## Bimetallic FeSe<sub>2</sub>/CoSe<sub>2</sub> Heterojunction Nanoparticles Anchored on Porous N-Doped Carbon Nanosheets for High-Rate Sodium-Ion Storage

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## **Experimental Section**

Synthesis of Fe/Co-MOF: Dissolve 0.523 g cobalt (II) nitrate hexahydrate, 0.121 g iron (III) chloride hexahydrate, and 0.25 g terephthalic acid (1,4-H2BDC) sequentially in 50 mL N, N-dimethylformamide (DMF) solution with vigorous stirring and sonication to ensure complete dissolution. Subsequently, add 10 mL deionized water, 10 mL ethanol, and 4 mL triethylamine (TEA) to the solution, followed by stirring at room temperature for 12 h. The precipitate was collected by centrifugation, washed alternately with acetone and ethanol three times, and finally dried in a vacuum oven at 60°C for 12 h to obtain Fe/Co-MOF powder.

Synthesis of FeSe<sub>2</sub>/CoSe<sub>2</sub>@NC: The as-prepared Fe/Co-MOF was placed in a tube furnace under 500 sccm argon flow as protective gas, then heated to 650 °C at a ramping rate of 2 °C min<sup>-1</sup> and maintained for 2 h, yielding FeCo@NC powder after natural cooling. The FeCo@NC powder was mixed with selenium powder at a 1:3 mass ratio in two separate zones of a ceramic boat (with selenium at the upstream position), and subsequently annealed in the tube furnace under 500 sccm argon flow at 500 °C for 2 h (heating rate: 2 °C min<sup>-1</sup>). The resulting powder after natural cooling was identified as FeSe<sub>2</sub>/CoSe<sub>2</sub>@NC.

Synthesis of Fe-MOF: Following the Fe/Co-MOF preparation procedure while omitting the addition of cobalt (II) nitrate hexahydrate and increasing the mass of iron (III) chloride hexahydrate to 0.607 g, while keeping all other steps unchanged, yields Fe-MOF.

Synthesis of Co-MOF: Using the Fe/Co-MOF preparation protocol but excluding iron (III) chloride hexahydrate and adjusting the mass of cobalt (II) nitrate hexahydrate to 0.655 g, while maintaining all other parameters, produces Co-MOF.

Synthesis of FeSe<sub>2</sub>@NC and CoSe<sub>2</sub>@NC: FeSe<sub>2</sub>@NC and CoSe<sub>2</sub>@NC were synthesized under identical conditions to FeSe<sub>2</sub>/CoSe<sub>2</sub>@NC by substituting Fe/Co-MOF with pre-synthesized Fe-MOF and Co-MOF, respectively, while maintaining the experimental protocol.

Synthesis of NC: The as-prepared FeCo@NC powder was mixed with 1 M HCl solution, then transfer to a 100 mL Teflon lined autoclave and maintained at 80 °C for

2 h. After hydrothermal impregnation, the mixture was washed by deionized water for several times and dried to gain the NC sample.

Material Characterization: The synthesized materials were systematically characterized using multiple analytical techniques. X-ray diffraction (XRD) patterns were collected on a D8 Advance diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5406$  Å) over a 20 range of 10-80° at a scan rate of 10° min<sup>-1</sup>, and phase identification was performed by comparing with standard PDF cards using Jade software. The electron paramagnetic resonance (EPR) spectra were obtained in the X-band with a magnetic field modulation of 100 kHz using a Bruker A300-10/12 EPR spectrometer at room temperature. X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi) was employed to analyze the elemental composition and chemical states, with data processed using Avantage software. Raman spectroscopy was applied to identify the vibrational modes of the materials and their crystal symmetry, using the LabRAM Soleil nano Raman spectrometer. Morphological and elemental distribution analyses were conducted using scanning electron microscopy (SEM, ZEISS Gemini 300). Further microstructural and crystallographic characterization, including high-resolution imaging and EDS mapping, was performed via transmission electron microscopy (TEM, FEI Tecnai F20, TF30), with data analyzed using Gatan Digital Micrograph. Additionally, Brunauer-Emmett-Teller (BET) surface area and pore size distribution were measured using a Micromeritics ASAP 2460 analyzer at 77 K, with samples degassed at 180°C for 10 h prior to measurement to eliminate adsorbed contaminants.

Electrochemical Measurements: The discharge capacity refers to sodiation capacity and charge capacity refers to de-sodiation capacity in this study. A slurry consisted of the powder samples, Super P carbon, and PVDF binder at a ratio of 8:1:1 (in weight) using NMP as solvent was prepared. Then the slurry was spread onto a copper foil using a doctor blade. Typically, the mass loading of active material in this study was 0.8-1.3mg cm<sup>-2</sup>. After the cutting and drying process, the as-prepared electrodes were assembled into 2032coin-type cells in an Ar-filled glovebox (H<sub>2</sub>O<0.1 ppm, O<sub>2</sub><0.1 ppm). The half-cell consisted of a piece of fleshly cut Na metal as the counter electrode, a glass fiber separator (Whatman GF/D), and 1 M NaPF<sub>6</sub> dissolved in DME (NP-035 purchased from DodoChem) as the electrolyte. The galvanostatic cycling test was performed using a LAND battery testing system under voltage ranges of 0.01–2.5 V (vs. Na/Na<sup>+</sup>). CV and EIS measurements were conducted on an electrochemical station (Bio-Logic, Inc., Seyssinet-Pariset, France). During EIS measurements, the batteries were tested by applying an amplitude signal of 5 mV ranging from 1 MHz to 0.01 Hz. Galvanostatic intermittent titration technique (GITT) measurements were carried out on the same NEWARE system with identical voltage cutoffs. The D<sub>Na<sup>+</sup></sub> values can be determined using the followed Equation:

