Electronic Supplementary Material (ESI) for Nanoscale.

Rational Design of Hierarchical $FeSe_2$ Encapsulated with Bifunctional Carbon Cuboids as Advanced Anode for Sodium-ion Batteries

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Experimental section

Chemicals: All chemicals were purchased and used without further purification. Flake graphite was purchased from XFNANO nanomaterials Technology Co. LTD. Potassium ferrocyanide trihydrate [$K_4Fe(CN)_6 \cdot 3H_2O$], potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4, 98.3%), hydrochloric acid (HCl, 30%), hydrogen peroxide (H_2O_2) and selenium (Se) powder were obtained from Sinopharm Chemical Reagent Shanghai Co. Polyvinylpyrrolidone (PVP, K30) was purchased from Sigma-Aldrich (USA).

Synthesis of $Fe_4[Fe(CN)_6]_3$@GO precursors: Through the modified Hummers method, graphene oxide (GO) was obtained from flake graphite powders. In a typical synthesis process, 50 mg GO was dissolved into 50 mL deionized water by ultrasonic treatment forming yellow solution. 110 mg $K_4Fe(CN)_6 \cdot 3H_2O$ and 2 g polyvinyl pyrrolidone (PVP) were added into the above solution. The mixture was stirred for 1 h, and then the suspensions were transferred into a Teflon-lined stainless steel autoclave (100 mL) to react under the temperature of 80 °C for 24 h. A precipitate was collected and washed with deionized water and ethanol for several times. The precursors were obtained after vacuum drying at 60 ℃ for overnight. For comparation, the bare $Fe_4[Fe(CN)_6]_3$ precursors were prepared at the same procedure only without GO addition.

Synthesis of $FeSe_2$*/NC@G composites*: The as-prepared precursors were placed at the downstream side of corundum boat and 2 g Se powder was located at the upstream side in the tube furnace. Then, the furnace was heated to 450 °C with a heating rate of 2 °C min^{-1} under Ar/H_2 (95/5, v/v) flow for 2 h.

Material Characterization: The morphological structure of samples were investigated by scanning electron microscopy (SEM, ZEISS, Simga300, 20 keV) and field- emission transmission electron microscopy (FE-TEM, JEM-2000CX, JEOL, 200 keV). The crystal structures of samples were analyzed by using X-ray diffractometer (Bruker D8 ADVANCE) with Cu Kα radiation (λ = 1.5418 Å). The X-ray photoelectronic spectroscopy (XPS) tests were carried out on a ESCALAB-250 spectrometer (Thermo Fisher Scientific). Nitrogen adsorption-desorption isotherm was characterized by a ASAP2020 (Automated Surface Area Analyzer) and the specific surface area was calculated by using the BET model based on the adsorption data in the linear relative pressure (p/p_0) range of 0.05–0.3. The Raman spectrum was performed by a Raman spectrometer (Horiba Xplora, λ = 532 nm). The thermogravimetric analysis (TGA) was conducted on a thermogravimetric analyzer (TGA, Thermo Gravimetric Analyzer, SDTA851). X-ray absorption fine structure (XAFS) spectroscopy of Fe K-edges were measured on 1W1B beamline at Beijing Synchroton Radiation Facility (BSRF) by scanning Si (111) monochromator.

Electrochemical Measurements: The working electrode was prepared by mixing the $FeSe_2$/NC@G or $FeSe_2$/NC powder, acetylene black, and polyvinylidene difluoride (PVDF) in a weight ratio of 70:20:10. The slurry was coated on Cu foil, and then dried at 100 °C overnight under vacuum and the loading density of the active materials is about 1.8 mg cm^{-2}. CR2032-type coin cells were assembled in an argon-filled glovebox. Na-metal foil use as counter electrode, and 1.0 M $NaClO_4$ dissolved in propylene carbonate (PC) with 5% fluoroethylene carbonate (FEC) used as electrolyte use as electrolyte. The charge-discharge tests were carried out on LAND CT2001A systems. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were tested on VSP electrochemical workstation (Bio-logic, France). For the full-cells test, the $Na_3V_2(PO_4)_3/C$ (NVP) cathode material was prepared as the previous report.[28] CR2032 coin-type cells were assembled using $FeSe_2$/NC@G anode and NVP cathode with the capacity ratio of 1:1.2. Specifically, the $FeSe_2$/NC@G anodes were pre-treated by charging/discharging 3 cycles at current density of 0.1 A g^{-1} and finally charged to 1.0 V at the same rate. Galvanostatic charge/discharge experiments were carried out between 1.0 and 3.0 V.

