

Supplementary Information

Synthesis of carbon-coated FeSe₂ nano microsphere with stable SEI film as anode materials for high-performance sodium-ion batteries

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1. Experimental

1.1 Synthesis of nano-microsphere Fe_3O_4 precursor

Weigh 0.246 g of $\text{Fe}(\text{AC})_2 \cdot 4\text{H}_2\text{O}$, 0.361 g of urea ($\text{CO}(\text{NH}_2)_2$), 0.074 g of NH_4F , and 0.036 g of CTAB (cetyl trimethyl ammonium bromide) into 60 mL of deionised water. Afterward, stir the mixture for 5 minutes to ensure thorough mixing. The resulting homogeneous solution is then transferred into a 100 mL reactor and subjected to a 12 h reaction at 120°C. Once the reaction is complete and the system has cooled to room temperature, collect the black precipitate from the reactor. Subsequently, wash it alternately with ethanol and deionised water, and finally dry the product at 70°C for 10 h to obtain the black powdery nano-microsphere Fe_3O_4 precursor.

1.2 Synthesis of nano-microsphere $\text{Fe}_3\text{O}_4@\text{PDA}$ composites

100 mg nano-microsphere Fe_3O_4 were first dispersed into 100 mL tris-buffer solution (PH=8.5) by ultrasonication for 2 h. Then, 60 mg of dopamine hydrochloride was added into the above solution, which was kept stirring for 24 h. The resultant product nano-microsphere $\text{Fe}_3\text{O}_4@\text{PDA}$ was collected through centrifugation and washed several times with absolute ethyl alcohol and deionized water, respectively, and dried at 70 °C overnight.

1.3 Synthesis of FeSe_2 and $\text{FeSe}_2@\text{NC}$ composites

The as-prepared nano-microsphere Fe_3O_4 and nano-microsphere $\text{Fe}_3\text{O}_4@\text{PDA}$ precursors and Se powders with a weight ratio of (1:3) were put in a corundum boat and calcined at 550 °C in Ar atmosphere for 3 h. Then the FeSe_2 and $\text{FeSe}_2@\text{NC}$ composites were obtained.

1.4 Materials characterization

The crystalline phase and morphology of the as-prepared Fe_3O_4 , FeSe_2 and

FeSe₂@NC composites was investigated by powder X-ray diffractometry (XRD, BRUKER D8 ADVANCE) with Cu-K α radiation ($\lambda=0.15406$ nm) and scanning electron microscopy (SEM, SU8010). The microstructure of FeSe₂ and FeSe₂@NC composites are further identified by transmission electron microscopy (TEM, TJEOL JEM 2100). The chemical composition and valence states of FeSe₂@NC is analysed by X-ray photoelectron spectroscope (XPS ESCALAB 250Xi, Thermo Scientific).

1.5 Cell fabrication and characterization

The sodium storage performance of FeSe₂ and FeSe₂@NC are evaluated with CR2025-type coin cells. The FeSe₂ and FeSe₂@NC are combined with Super-P (SP) and polyvinylidene fluoride (PVDF) binder in a mass ratio of 7:2:1 in N-methylpyrrolidone (NMP) to create a homogeneous slurry. This slurry is then cast onto copper foil and dried in a vacuum at 110 °C for 12 h. After drying, electrode discs with a diameter of 12.5 mm are punched out and weighed, resulting in an active material loading density of approximately~1.4 mg/cm². Electrochemical cells are assembled in an argon-filled glove box where the levels of O₂ and H₂O are maintained below 0.01 ppm. The electrolyte used is 1 M NaPF₆ in diethylene glycol dimethyl ether (DEGDME), with sodium foil serving as both the anode and counter electrode. A Whatman glass microfiber filter (Whatman GF/F) is employed as the separator. Galvanostatic charge/discharge measurements are conducted within a voltage range of 0.1 to 3.0 V using a multichannel battery testing system (LAND CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) for the prepared anodes are performed using an electrochemical workstation (Metrohm Autolab PGSTAT302N) with a voltage window of 0.1 to 3.0 V. Galvanostatic intermittent titration technique (GITT) measurements were carried out by applying a constant current of 50 mA g⁻¹ for 300 s followed by a 900 s relaxation to reach

equilibrium. In the full-cell configuration, $\text{FeSe}_2@\text{NC}$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) were employed as the anode and cathode materials, respectively, with a mass ratio of approximately 1:3 between anode and cathode. Galvanostatic charge/discharge measurements are conducted within a voltage range of 0.5 to 3.5 V using a multichannel battery testing system (LAND CT2001A).