$$D_{Na^{+}} = \frac{4}{\pi\tau} \left( \frac{m_B V_M}{M_B S} \right)^{2} \cdot \left( \frac{\Delta E_s}{\Delta E_t} \right)^2$$
(1)

where  $\tau$  is the relaxation time (s), m<sub>B</sub> is the mass of the active materials, V<sub>M</sub> is the molar volume of the active materials, S is the contact area between the active materials and electrolyte,  $\Delta E_s$  denotes the potential variation in two consecutive relaxation periods, and  $\Delta E_{\tau}$  stands for the potential variation between static state and equilibrium state.

 $Na_3V_2(PO_4)_3$  (NVP) was selected as the cathode material. The NVP cathode was prepared through blending the NVP power, Super P, and PVDF in a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP), and then casting onto Al foils. After dried in vacuum oven at 100 °C, NVP cathode was firstly assembled into half cells and tested over a potential range of 2.0-3.8 V. The FeSe<sub>2</sub>/CoSe<sub>2</sub>@NC//NVP full cell with a N/P ratio of ~1:1.2 was measured within a voltage window of 1.0-3.5 V.

Computational Methods: All the DFT calculations were conducted based on the Vienna Ab-inito Simulation Package (VASP).<sup>[1-2]</sup> The exchange-correlation effects were described by the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) method.<sup>[3-4]</sup> The core-valence interactions were accounted by the projected augmented wave (PAW) method.<sup>[5]</sup> The energy cutoff for plane wave expansions was set to 400 eV, and the  $2 \times 2 \times 1$  Monkhorst-Pack grid k-points were selected to sample the Brillouin zone integration. The structural optimization was completed for energy and force convergence set at  $1.0 \times 10^{-4}$  eV and  $0.05 \text{ eV} \text{ Å}^{-1}$ , respectively. DFT-D3 method was used to describe van der Waals (vdW) interactions.<sup>[6]</sup>



Figure S1. (a-b) SEM images at different magnifications of Fe-Co MOF.



**Figure S2.** (a-b) SEM images at different magnifications, (c-d) STEM images, (e) HR-TEM image, (f) the corresponding SAED pattern, and (g) EDS of Fe-Co/NC.



**Figure S3.** XRD pattern of Fe-Co/NC.



Figure S4. SEM images of the (a-b) CoSe<sub>2</sub>/NC and (c-d) FeSe<sub>2</sub>/NC.



Figure S5. XRD of the (a) FeSe<sub>2</sub>/NC and CoSe<sub>2</sub>/NC.



Figure S6. (a) XPS spectra of C 1s for  $FeSe_2/CoSe_2@NC$ . (b) XPS spectra of Se 3d for  $FeSe_2@NC$ ,  $CoSe_2@NC$ , and  $FeSe_2/CoSe_2@NC$ .



**Figure S7.** (a) N<sub>2</sub> adsorption-desorption isotherms and (b) pore size distribution of FeSe<sub>2</sub>/CoSe<sub>2</sub>@NC.



Figure S8. CV curves of (a) FeSe<sub>2</sub>@NC and (b) CoSe<sub>2</sub>@NC.



Figure S9. Charge/discharge curves at different current densities of FeSe<sub>2</sub>/CoSe<sub>2</sub>@NC.



Figure S10. Electrochemical performances of the nitrogen-doped carbon (NC) anodes: (a) Rate performance and (b) cycling performance at 1 A  $g^{-1}$ .



Figure S11. (a, b) SEM and (c) TEM images for  $FeSe_2/CoSe_2@NC$  after 500 cycles.



**Figure S12.** (a) CV curves at different sweep rates and (b) the corresponding  $\log i$  vs.  $\log v$  plots at each peak and the corresponding linear fits of CoSe<sub>2</sub>@NC. (c) CV curves at different sweep rates and (d) the corresponding  $\log i$  vs.  $\log v$  plots at each peak and the corresponding linear fits of FeSe<sub>2</sub>@NC electrode.



**Figure S13.** (a) GITT curves, (b) EIS results before cycling, and (c) corresponding plots between  $\omega^{-1/2}$  and Z' of CoSe<sub>2</sub>@NC, FeSe<sub>2</sub>@NC, and FeSe<sub>2</sub>/CoSe<sub>2</sub>@NC electrode.



**Figure S14.** (a) Galvanostatic charge/discharge curves at 1 A  $g^{-1}$  in the initial three cycles and (b) cycling performance of Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>@C cathode. (c) Rate and (d) cycling performance at 1 A  $g^{-1}$  of FeSe<sub>2</sub>/CoSe<sub>2</sub>@NC//NVP full cell.

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