

Supporting Information

Direct Synthesis of Metal Selenide Hybrids as Superior Sodium

Storage Anode

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1. Experimental section

1.1 Preparation of the Fe-Co precursors

In a typical synthesis, 177.58 mg $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 191.4 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 166 mg terephthalic acid were dissolved in 30 ml N,N-dimethyl acetamide and mixed together to form a uniform solution under continuous stirring for 1 h. Then the above mixture was poured into 50 ml Teflon-lined autoclave, setting the temperature to 150 °C and keeping for 3 h. When the temperature drops to room temperature, the resulting solution was washed several times with ethanol and centrifuged to collect the precursors. Finally, the Fe-Co precursor was put in the oven and dried at 60 °C for overnight. As a reference, single metal Fe and Co precursors were prepared by the same way but only adding $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively.

1.2 Preparation of the $\text{FeSe}_2/\text{CoSe}_2$ hybrid

Two solutions (A and B) were prepared separately to synthesis $\text{FeSe}_2/\text{CoSe}_2$ hybrid. For the solution A, 50 mg Fe-Co precursor was dissolved in 25 ml deionized water under continuous stirring. Solution B was prepared by 150 mg Na_2SeO_3 dissolved in 4 ml $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ under stirring until turns to red. Then Solution A was slowly dribbled into solution B. After continuous stirring for 30 minutes, the above mixture was poured into 50 mL transferred into Teflon-lined stainless steel autoclave and heated at 150 °C for 8 h. After naturally cooled to room temperature, $\text{FeSe}_2/\text{CoSe}_2$ nanoparticles were purified with absolute ethanol and deionized water and collected by filtration. Finally, the obtained $\text{FeSe}_2/\text{CoSe}_2$ nanoparticles were dried at 60 °C under vacuum overnight. As a reference, individual FeSe_2 nanoparticles and CoSe_2 nanoparticles were prepared by the same way but only adding Fe precursors or Co precursors, respectively. The

previously prepared individual FeSe₂ and CoSe₂ were ground in agate mortar with same proportions to obtain the mechanical mixture (FeSe₂:CoSe₂ =1:1).

1.3 Preparation of full cell cathode material Na₃(VPO₄)₂F₃

The cathode material of full cell Na₃(VPO₄)₂F₃ was synthesized by an improved method. First, VCl₃ and NaF were dissolved in deionized water with a molar ratio of 1:3. Second, H₃PO₄ and NaOH were slowly dropped in the suspension to adjust the PH about 4.0. Then the obtained suspension was placed in 60 °C oven for 24 h and centrifuged to collect. Finally, the collected Na₃(VPO₄)₂F₃ was dried in 60 °C oven.

2. Materials Characterizations

Field emission electron scanning microscopy (FESEM) and energy dispersive spectroscopy (EDS) were used to observe the morphology of the materials, and transmission electron microscopy (TEM) was used to analyze the microstructure of the materials. The crystal and phase structure of the materials were detected by X-ray diffraction (XRD-7000) of Cu K α radiation at 1.5406 Å. The X-ray photoelectron spectroscopy (XPS) of the product was obtained with the Thermo Scientific Escalab 250xi spectrometer.

3. Electrochemical measurements

The active material FeSe₂/CoSe₂, carbon black and polyvinylidene fluoride binder were evenly mixed at a mass ratio of 7:2:1, followed by the addition of N-methyl-2-pyrrolidone (NMP). The resulting paste was coated on the copper foil with a diameter of 1 cm, and the mass loading of each electrode slice is approximately 0.7 mg cm⁻². Then the electrode was transferred to a vacuum oven at 120 °C for 12 h to remove the NMP. The assembly of CR2032 battery is completed in a glove box filled with Ar, with

metal sodium as the counter electrode, glass fiber as the separator, NaPF₆ in DOL: Diglyme =1:1 as the electrolyte. In full cell, the cathode of Na₃(VPO₄)₂F₃ was prepared by the same way of FeSe₂/CoSe₂ electrode. The mass loading of cathode and anode are 1.5 mg cm⁻² and 1 mg cm⁻², respectively. Constant current charge-discharge experiments were carried out with Land Battery Test System (Wuhan, China) under a voltage window of 0.4-2.9 V. The CV at different sweep rates was measured using a CHI 660E electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was evaluated by Zahner electrochemical workstation (Zennium, IM6, Germany).

