

## Supplementary Information

### **Synthesis of carbon-coated FeSe<sub>2</sub> nano microsphere with stable SEI film as anode materials for high-performance sodium-ion batteries**

Zhiya Lin <sup>a,c,1</sup>, Yidan Chen <sup>b,1</sup>, Zhilong Wu <sup>b</sup>, Shaoming Ying <sup>b\*</sup>, Xiaohui Huang <sup>b\*</sup>

<sup>a</sup> College of Mathematics and Physics, Ningde Normal University, Ningde,  
352100, China.

<sup>b</sup> Fujian Provincial Key Laboratory of Featured Materials in Biochemical Industry,  
College of Chemistry and Materials, Ningde Normal University, Ningde 352100,  
PR China.

<sup>c</sup> College of Physics and Energy, Fujian Normal University, Fujian Provincial  
Solar Energy Conversion and Energy Storage Engineering Technology Research  
Center, Fuzhou, 350117, China.

\*Corresponding author:

Xiaohui Huang E-mail: 11429721@qq.com

Shaoming Ying E-mail: yingshaoming@126.com

<sup>1</sup> Z. Y. Lin and Y. D. Chen contributed equally to this work.

## **1. Experimental**

### **1.1 Synthesis of nano-microsphere Fe<sub>3</sub>O<sub>4</sub> precursor**

Weigh 0.246 g of Fe(AC)<sub>2</sub>·4H<sub>2</sub>O, 0.361 g of urea (CO(NH<sub>2</sub>)<sub>2</sub>), 0.074 g of NH<sub>4</sub>F, 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<sub>3</sub>O<sub>4</sub> precursor.

### **1.2 Synthesis of nano-microsphere Fe<sub>3</sub>O<sub>4</sub>@PDA composites**

100 mg nano-microsphere Fe<sub>3</sub>O<sub>4</sub> 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 Fe<sub>3</sub>O<sub>4</sub>@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<sub>2</sub> and FeSe<sub>2</sub>@NC composites**

The as-prepared nano-microsphere Fe<sub>3</sub>O<sub>4</sub> and nano-microsphere Fe<sub>3</sub>O<sub>4</sub>@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<sub>2</sub> and FeSe<sub>2</sub>@NC composites were obtained.

### **1.4 Materials characterization**

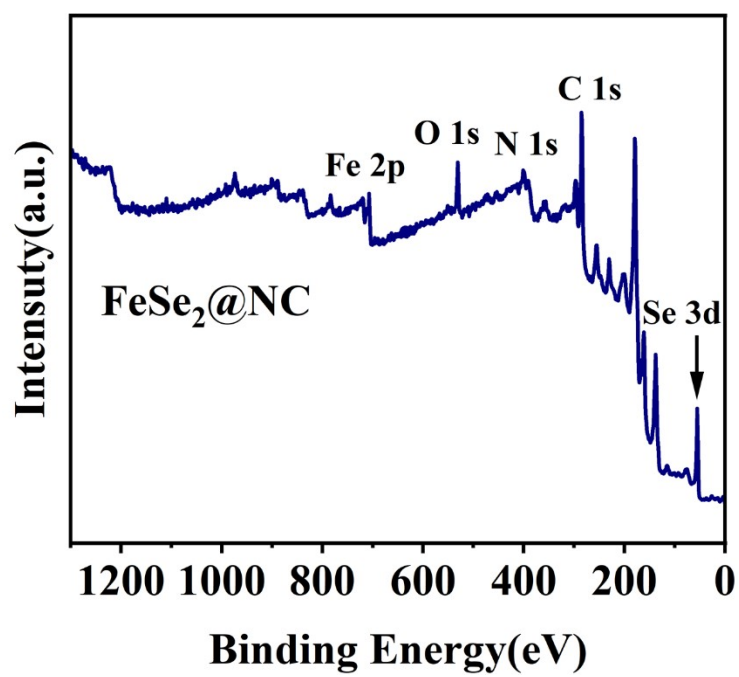
The crystalline phase and morphology of the as-prepared Fe<sub>3</sub>O<sub>4</sub>, FeSe<sub>2</sub> and

FeSe<sub>2</sub>@NC composites was investigated by powder X-ray diffractometry (XRD, BRUKER D8 ADVANCE) with Cu-K $\alpha$  radiation ( $\lambda=0.15406$  nm) and scanning electron microscopy (SEM, SU8010). The microstructure of FeSe<sub>2</sub> and FeSe<sub>2</sub>@NC composites are further identified by transmission electron microscopy (TEM, TJEOL JEM 2100). The chemical composition and valence states of FeSe<sub>2</sub>@NC is analysed by X-ray photoelectron spectroscopy (XPS ESCALAB 250Xi, Thermo Scientific).

