

## Supporting Information

### Phosphate-modified Co-Ni phosphide heterostructure formed by interfacial and electronic tuning for boosted faradaic properties

Zhan Li,<sup>a</sup> Hongyu Mi,<sup>\*a</sup> Chenchen Ji,<sup>\*a</sup> Fengjiao Guo,<sup>a</sup> Pengtao Qiu,<sup>b</sup> Kongjun Ma,<sup>a</sup> Shixue He,<sup>a</sup> Dandan Wu,<sup>a</sup> Haonan Cui,<sup>a</sup> Nianjun Yang<sup>\*c</sup>

#### 1. Experiment section

##### 1.1 Materials

The carbon cloth (CC, Model Number: WOS1003, Diameter of the carbon fiber: 9  $\mu\text{m}$ ) was purchased from Carbon Technology Co., Ltd. The polyvinyl pyrrolidone (PVP,  $M_n = 1,300,000$ ), polyvinyl alcohol (PVA) and sodium hypophosphite ( $\text{NaH}_2\text{PO}_2$ , AR) were purchased from Aladdin. The aqueous ammonia ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ , ~25 %) was purchased from Sichuan Xilong Science Co. Ltd. The potassium hydroxide (KOH, AR) and selenium power (Se, AR) were purchased from Tianjin Beilian Fine Chemicals Development Co. Ltd. The cobalt chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , AR) was purchased from Tianjin Zhiyuan Chemical Reagent Co. Ltd. The ammonium fluoride ( $\text{NH}_4\text{F}$ , AR) and nickel chloride hexahydrate ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , AR) were purchased from Tianjin Baishi Chemical Co. Ltd. The urea ( $\text{CH}_4\text{N}_2\text{O}$ , AR) was purchased from Tianjin Fengchuan Chemical Reagent Technology Co. Ltd. The potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ , AR) was purchased from Tianjin Hengxing Chemical Reagent Manufacturing Co. Ltd. The sodium sulfide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , AR) was purchased from Tianjin Hedong Hongyan Reagent Factory.

##### 1.2 Pretreatment of the CC

Typically, 0.5 g PVP was dissolved in 100 mL of deionized (DI) water. Then, a CC ( $4 \times 3 \text{ cm}^2$ ) was put into the PVP solution with mild stirring for 2 h. After, the CC was washed with DI water and dried at 60  $^\circ\text{C}$ .

### 1.3 Synthesis of the CoP@Ni<sub>2</sub>P-CC

In a typical synthesis, 0.65 g CoCl<sub>2</sub>·6H<sub>2</sub>O, 1.71 g urea and 0.14 g NH<sub>4</sub>F were dissolved in 40 mL DI water. Then, the pretreated CC (2 × 3 cm<sup>2</sup>) was put into the solution with mild sonication and then transferred into a 100 mL Teflon-lined stainless-steel autoclave, which was maintained at 120 °C for 6 h. After the autoclave was cooled down to room temperature, the as-obtained Co precursor on CC was ultrasonically cleaned with DI water and dried at 60 °C for 12 h. The Co precursor on CC was suspended into a 100 mL mixture solution which consists of 2 g K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 6.6 g NiCl<sub>2</sub>·6H<sub>2</sub>O. Then, 5 mL NH<sub>3</sub>·H<sub>2</sub>O was added into the above solution and the chemical bath deposition (CBD) process was continued for 1 h. After that, the as-obtained Co@Ni precursor on CC was obtained, which was washed with DI water and ethanol and dried at 60 °C for 12 h. The as-prepared Co@Ni precursor on CC and 200 mg NaH<sub>2</sub>PO<sub>2</sub> powders were placed downstream and upstream, respectively. The sample was calcined at 300 °C for 2 h under Ar atmosphere with a ramp rate of 2 °C min<sup>-1</sup>. After the furnace cooled down to room temperature, the CoP@Ni<sub>2</sub>P-CC was obtained.

### 1.4 Synthesis of the Co<sub>3</sub>S<sub>4</sub>@Ni<sub>3</sub>S<sub>4</sub>-CC

300 mg Na<sub>2</sub>S·9H<sub>2</sub>O was dissolved in 20 mL DI water and stirred for 15 min. A piece of the Co@Ni precursor was put into the above solution and then transferred into a 50 mL Teflon-lined stainless-steel autoclave and maintained at 160 °C for 12 h. After cooling down to room temperature, the CC was rinsed and dried to get the Co<sub>3</sub>S<sub>4</sub>@Ni<sub>3</sub>S<sub>4</sub>-CC.