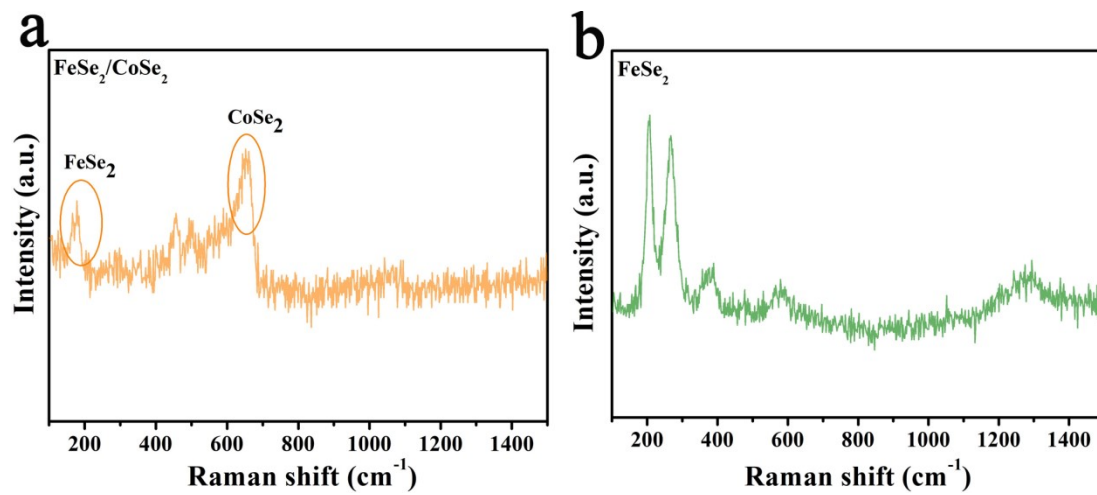


Figure S1. Raman shift of (a) FeSe₂/CoSe₂ and (b) FeSe₂.

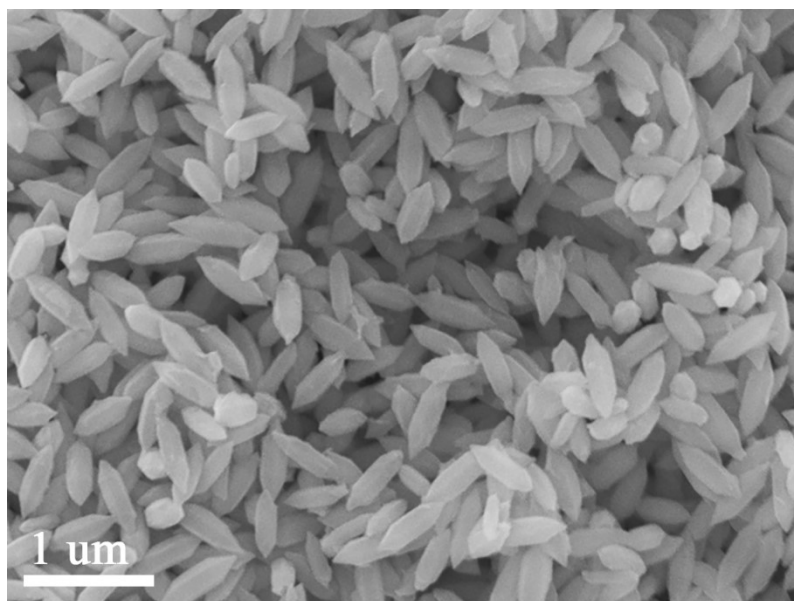


Figure S2. SEM image of Fe-Co precursors.

