from Chengdu Organic Chemicals Co. Ltd., which were produced by the chemical vapor deposition method. *N,N*-dimethylformamide (DMF) and ethanol were obtained from Shanghai Chemical Reagent Company. Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), thiourea ($CS(NH_2)_2$), urea ($CO(NH_2)_2$) and $NaH_2PO_2 \cdot H_2O$ were supplied by China Medicine Company. De-ionized (DI) water was used throughout all the experiments.

2. Preparation of electrospun CNT/CNF membranes

CNT/CNF membranes were prepared via a facile co-electrospinning method, followed by pre-oxidation and carbonization. First, pristine CNTs were treated with a mixture of HNO_3 and H_2SO_4 (v/v = 1/1) at 70 °C for 1 h. The suspension was filtrated and washed for several times, followed by drying to obtain acid-treated CNTs. Second, certain amount of acid-treated CNT was dispersed in 5 mL DMF under ultrasonication. Meanwhile, 1.0 g PAN powder was dissolved in 5 mL DMF under vigorous stirring to form a homogeneous solution. Then, the above solutions were further mixed together to form a uniform bicomponent spinning solution. Finally, the CNT/PAN mixture was sucked into a syringe with a stainless steel needle for the co-electrospinning process. It was carried

out under an applied voltage of 20 kV and a distance of 17 cm between the needle tip and the collector. The obtained CNT/PAN membranes were then pre-oxidized at 250 °C for 2 h with a heating rate of 1 °C min^{-1} in an air atmosphere, followed by carbonization in a nitrogen flow at 800 °C for 2 h. Thus, with PAN nanofibers turning into carbon nanofibers, the CNT embedded carbon nanofiber (CNT/CNF) membranes were prepared.

3. Preparation of P-$NiCo_2S_4$@CNT/CNF membranes

$NiCo_2S_4$@CNT/CNF membranes were prepared through a one-step hydrothermal procedure. Briefly, $Ni(NO_3)_2 \cdot 6H_2O$ (1 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (2 mmol), thiourea (8 mmol) and urea (4 mmol) were dissolved in 30 mL DI water under vigorous magnetic stirring for 20 min. After that, the transparent pink solution was transferred into a 50 mL Teflon-lined stainless steel autoclave with a piece of CNT/CNF membrane (2 × 2 cm^2) completely immersed into the solution. The autoclave was sealed and maintained at 160 °C for 12 h. After cooling down to room temperature, the obtained hybrid membranes were rinsed with DI water and ethanol for several times, and finally dried at 80 °C for 8 h.

P-doped $NiCo_2S_4$@CNT/CNF membranes were synthesized through a phosphidation reaction in the tube furnace. 100 mg of $NaH_2PO_2 \cdot H_2O$ was placed at the upstream position within the reactor tube while a piece of $NiCo_2S_4$@CNT/CNF membrane was placed at the downstream position. The phosphidation reaction was performed at 300 °C for 1 h with a heating rate of 2

°C min^{-1} under a steady flow of N_2 gas. After cooling down naturally, the phosphorus-doped hybrid product was prepared, and denoted as P-$NiCo_2S_4$@CNT/CNF.

4. Characterization

Morphology of the products was observed using a field emission scanning electron microscope (FESEM, Ultra 55, Zeiss) at an acceleration voltage of 5 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy were performed under an acceleration voltage of 200 kV with a JEOL JEM2100 TEM. X-ray diffraction (XRD) experiments were conducted from 2θ = 5° to 70° on an X'Pert Pro X-ray diffractometer with Cu Kα radiation (λ = 0.1542 nm) under a voltage of 40 kV and a current of 40 mA. X-ray photoelectron spectroscopy (XPS) analyses were made with Thermo Scientific ESCALAB 250Xi using an Al Kα sources 1486.6 eV anode. All XPS spectra were corrected using C1s line at 284.6 eV. The electrical conductivity of the samples was measured with a 4-point probes resistivity measurement system (RTS-8).

Table S1 Electrical conductivities for CNF and CNT/CNF membranes.