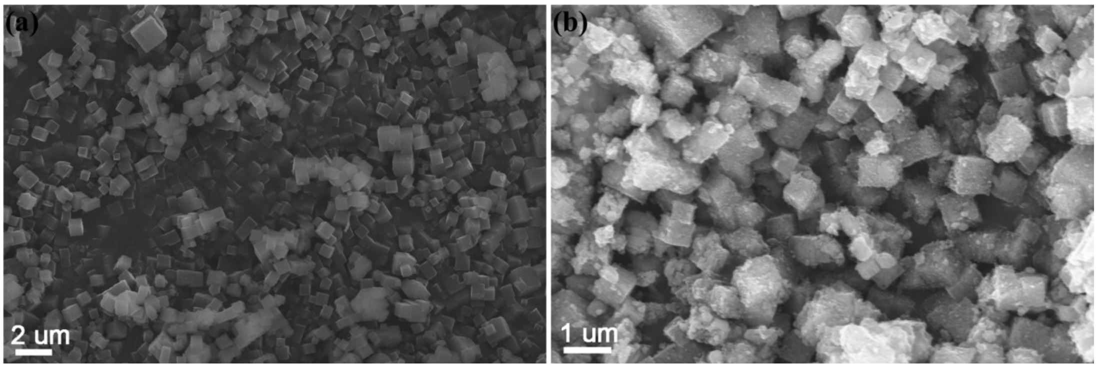

Figure S1. SEM images for the as-prepared samples. (a) $Fe_4[Fe(CN)_6]_3$ precursors, (b) $FeSe_2$/NC.

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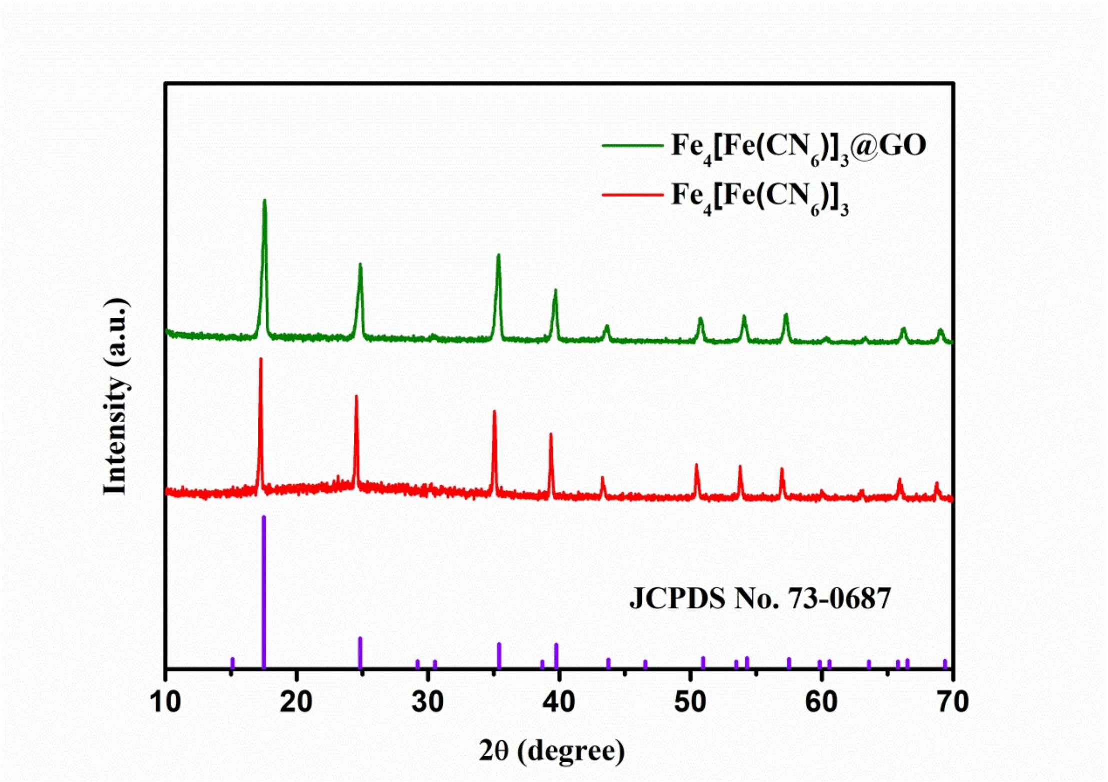

Figure S2. XRD patterns of the as-prepared precursors. (a) $Fe_4[Fe(CN)_6]_3$, (b) $Fe_4[Fe(CN)_6]_3$@GO.