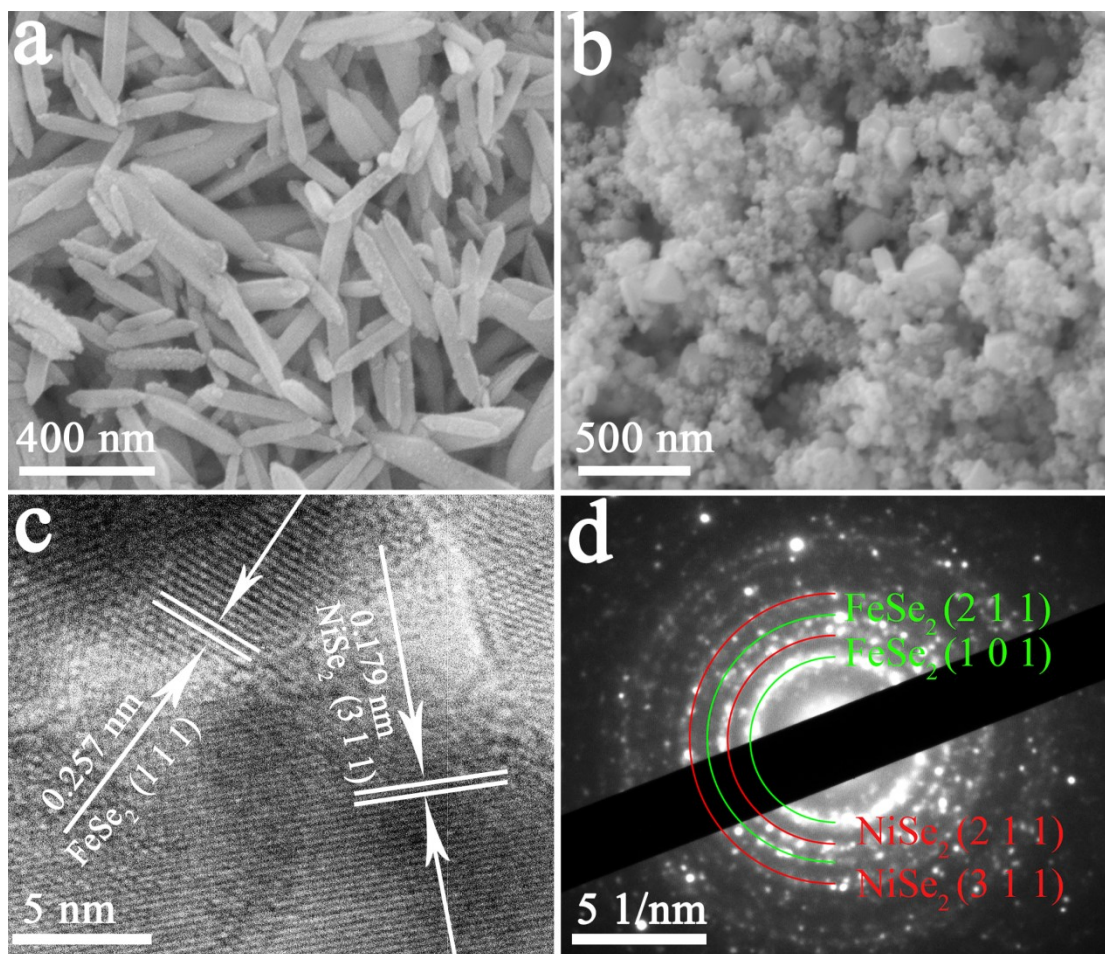


Figure S3. (a-b) FESEM images of Fe-Ni precursor and FeSe₂/NiSe₂ composites. (c) HRTEM images of FeSe₂/NiSe₂ composites. (d) Electron diffraction pattern of FeSe₂/NiSe₂ composites.

