

Electronic Supplementary Information

Construction of Bimetallic Nickel Cobalt Selenides Pompon as Superior Anode for High Performance Sodium Storage

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1. Materials Characterizations

The morphology was observed by field emission scanning electron microscopy (FESEM) using JSM-7800F (Japan) with Energy-dispersive spectroscopy (EDS), and the microstructure of the material was analyzed by transmission electron microscopy (TEM) of JEM-2100 (Japan). Cu K α radiation X-ray diffraction (XRD-7000) with a wavelength of 1.5406 Å was used to exam the crystal structure of the material. The X-ray photoelectron spectroscopy (XPS) of the products were obtained from a Thermo Scientific Escalab 250xi spectrometer. The analysis of pore size and specific surface area was mainly based on Autosorb-1 (Quantachrome Instruments, USA).

2. Electrochemical Measurements

The electrochemical properties of the material are mainly manifested by the CR2032 cells assembled in a glove box filled with Ar. The preparation process of the anode working electrode followed a conventional method. Typically, the active materials, carbon black and polyvinylidene fluoride binder were homogeneously mixed at a mass ratio of 8:1:1 with N-methyl-2-pyrrolidone (NMP) as solvent. Then the obtained slurry was pasted onto a polished and clean Cu foil and transferred to a 120 °C vacuum oven for 12 h to remove the NMP solvent. The mass loading of each electrode slice (12mm diameter) is approximately 1.0 mg cm⁻², and the thickness of active material is about 10 μm. The glass fiber and metal sodium slices were employed as the separator and counter electrode, respectively. The injected electrolyte component was 1 mol L⁻¹ sodium trifluoromethanesulfonate (NaCF₃SO₃) in diethylene glycol dimethyl ether (DEGDME). The galvanostatic charge/discharge test

was performed by Land battery test system (Wuhan, China) in a voltage window of 0.4 V - 2.9 V at desired current density. The cyclic voltammetry (CV) of the cell at different sweep speeds from 0.1-1.0 mV s⁻¹ was completed by the CHI 660E electrochemical workstation. Zahner electrochemical workstation (Zennium, IM6, Germany) was applied to investigate the electrochemical impedance spectroscopy (EIS).

Supplementary Figures

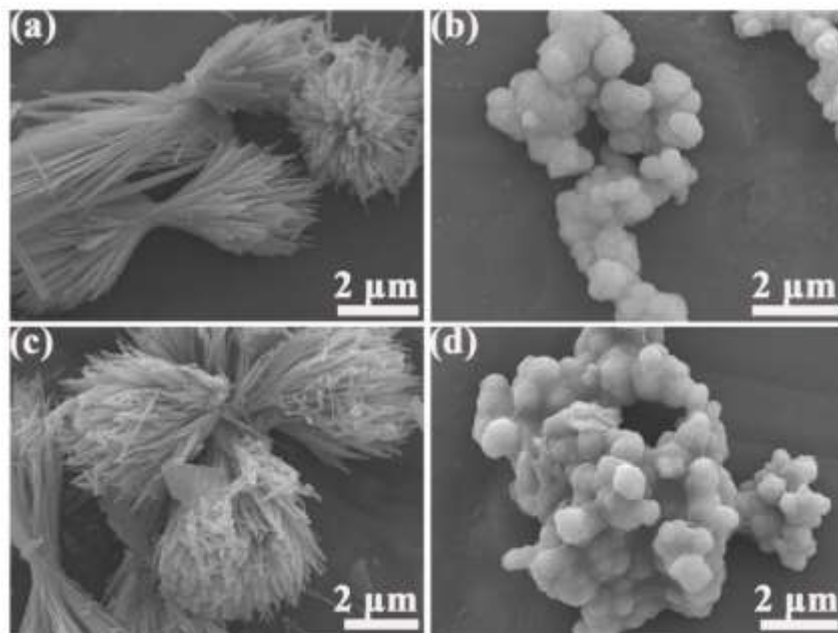


Fig. S1. (a-b) FESEM images of Co and Ni precursor. (c-d) FESEM images of Co_9Se_8 and $\text{Ni}_{0.85}\text{Se}$ composites.