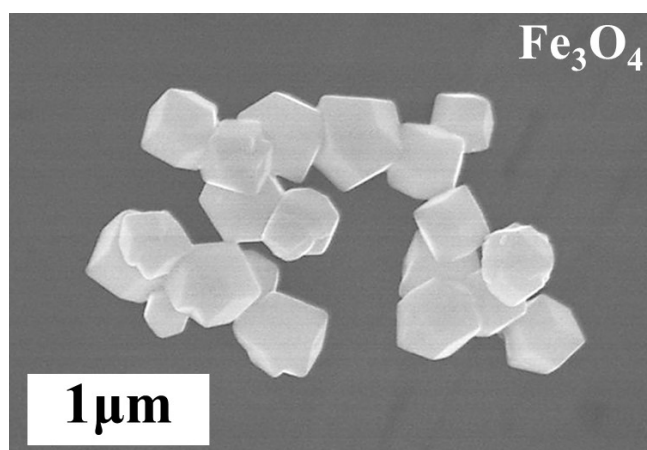
### 1.5 Cell fabrication and characterization

The sodium storage performance of FeSe<sub>2</sub> and FeSe<sub>2</sub>@NC are evaluated with CR2025-type coin cells. The FeSe<sub>2</sub> and FeSe<sub>2</sub>@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/cm<sup>2</sup>. Electrochemical cells are assembled in an argon-filled glove box where the levels of O<sub>2</sub> and H<sub>2</sub>O are maintained below 0.01 ppm. The electrolyte used is 1 M NaPF<sub>6</sub> 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<sup>-1</sup> 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 FeSe<sub>2</sub>@NC powders