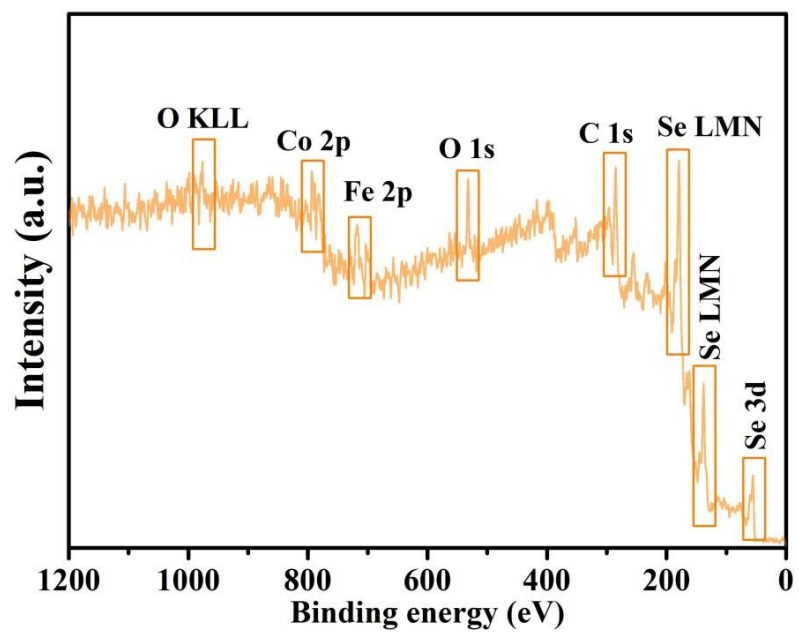


Figure S4. XPS survey spectrum of the FeSe₂/CoSe₂.

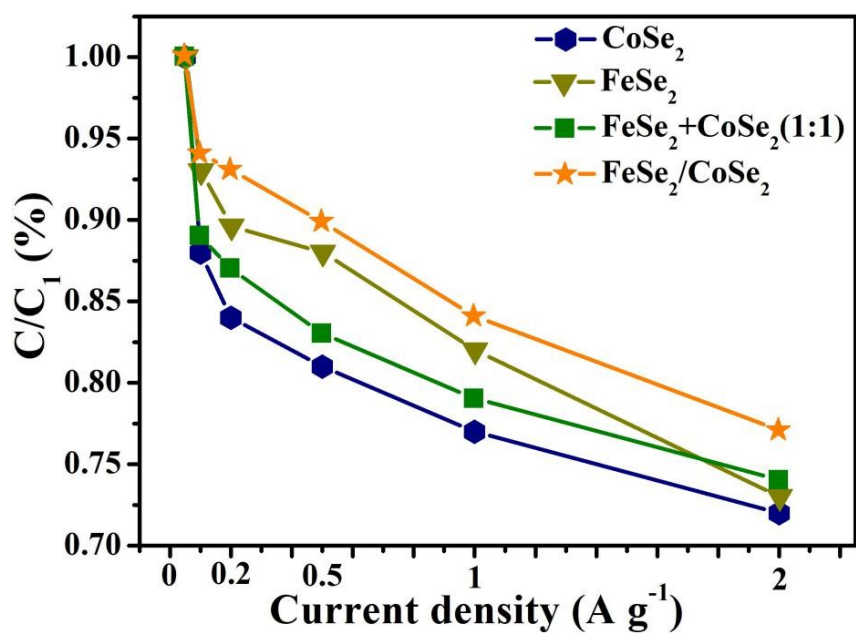


Figure S5. Ratio of capacity to reference capacity at different current densities.

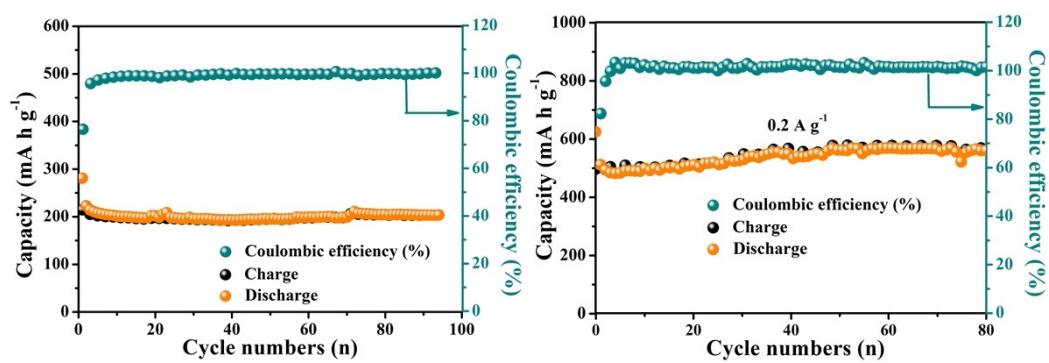


Figure S6. (a) FeSe₂/CoSe₂ cycle performance at high mass loading of 1.75 mg cm⁻² and (b) low current density of 0.2 A g⁻¹.