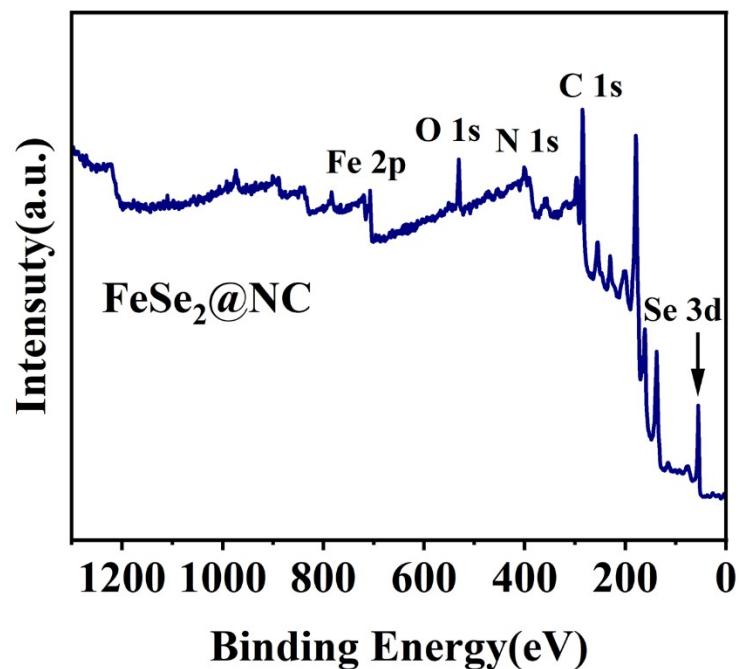


Fig. S1 XPS of full survey spectra of $\text{FeSe}_2@\text{NC}$ powders

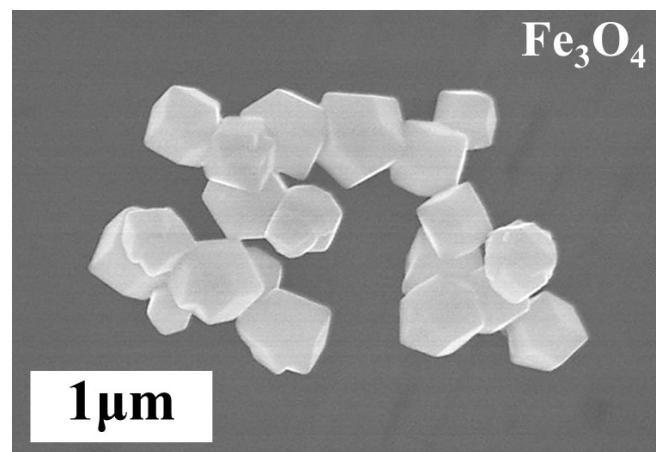


Fig. S2 SEM images of Fe_3O_4 -precursor,

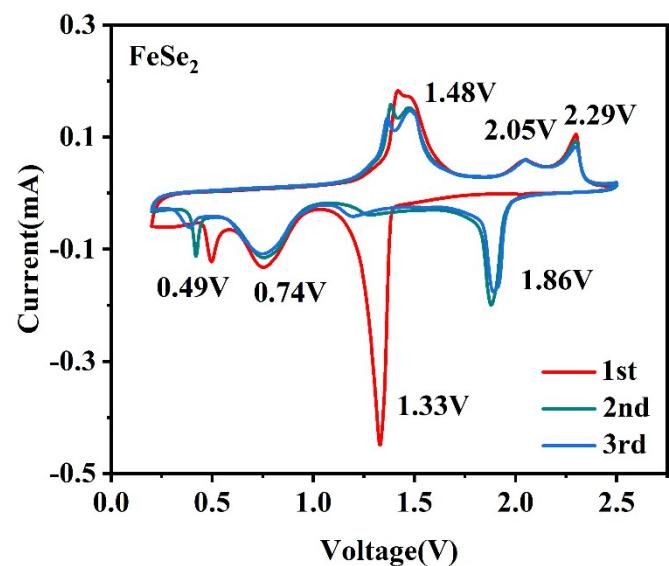


Fig. S3 CV curve of FeSe₂