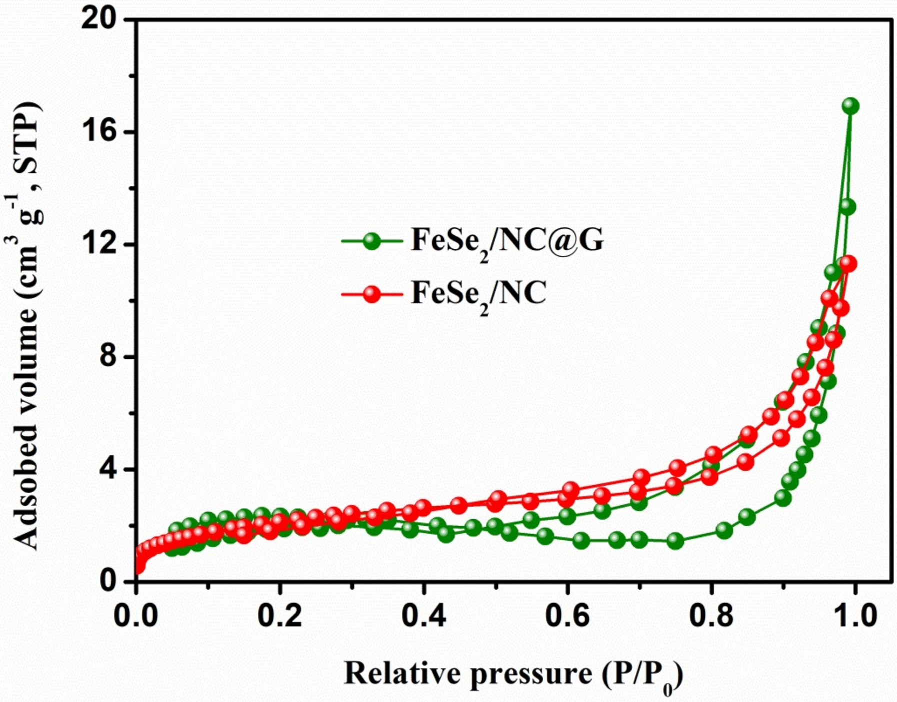

Figure S3. Nitrogen adsorption-desorption isotherms of the $FeSe_2$/NC and $FeSe_2$/NC@G samples.

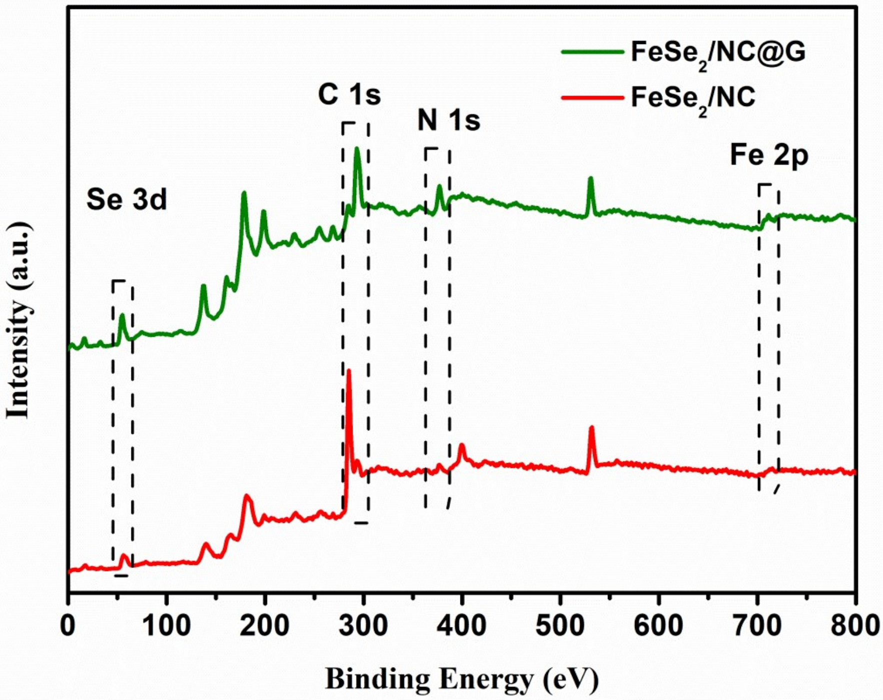

Figure S4. XPS survey spectra for the as-prepared $FeSe_2$/NC and $FeSe_2$/NC@G samples.