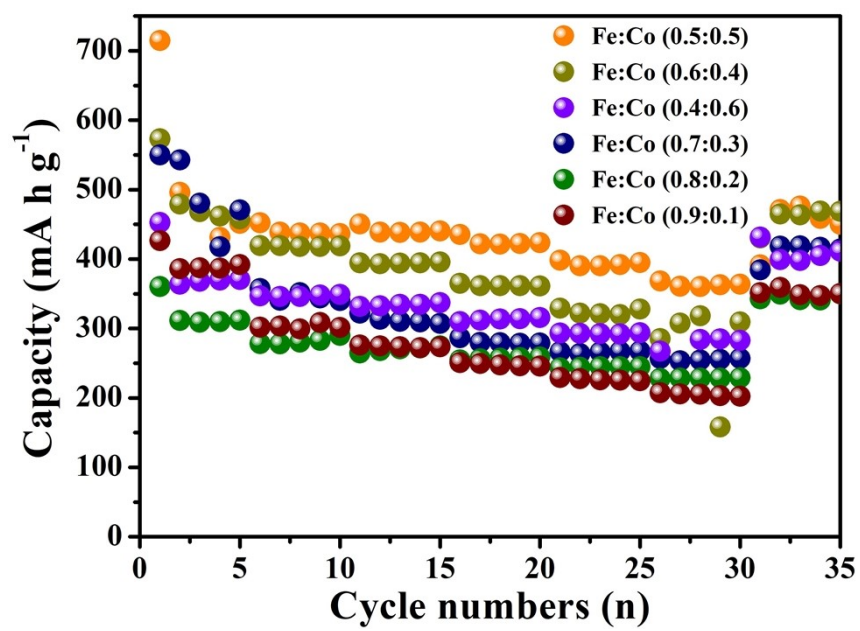


Figure S7. Rate performance at different ratio of Fe/Co.

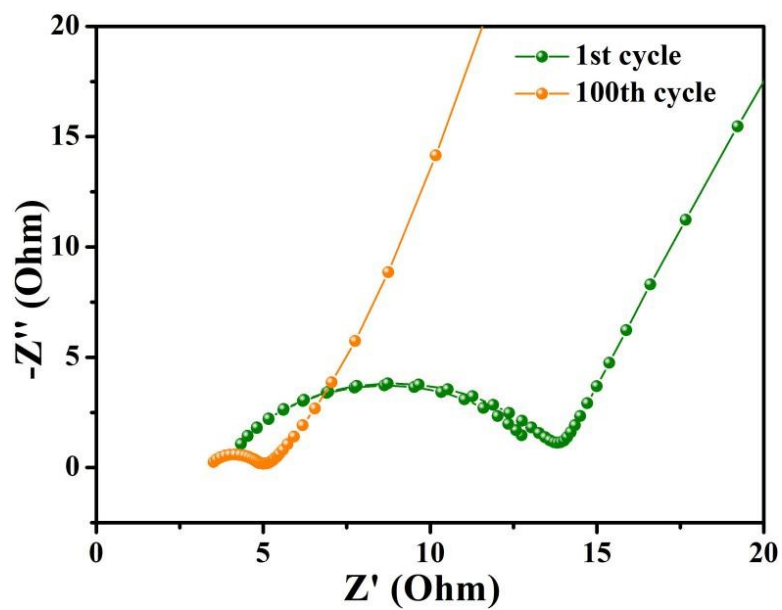
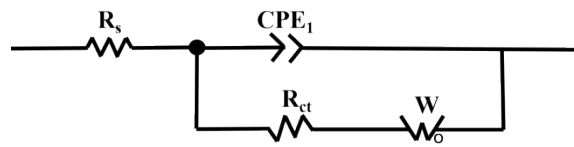


Figure S8. Comparison of Nyquist graphs of $\text{FeSe}_2/\text{CoSe}_2$ after 1 and 100 cycles.



R_s , R_{ct}/CPE_1 and W are related to solution, charge transfer, and ion diffusion impedance, respectively.