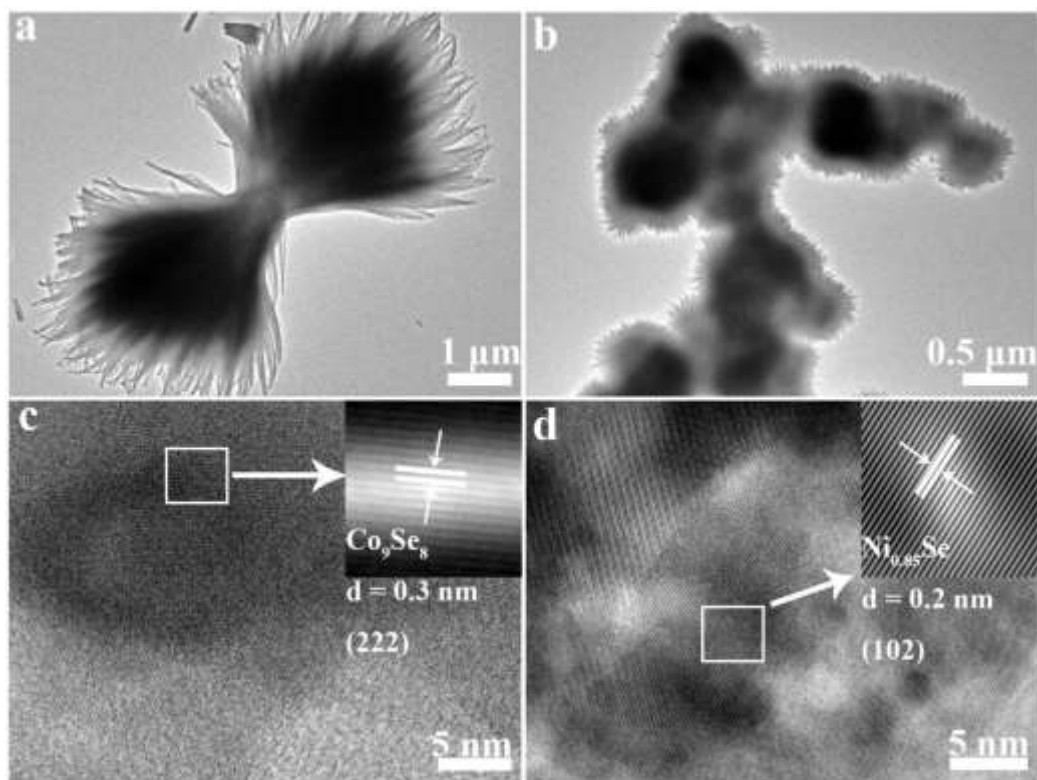


Fig. S2. (a-b) Low-magnification TEM images of Co_9Se_8 and $\text{Ni}_{0.85}\text{Se}$. (c-d) High-magnification TEM images of Co_9Se_8 and $\text{Ni}_{0.85}\text{Se}$.