Sample	1	2	3	4	5	Average (Ω • cm)
CNF	126.8	130.1	124.3	134.8	130.4	129.3
CNT/CNF	51.8	51.4	53.0	53.9	52.2	52.5

Electrical conductivity:

CNF: $1 \div (129.3 \div 100) = 0.77$ S m^{-1}

CNT/CNF: $1 \div (52.5 \div 100) = 1.90$ S m^{-1}

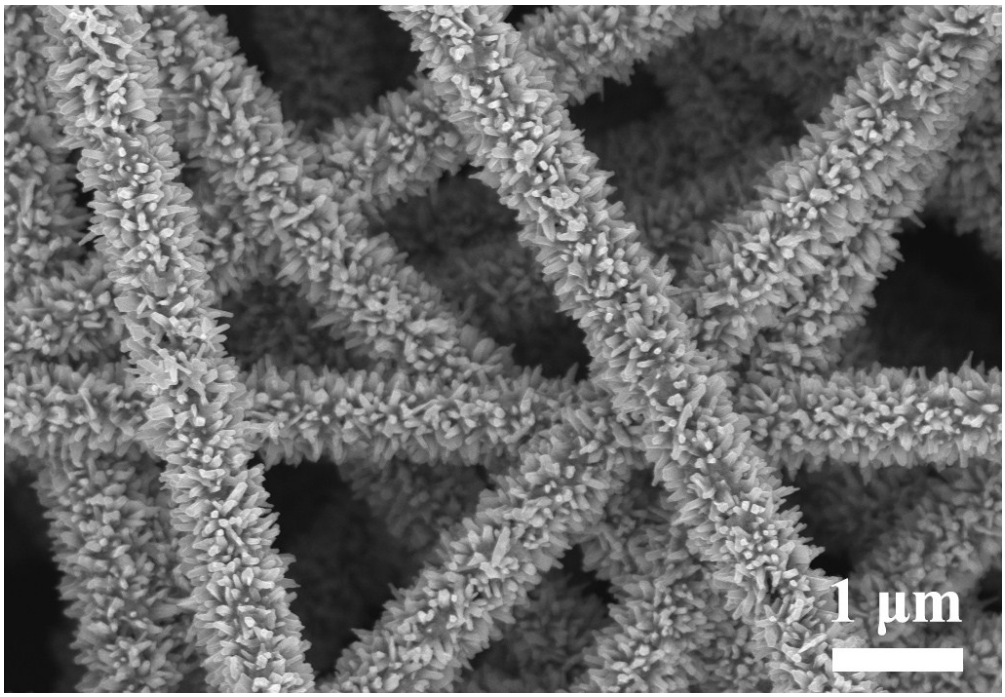

Fig. S1 FESEM images of $NiCo_2S_4$@CNF hybrid.

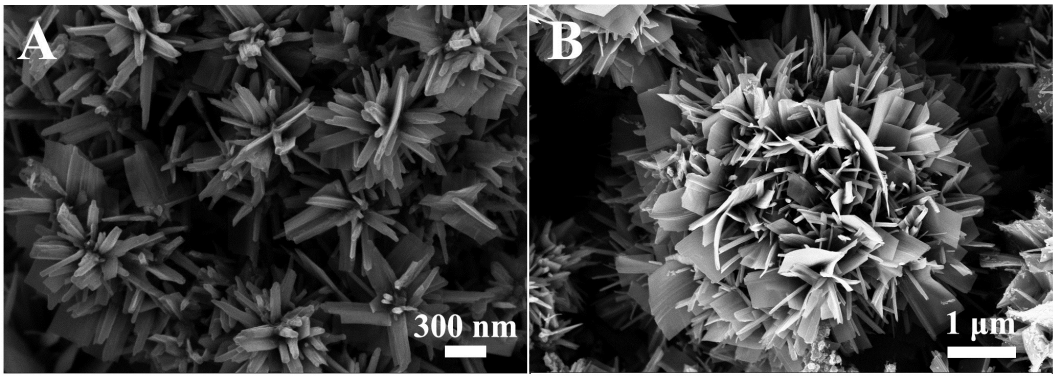

Fig. S2 FESEM images of $NiCo_2S_4$ without template.