### 1.5 Synthesis of the CoSe<sub>2</sub>@NiSe<sub>2</sub>-CC

3 g KOH and 0.1 g Se powder were put into 20 mL DI water and stirred for 1 h. After that, a piece of the Co@Ni precursor was put into the mixed solution and then transferred into a 50 mL Teflon-lined stainless-steel autoclave and maintained at 120 °C for 6 h to obtain the CoSe<sub>2</sub>@NiSe<sub>2</sub>-CC.

### 1.6 Synthesis of the Co<sub>3</sub>O<sub>4</sub>@NiO-CC

The as-prepared Co@Ni precursor was annealed at 300 °C with a heating rate of 2 °C min<sup>-1</sup> under air atmosphere and then cooling down to room temperature, forming the Co<sub>3</sub>O<sub>4</sub>@NiO-CC.

### 1.7 Material characterization

Scanning electron microscope (SEM, SU-8010), transmission electron microscope (TEM, Hitachi-600), and high resolution TEM analyses (FEI Tecnai G2 F20) were used to investigate the structure and morphology of the prepared samples. Powder X-ray diffraction (XRD, Brüker D8 Advance X-ray diffractometer) was utilized to analyze the crystallographic structures of the prepared samples. X-ray energy dispersive spectroscopy (EDX) spectra were obtained by SU-8010. X-ray photoelectron spectroscopy (XPS) tests were carried out by ESCALAB 250Xi.

### 1.8 Electrochemical measurement

The electrochemical measurements were carried out by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) on an electrochemical workstation (CHI 760E, Shanghai Chenhua) in a three-electrode system. The specific capacities ( $Q_m$ ) were calculated from the GCD curves according to the following equation:<sup>1</sup>

$$Q_m = \frac{2I \int V dt}{mV} \quad (1)$$

where  $I$  (A) is the discharge current,  $\int V dt$  is the integral area under a discharge curve,  $m$  (g) is the mass loading of the active materials, and  $V$  (V) is the voltage or the potential window.

### 1.9 Fabrication of the FHSC device

The FHSC device was fabricated by using the CoP@Ni<sub>2</sub>P-CC cathode, an activated carbon (AC) anode with a piece of PVA/KOH gel film as a separator, respectively. The AC anode was prepared by pressing a well-dispersed film with 80 wt% samples, 10 wt% polytetrafluoroethylene (PTFE) binder and 10 wt% acetylene black on the graphite paper current collector. The polyvinyl alcohol/KOH (denoted as PVA/KOH) gel was obtained by dissolving 1.0 g PVA into 8 mL DI water and stirring at 85 °C for

2 h. After that, a mixed solution with 1 g KOH and 2 mL DI water was poured into the as-formed PVA gel and stirred at room temperature for 30 min. The mass ratio between the cathode and the anode materials in the as-fabricated FHSC device was obtained according to the following formula:<sup>2</sup>

$$\frac{Q_{m+}}{Q_{m-}} = \frac{m_-}{m_+} \quad (2)$$

where  $Q_m$  is the specific capacity and  $m$  is mass of the active materials. In this work, the mass ratio was  $m_{AC}:m_{Ni_2P@CoP-CC} = 2.04$ .

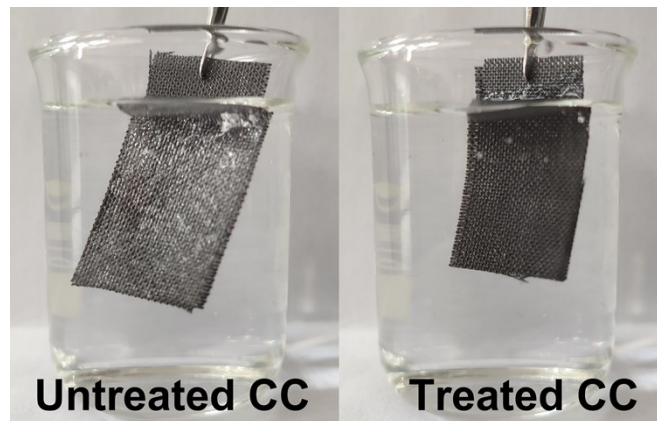
The energy density and power density of the as-assembled FHSC were calculated via the equations (3) and (4):<sup>1</sup>

$$E = \frac{I \int V dt}{3.6m} \quad (3)$$

$$P = \frac{3600E}{t} \quad (4)$$

## 2. Result and discussion

Compared with the CC substrate without PVP treatment (Fig. S1a), Fig. S1b clearly demonstrates that the CC substrate after PVP treatment possess an enhanced hydrophilicity without bubbles on its surface when they were put into the DI water, which is beneficial for the growth of active materials.