Figure S9. The equivalent circuit for $FeSe_2/CoSe_2^{[1]}$.

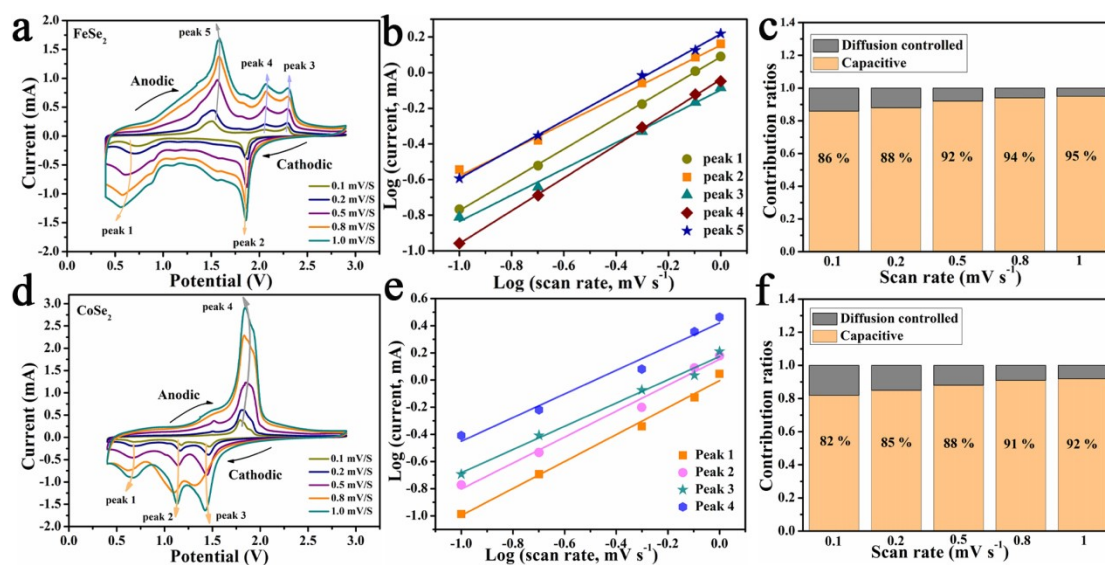


Figure S10. CV curves at different scan rates of (a) FeSe₂ and (d) CoSe₂. Log (scan rate) versus log (peak current) at different redox peaks of (b) FeSe₂ and (e) CoSe₂. Percentage of capacitive contribution at different scanning rates of (c) FeSe₂ and (f) CoSe₂.

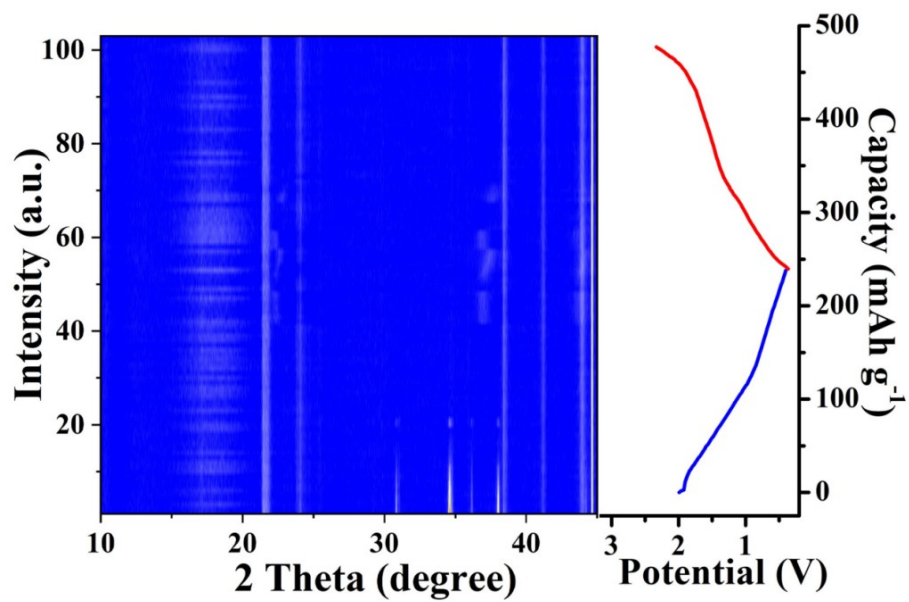


Figure S11. Contour plots of in-situ XRD results of the FeSe₂/CoSe₂ during the initial cycle.