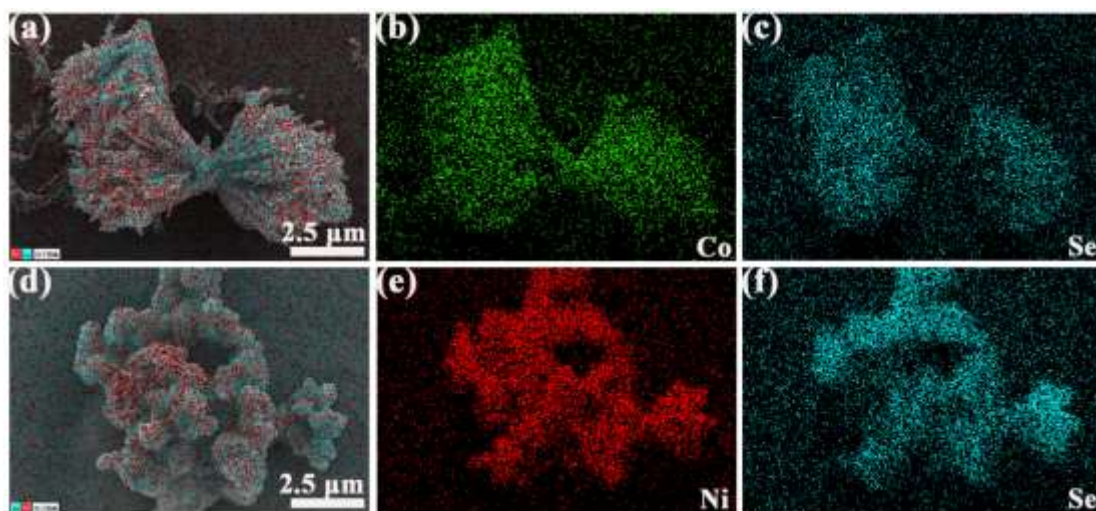


Fig. S3. EDS mapping images of (a-c) Co_9Se_8 and (d-f) $\text{Ni}_{0.85}\text{Se}$.

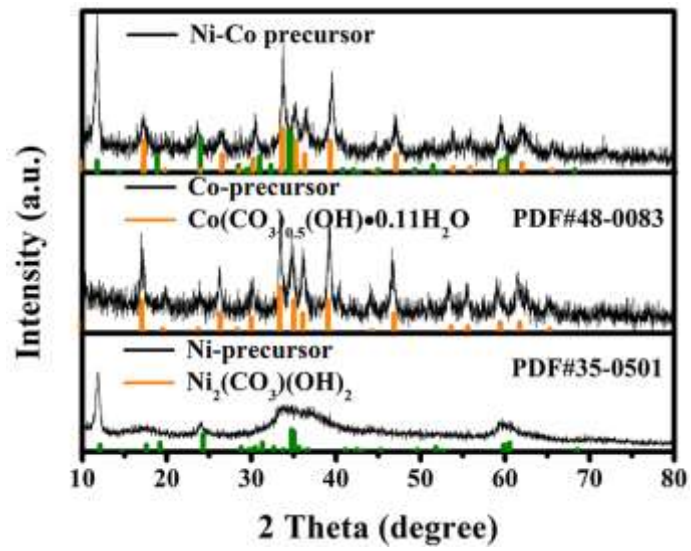


Fig. S4. XRD patterns of Ni-Co, Co and Ni precursor.

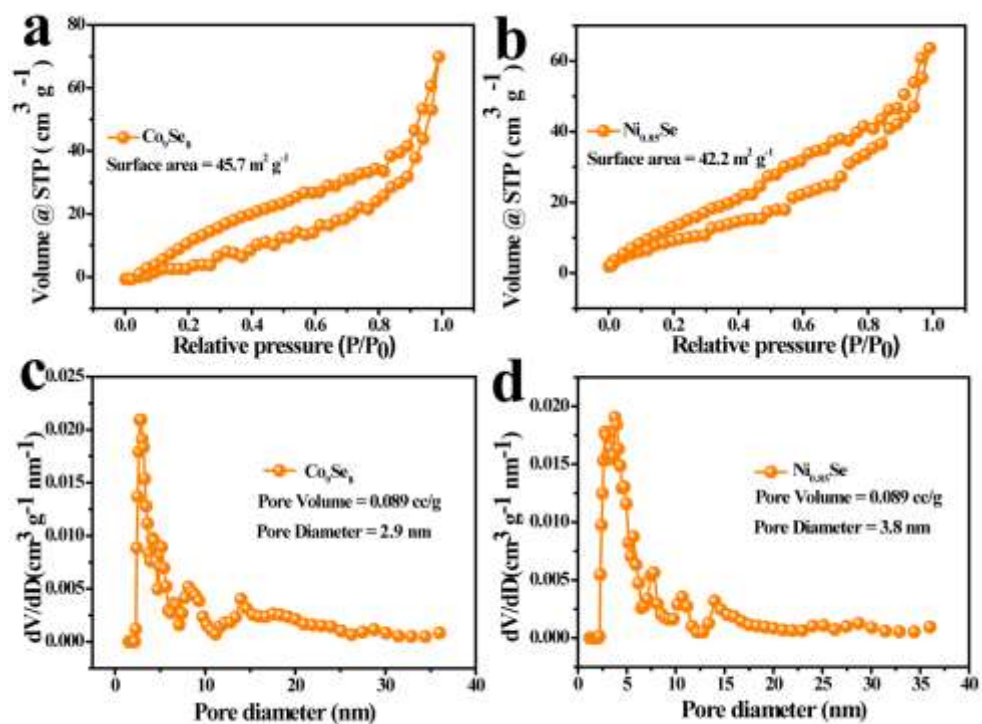


Fig. S5. Nitrogen sorption isotherms of (a) Co₉Se₈ and (b) Ni_{0.85}Se. Pore size distribution of (c) Co₉Se₈ and (d) Ni_{0.85}Se.