**Fig. S1** CC before and after PVP treatment.

The valence states of the  $Co_3S_4@Ni_3S_4-CC$ ,  $CoSe_2@NiSe_2-CC$  and  $Co_3O_4@NiO-CC$  samples were measured by XPS measurements. As show in Fig. 2c and 2d, the Ni  $2p_{3/2}$  core level spectrum of the  $Co_3S_4@Ni_3S_4-CC$  shows two peaks at binding

energies of 856.6 and 853.5 eV correspond to the  $\text{Ni}^{3+}$  and  $\text{Ni}^{2+}$ .<sup>3,4</sup> At the same time, the peaks for Co  $2p_{3/2}$  core level spectrum at 781.8 and 779 eV contribute to the  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$ .<sup>3,5</sup> Similarly, for  $\text{CoSe}_2@\text{NiSe}_2\text{-CC}$  sample, the typical peaks for  $\text{Ni}^{3+}$  and  $\text{Ni}^{2+}$  were observed at 855.9 and 853.8 eV,<sup>6</sup> and typical peaks for  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  were located at 781.3 and 779 eV.<sup>7</sup> The Ni  $2p_{3/2}$  core level spectrum of  $\text{Co}_3\text{O}_4@\text{NiO-CC}$  was fitted with the binding energies of 856.5 and 854.2 eV, corresponding to the  $\text{Ni}^{3+}$  and  $\text{Ni}^{2+}$ .<sup>8,9</sup> And the peaks at binding energies of 781.4 and 775.4 eV contribute to the  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  species.<sup>10,11</sup>

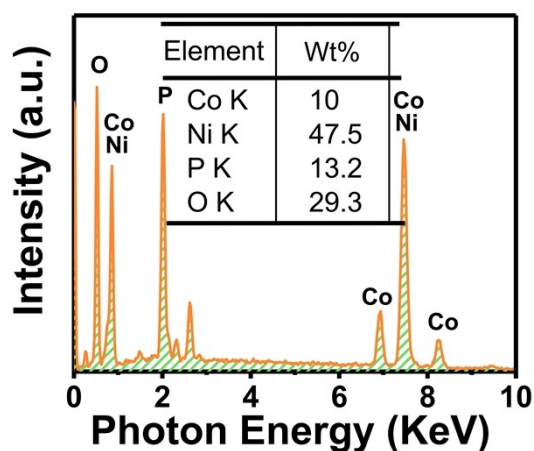


Fig. S2 EDX pattern of the  $\text{CoP}@\text{Ni}_2\text{P-CC}$ .

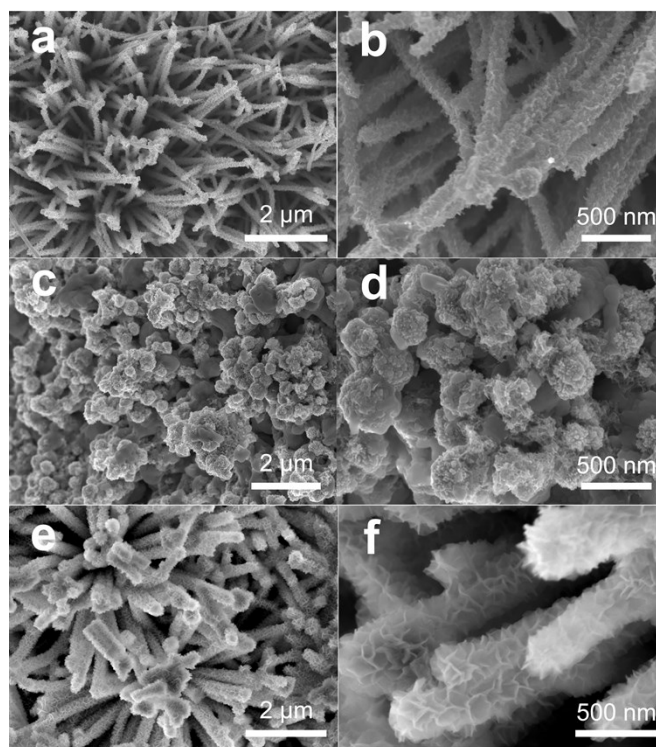


Fig. S3 SEM images of the (a-b)  $\text{Co}_3\text{S}_4@\text{Ni}_3\text{S}_4\text{-CC}$ , (c-d)  $\text{CoSe}_2@\text{NiSe}_2\text{-CC}$ , (e-f)  $\text{Co}_3\text{O}_4@\text{NiO-CC}$  samples.