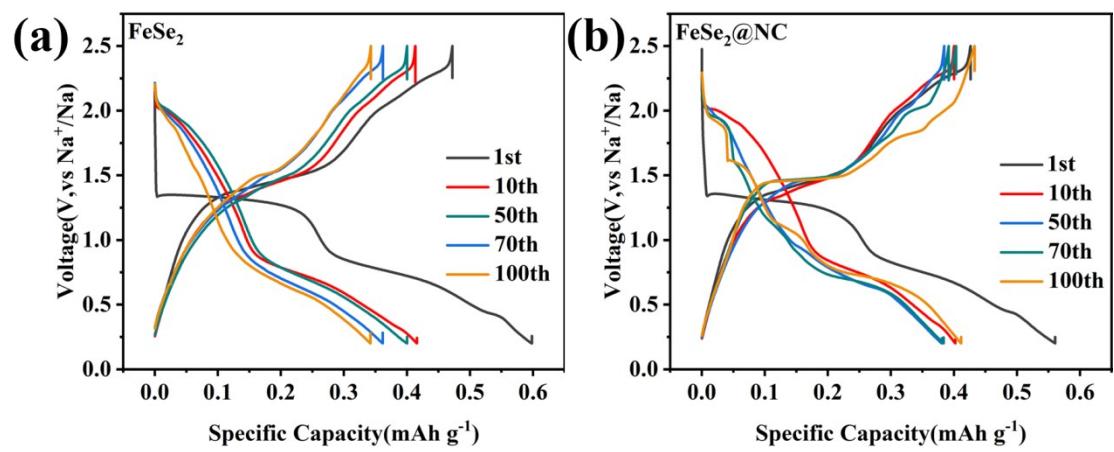


Fig. S4 galvanostatic charge-discharge curves of (a) FeSe_2 and (b) $\text{FeSe}_{2z}\text{@NC}$.

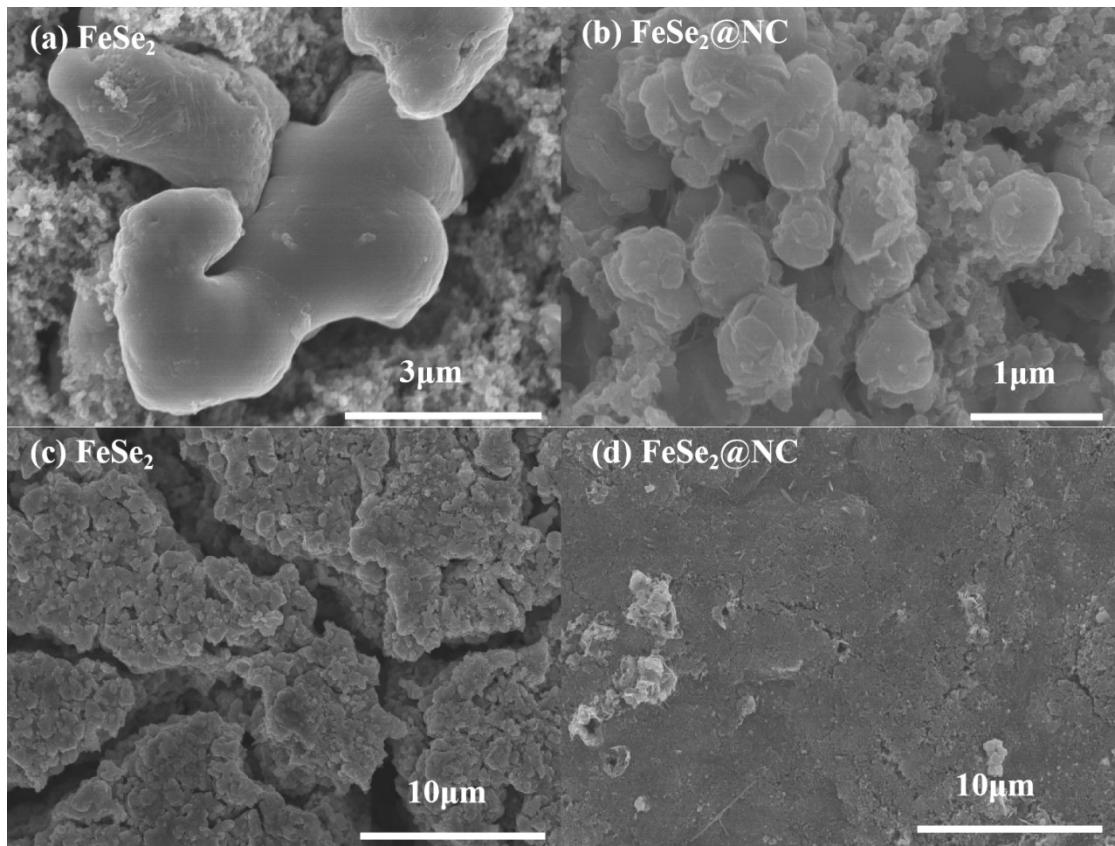


Fig. S5 The surface morphologies of (a, b) FeSe_2 and (c, d) $\text{FeSe}_2@\text{NC}$ electrodes after 100 cycles.