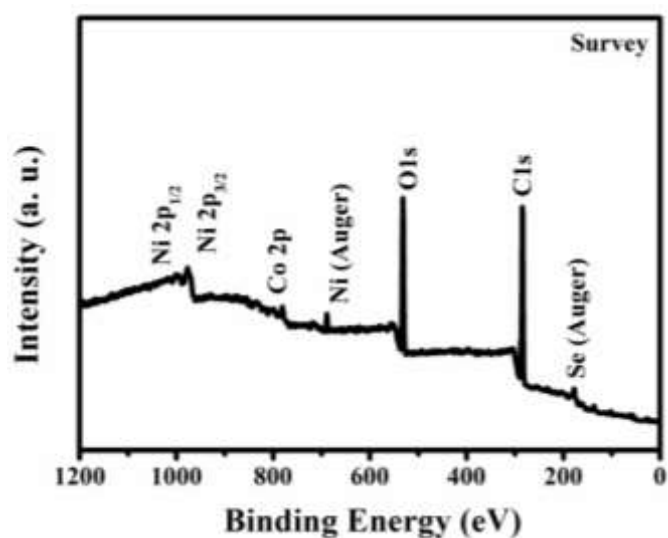


Fig. S6. XPS survey spectrum of NiCo₂Se₄.

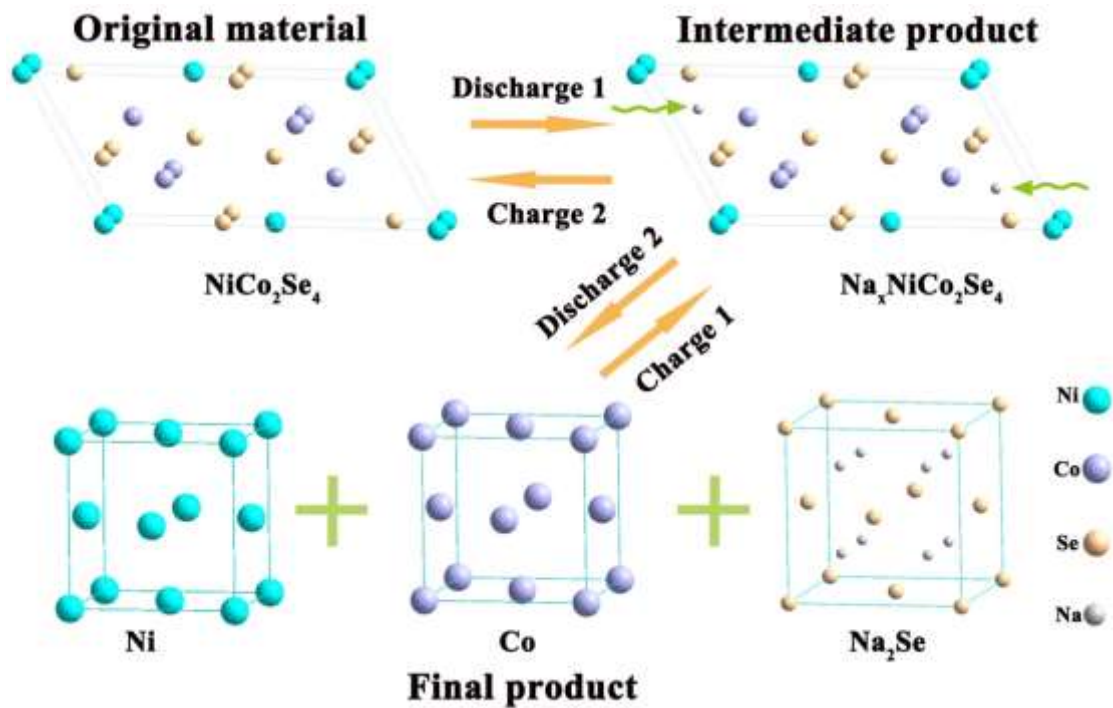


Fig. S7. Charging/discharging mechanism schematic.