**Fig. S2** SEM images of Fe<sub>3</sub>O<sub>4</sub>-precursor,

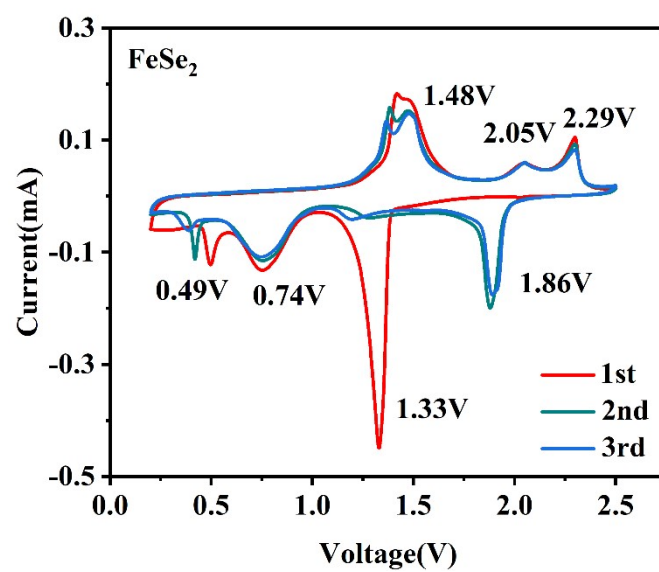
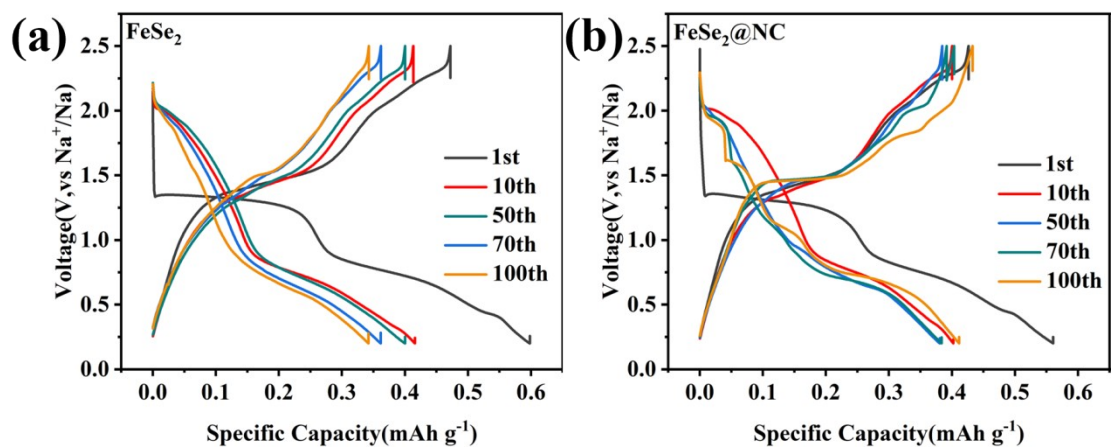
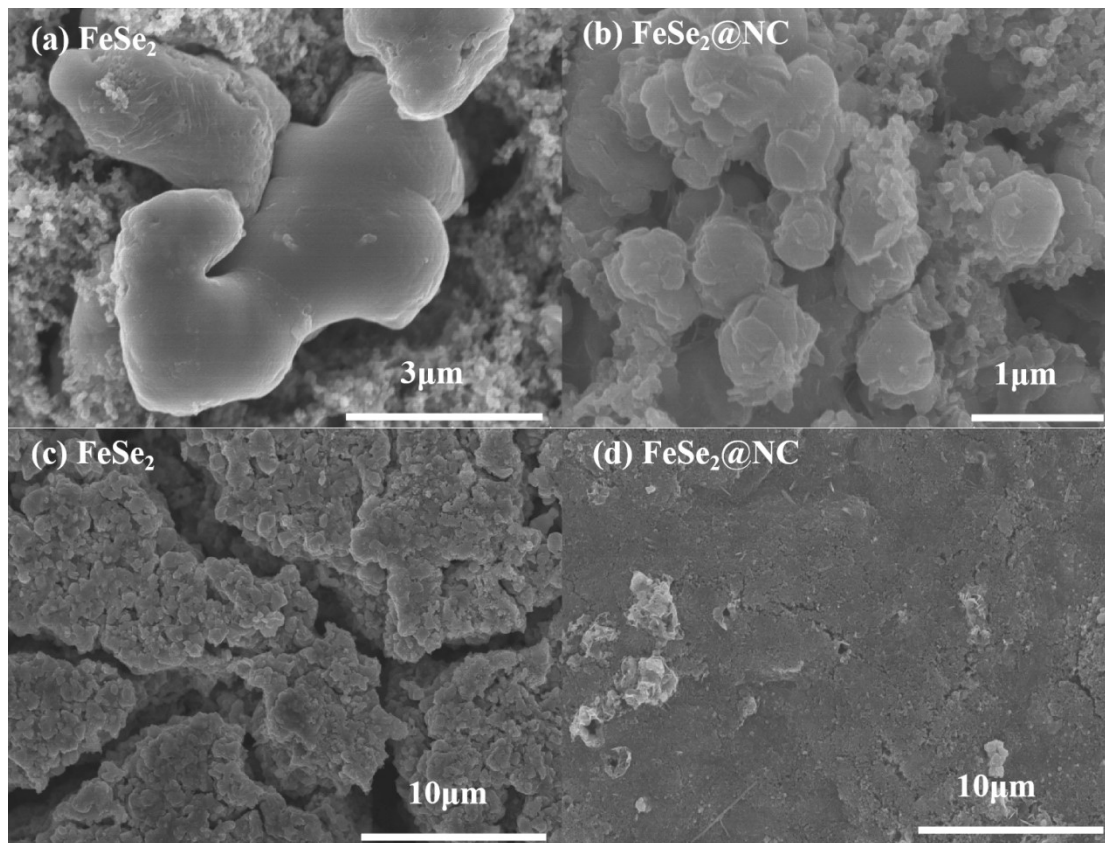