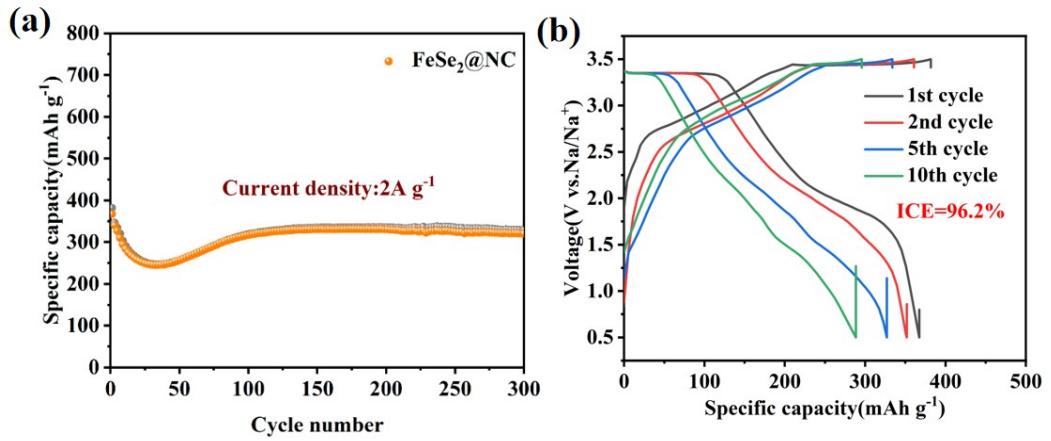


Fig. S6 (a) Long cycling performance of $\text{FeSe}_2@\text{NC}$ || NVP full cell at a current density of 2.0 A g^{-1} .

(b) charge/discharge curves for the $\text{FeSe}_2@\text{NC}||\text{NVP}$ full cell