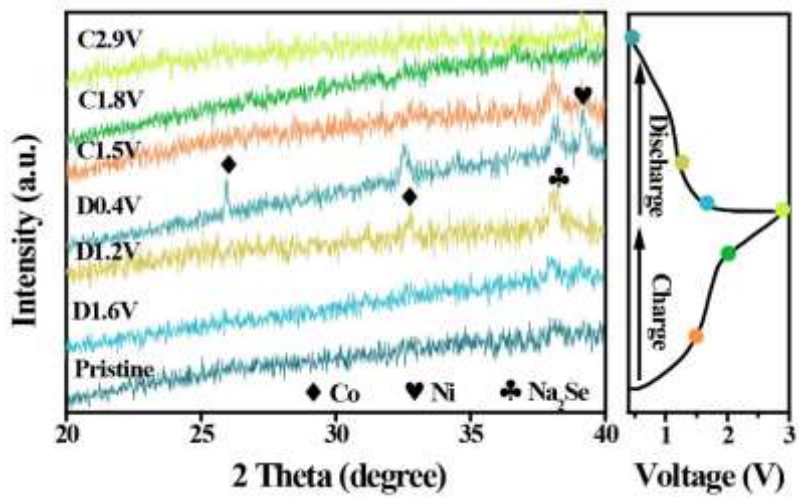


Fig. S8. Ex situ XRD pattern of NiCo_2Se_4 electrodes during charge/discharge.

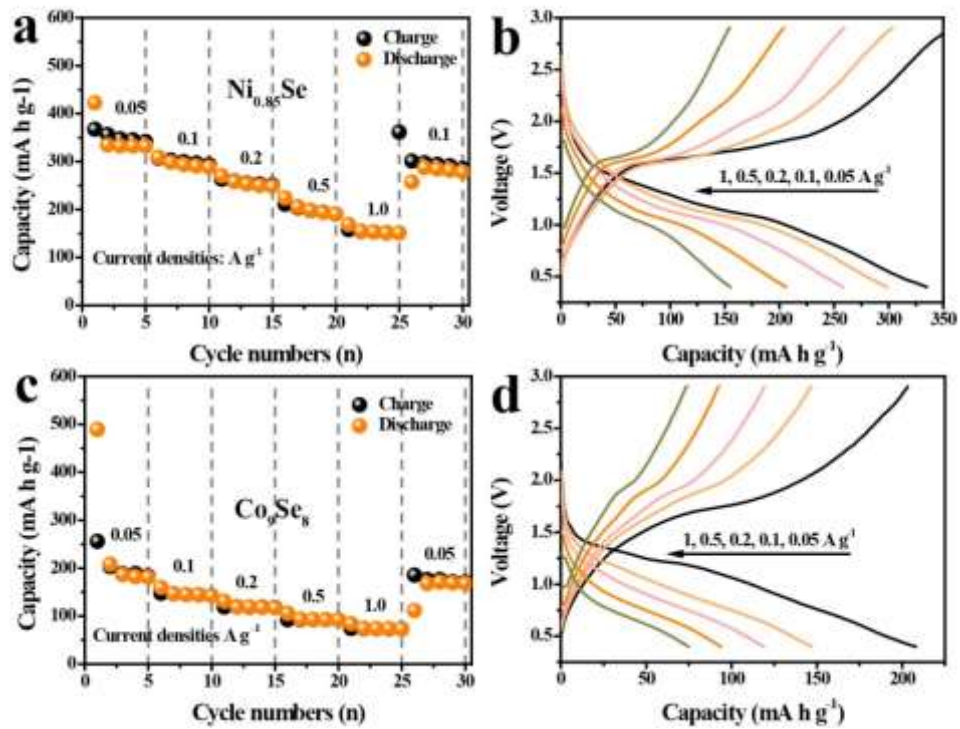


Fig. S9. Rate performance of $\text{Ni}_{0.85}\text{Se}$ and Co_9Se_8 .