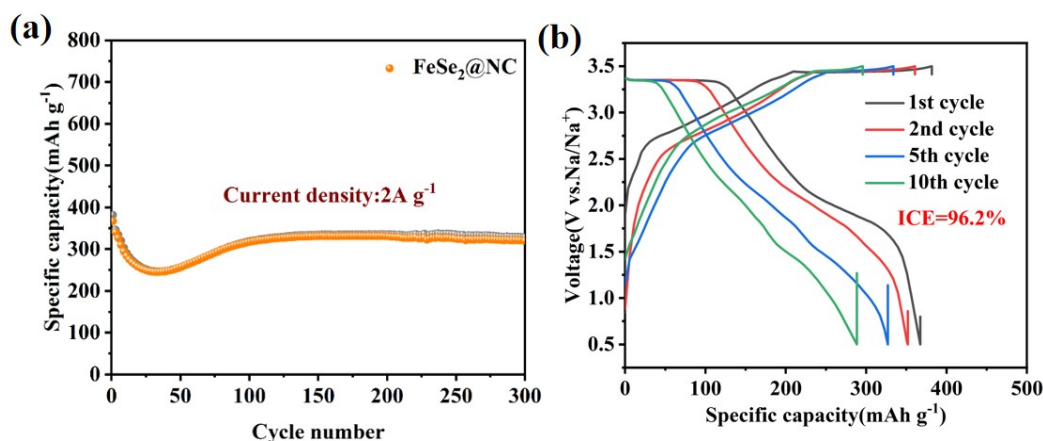
Fig. S3 CV curve of FeSe<sub>2</sub>



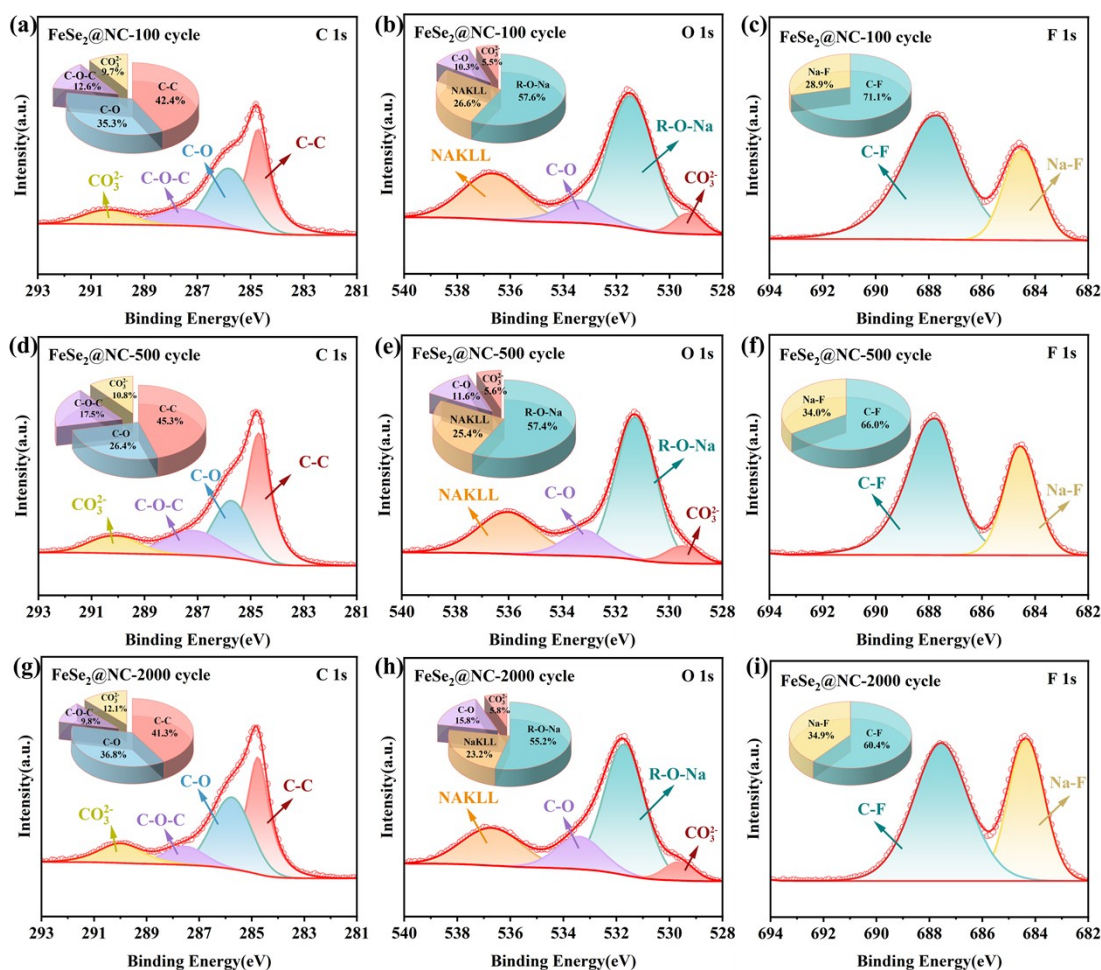
**Fig. S4** galvanostatic charge-discharge curves of (a)  $\text{FeSe}_2$  and (b)  $\text{FeSe}_2@\text{NC}$ .