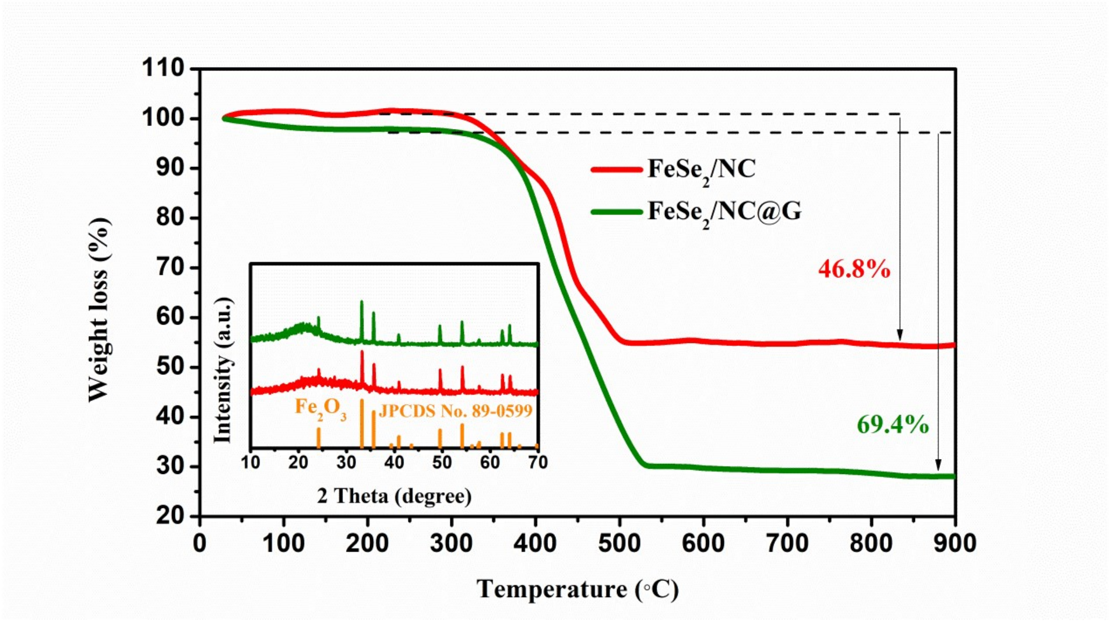

Figure S5. TGA curves for the $FeSe_2$/NC and $FeSe_2$/NC@G samples. Inset is the XRD patterns of the $FeSe_2$/NC and $FeSe_2$/NC@G composites after TGA test.

The content of $FeSe_2$ can be calculated by element quality conservation during TGA test. In a typical calculation, we suppose the weight of $FeSe_2$/NC@G is x mg. Thus, after annealing, the weight of Fe_2O_3 is 0.694x mg.

$2FeSe_2 + 7/2O_2 \rightarrow Fe_2O_3 + 2SeO_2$

According to above equation, the content of $FeSe_2$ should be 40.9% in the $FeSe_2$/NC@G. Similarly, the content of $FeSe_2$ in $FeSe_2$/NC is 71.2 %.

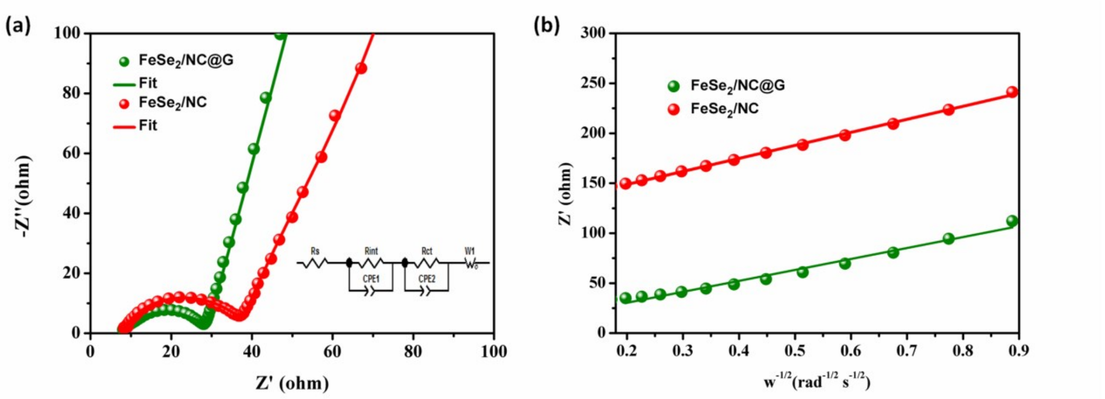

Figure S6. (a) Nyquist plots of $FeSe_2$/NC and $FeSe_2$/NC@G electrodes. Insets depict the equivalent circuit and enlarged spectra high frequency. (b) Linear fitting between Z' and reciprocal of the square root of the angular frequency in the low-frequency region.