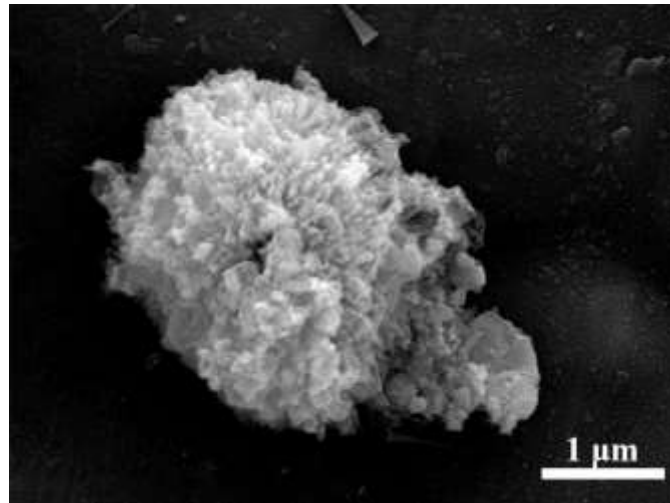


Fig. S10. FESEM image of NiCo_2Se_4 after circulation.

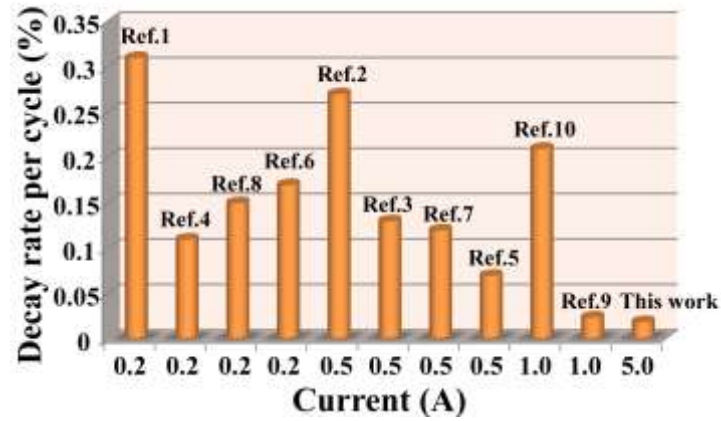


Fig. S11. Comparisons of the decay rate per cycle with other works.

Table 1. Summary for the cycle life of the representative selenide-based anode materials for SIBs.

Materials	Current density (mA g ⁻¹)	Cycles	Capacity (mAh g ⁻¹)	Capacity decay rate per cycle(%)	Ref.
NiCo ₂ Se ₄	5000	2500	230	0.019%	This work
(NiCo)/CoSe ₂	200	80	497	0.31%	1 ⁻²⁰¹⁷
Ni _{1.5} CoSe ₅	500	80	360	0.27%	2 ⁻²⁰¹⁸
Ni _{1.8} Co _{1.2} Se ₄	500	100	379.3	0.13%	3 ⁻²⁰¹⁸
C@Ni _x Co _{1-x} Se ₂ /CNF	200	100	499	0.11%	4 ⁻²⁰¹⁷
NiCoSe ₂ @C	500	250	338.3	0.07%	5 ⁻²⁰¹⁹
CNT-CoSe ₂ @NC	200	120	404	0.17%	6 ⁻²⁰¹⁹
CoSe/NC-L	500	150	397	0.12%	7 ⁻²⁰¹⁹
CoSe ₂ @NC	200	100	555	0.15%	8 ⁻²⁰¹⁸
Co _{0.85} Se NSs@rGO	1000	800	382	0.024%	9 ⁻²⁰¹⁸
NiSe ₂ /NC	1000	150	308	0.21%	10 ⁻²⁰¹⁸

Table 2. Kinetic parameters of NiCo₂Se₄, Ni_{0.85}Se and Co₉Se₈ obtained from equivalent circuit fitting.

Anode material	R _{ct} (Ω)
NiCo ₂ Se ₄	26.46
Ni _{0.85} Se	40.13
Co ₉ Se ₈	43.54

Table 3. The D_{Na⁺} values for the electrochemistry processes of NiCo₂Se₄, Ni_{0.85}Se and Co₉Se₈.

Anode material	Diffusion coefficient (cm ² s ⁻¹)
NiCo ₂ Se ₄	4.22 × 10 ⁻¹²
Ni _{0.85} Se	1.77 × 10 ⁻¹³
Co ₉ Se ₈	9.63 × 10 ⁻¹³

References

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