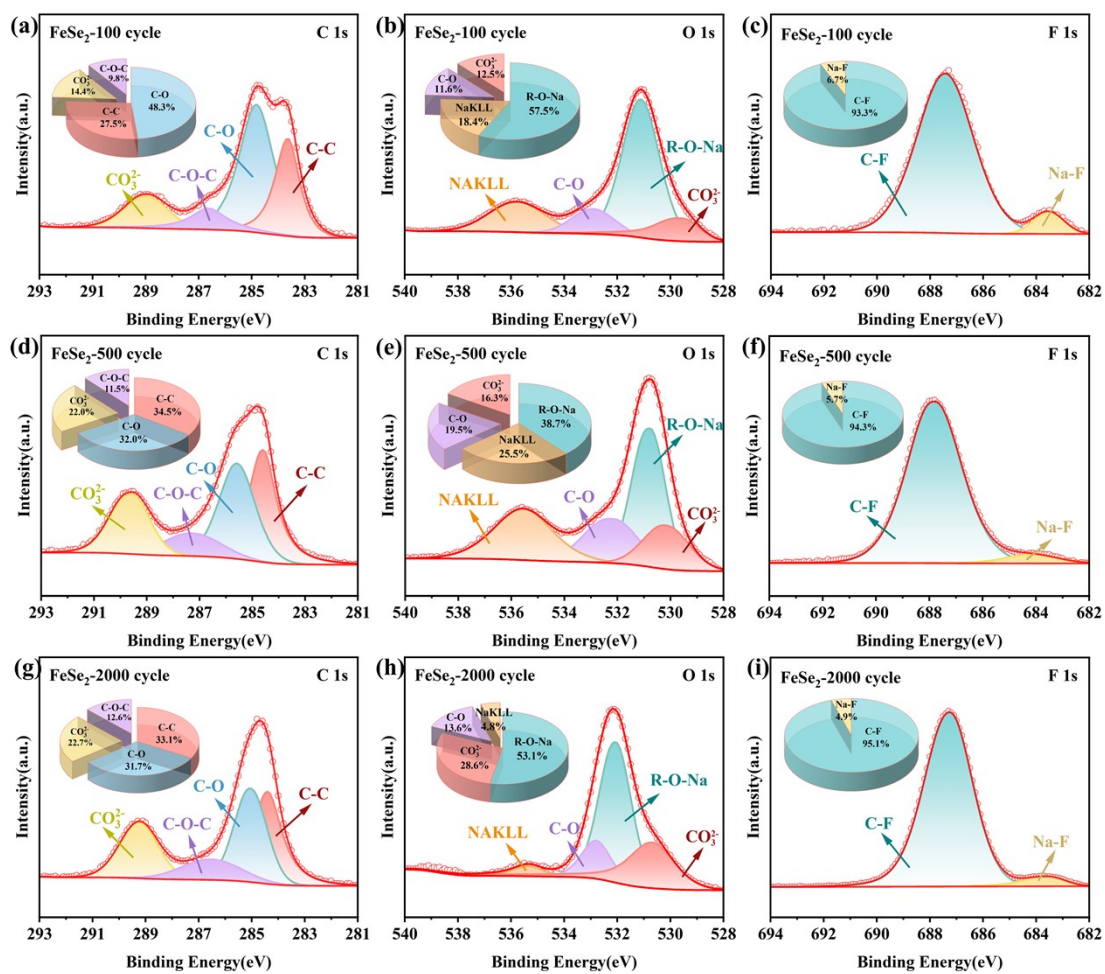
**Fig. S5** The surface morphologies of (a, b)  $\text{FeSe}_2$  and (c, d)  $\text{FeSe}_2@\text{NC}$  electrodes after 100 cycles.



**Fig. S6** (a) Long cycling performance of FeSe<sub>2</sub>@NC || NVP full cell at a current density of 2.0 A g<sup>-1</sup>. (b) charge/discharge curves for the FeSe<sub>2</sub>@NC || NVP full cell



**Fig. S7** (a) C 1s, (b) O 1s and (c) F 1s XPS spectrums of FeSe<sub>2</sub>@NC, extracted from coin cells after 200,500 cycles and 1000 cycles



**Fig. S8** (a) C 1s, (b) O 1s and (c) F 1s XPS spectra of FeSe<sub>2</sub>, extracted from coin cells after 200,500 cycles and 1000 cycles