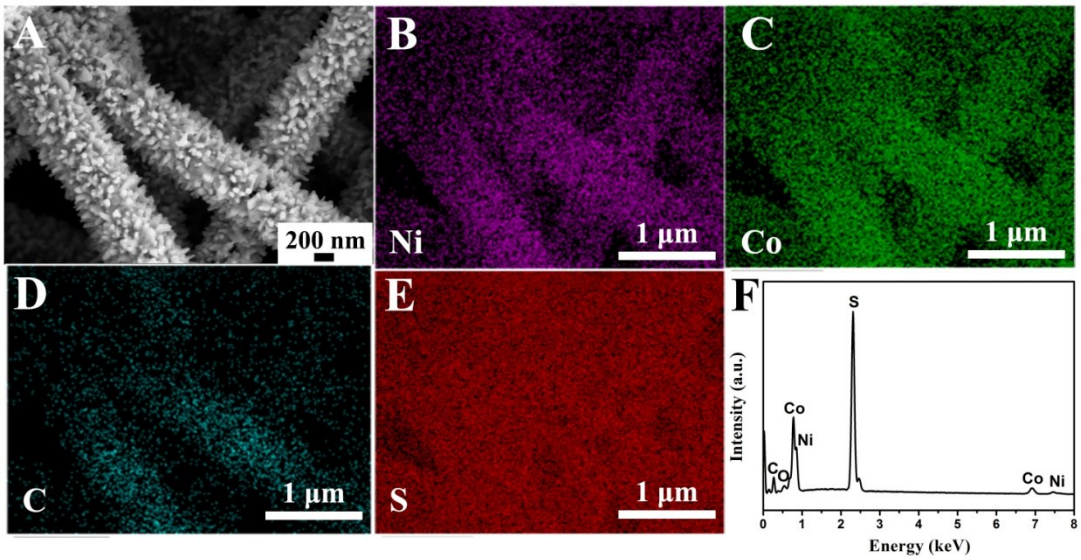

Fig. S3 EDS mapping images and spectrum of $NiCo_2S_4$@CNT/CNF hybrid.