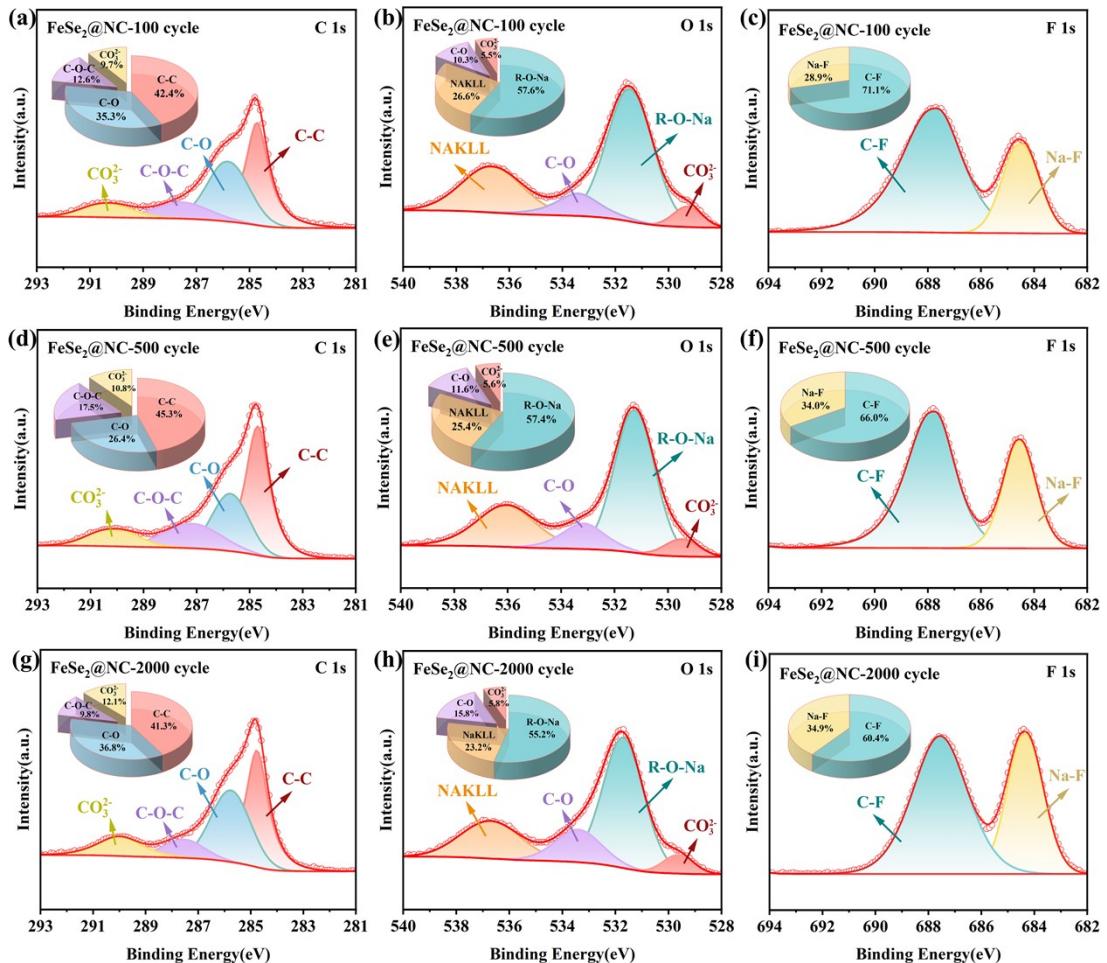


Fig. S7 (a) C 1s, (b) O 1s and (c) F 1s XPS spectra of $\text{FeSe}_2@\text{NC}$, extracted from coin cells after 100, 500, and 1000 cycles

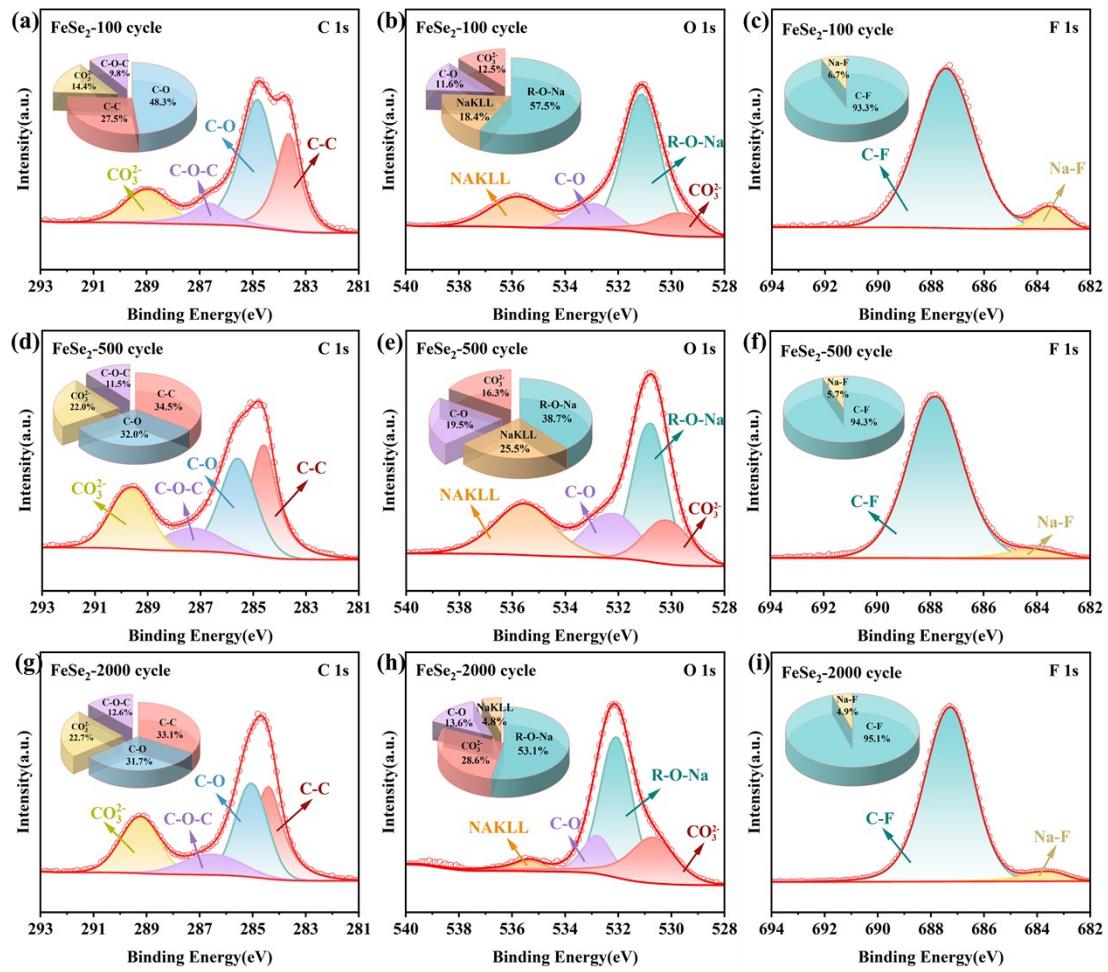


Fig. S8 (a) C 1s, (b) O 1s and (c) F 1s XPS spectra of FeSe₂, extracted from coin cells after 200,500 cycles and 1000 cycles