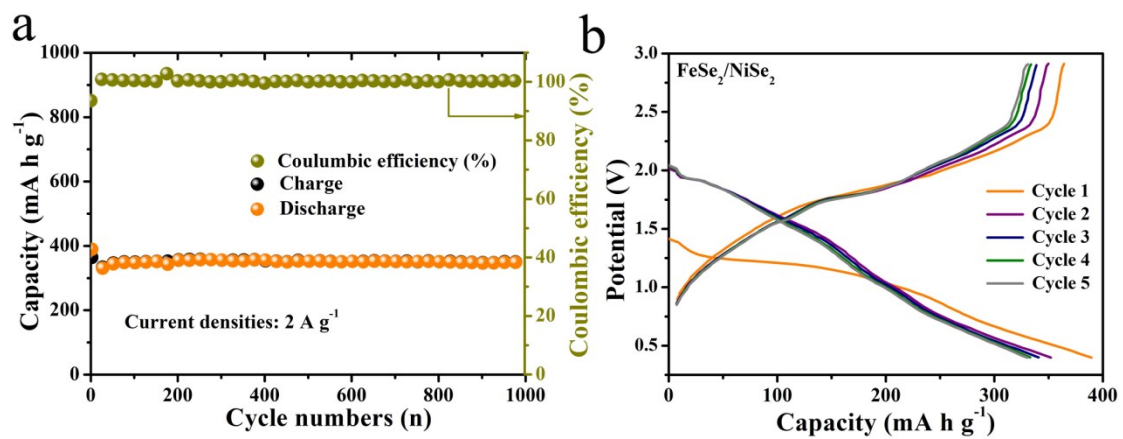


Figure S12. (a) Cycling performance of FeSe₂/NiSe₂ at 2 A g⁻¹. (b) Charging and discharging curves of FeSe₂/NiSe₂ first 5 cycles.

Table S1. Fitting results of EIS in Figure 4a with the proposed equivalent circuit.

R_s represents the series resistance, R_{ct} indicates the charge-transfer resistance and CPE

Samples	$R_s(\Omega)$	$R_{ct}(\Omega)$	$\sigma(\Omega \text{ cm}^2 \text{ s}^{-1/2})$	$D_{Na^+}(\text{cm}^2 \text{ s}^{-1})$
FeSe₂/CoSe₂	3.5	2.1	1.67	4.95×10^{-17}
FeSe₂	3.8	4.6	39.87	8.68×10^{-20}
CoSe₂	5.09	9.6	16.92	2.88×10^{-20}
FeSe₂:CoSe₂(1:1)	4.69	7.15	69.28	4.82×10^{-19}

expresses the constant phase element^[2].

Table S2. Slope values of each peak in figure 5d^[3]

Peak	Slope value
Peak1	0.98
Peak2	0.87
Peak3	0.87
Peak4	0.90
Peak5	0.81
Peak6	0.95

Table S3. ICP test of different Fe/Co ratio in figure S6.

Fe/Co ratio	Concentration of Fe (mg/L)	Concentration of Co (mg/L)
0.5:0.5	8.619	8.614
0.6:0.4	6.826	4.335
0.4:0.6	7.563	11.245
0.7:0.3	8.363	3.583
0.8:0.2	7.846	1.982

Reference

- [1] Choi. W, Shin. HC, Kim. JM, Choi. JY, Yoon. WS, Modeling and applications of electrochemical impedance spectroscopy (EIS) for lithium-ion batteries, *J. Electrichem. Sci. Technol*, 2020, 11, 1-13.
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- [3] A. Veronica, C. Jeremy, L. Michael A, K. Jong, T. Pierre, T. Sarah, A. Hector, S. Patrice, D. Bruce, High-rate electrochemical energy storage through Li⁺ intercalation pseudocapacitance, *Nat. Mater*, 2013, 12, 518-522.