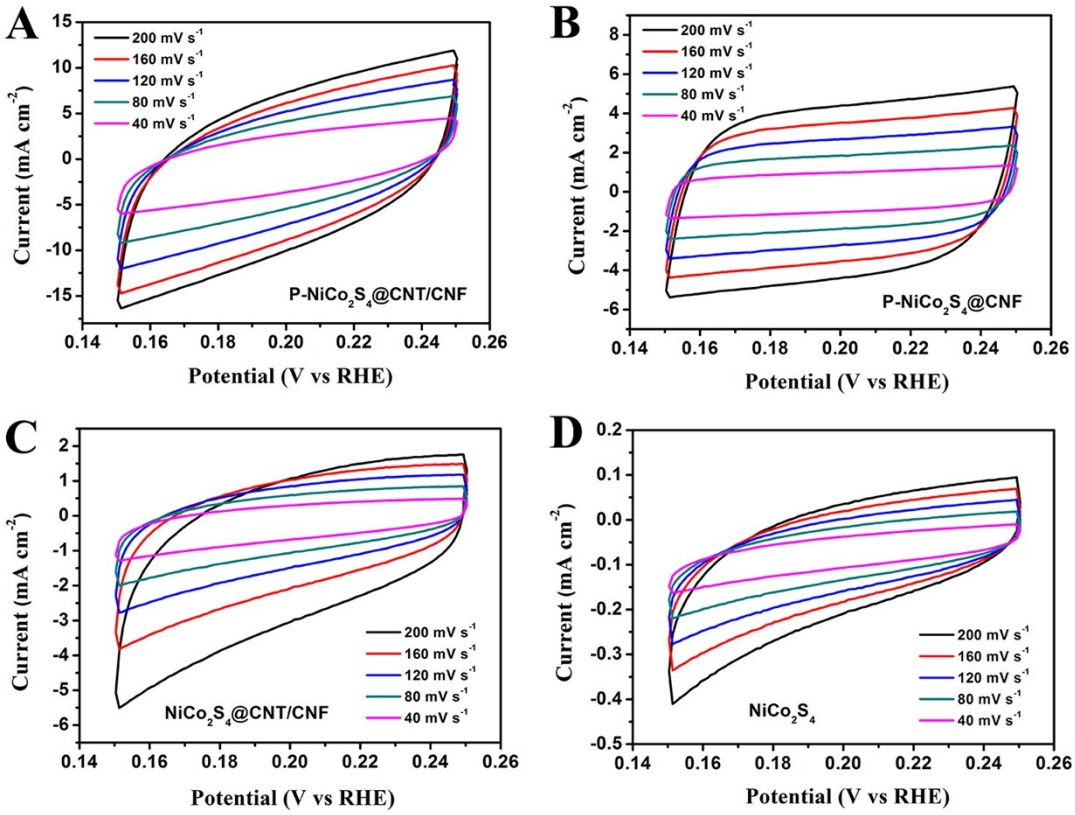

Fig. S4 Cyclic voltammetry (CV) curves of (A) P-$NiCo_2S_4$@CNT/CNF hybrid, (B) P-$NiCo_2S_4$@CNF hybrid, (C) $NiCo_2S_4$@CNT/CNF hybrid, and (D) $NiCo_2S_4$ in the region of 0-0.2 V vs. RHE.

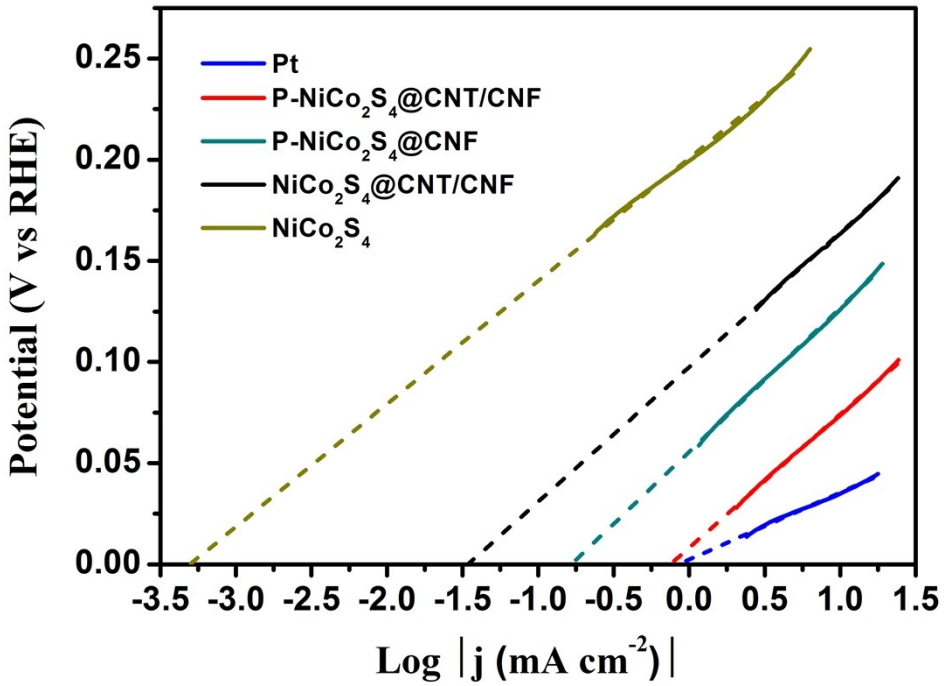

Fig. S5 Calculated exchange current densities of various samples by using extrapolation methods.

Table S2 Calculations of the exchange current densities of various samples.

Sample	Log(| j (mA cm^{-2}) |) at η = 0 V	Exchange current density j_0 (mA cm^{-2})
P-$NiCo_2S_4$@CNT/CNF	-0.10	0.79
P-$NiCo_2S_4$@CNF	-0.75	0.18
$NiCo_2S_4$@CNT/CNF	-1.44	0.04