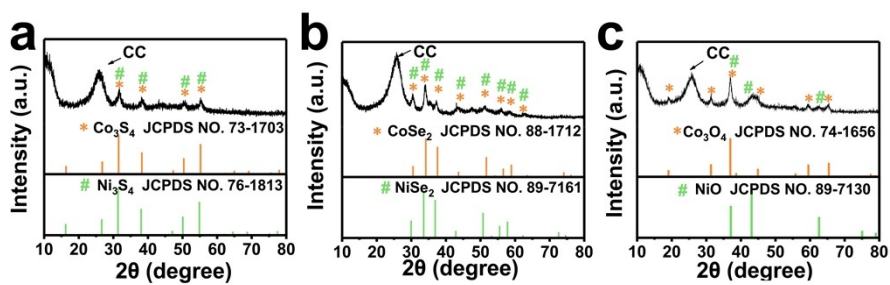


Fig. S4 XRD patterns of the (a) Co<sub>3</sub>S<sub>4</sub>@Ni<sub>3</sub>S<sub>4</sub>-CC, (b) CoSe<sub>2</sub>@NiSe<sub>2</sub>-CC, and (c) Co<sub>3</sub>O<sub>4</sub>@NiO-CC samples.

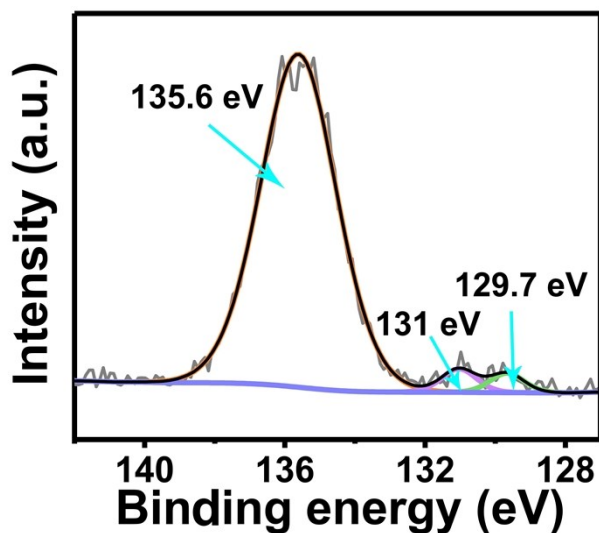


Fig. S5 XPS spectrum of the P 2p region for the CoP@Ni<sub>2</sub>P-CC sample.

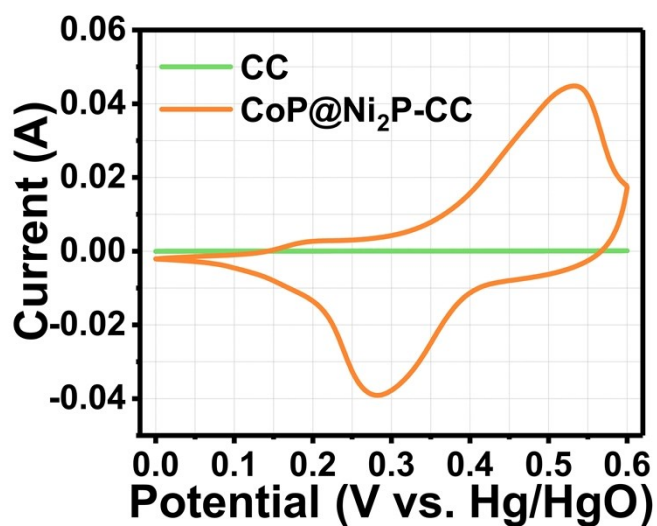


Fig. S6 CV curves for the blank CC and CoP@Ni<sub>2</sub>P-CC at 10 mV s<sup>-1</sup>.

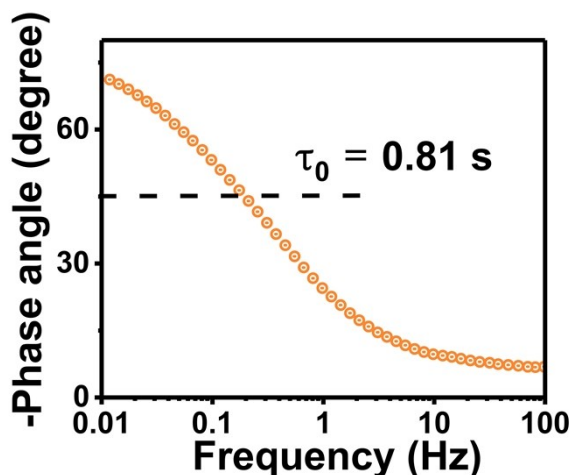


Fig. S7 Bode plot of the CoP@Ni<sub>2</sub>P-CC.

### Notes and references

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