The Na^+ diffusion coefficient can be calculated from the formula as following:

$$D = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2} \qquad (1)$$

Where R is the gas constant and F is the Faraday constant. T is the temperature of environment experiment. A is the surface area of the electrode. n is the number of the electrons per molecule. σ is the slope of the line $Z' \sim \omega^{-0.5}$. C is the sodium ion concentration in the bulk electrode.

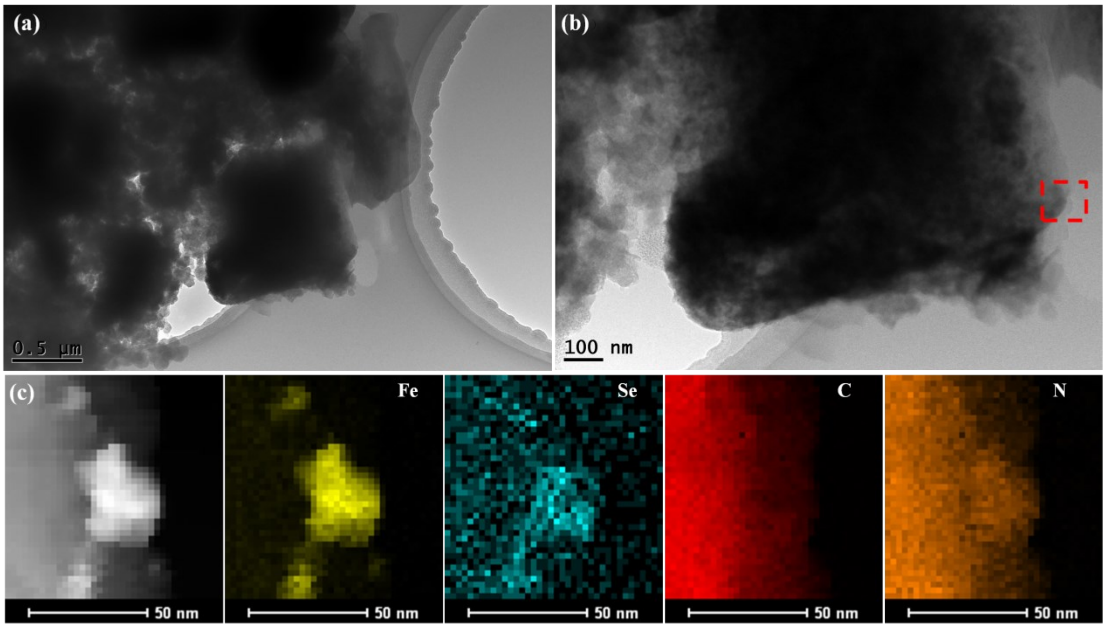

Figure S7. Ex-situ TEM images of $FeSe_2$/NC@G electrodes after 100 cycles at 0.5 A g^{-1}.

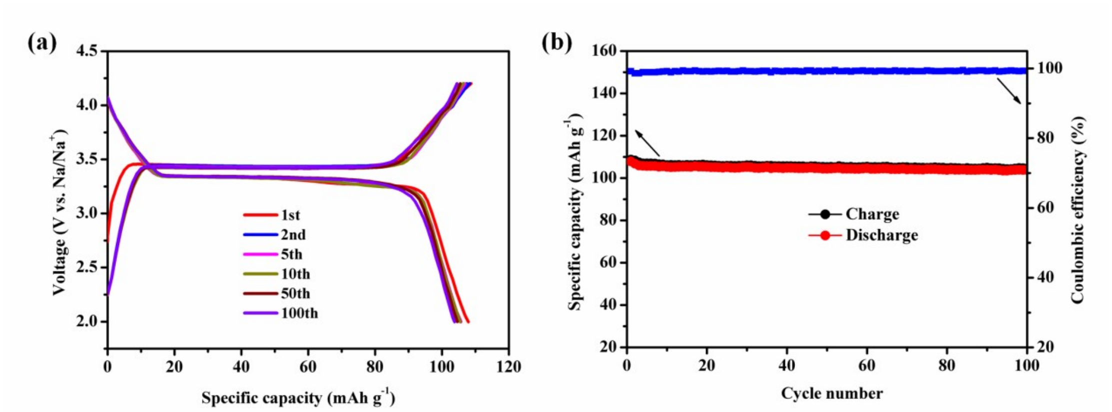

Figure S8. (a) The charge-discharge profiles of $Na_3V_2(PO_4)_3$/C cathode at 0.12 A g^{-1}. (b) the cycling test of $Na_3V_2(PO_4)_3$/C cathode at 0.12 A g^{-1}.

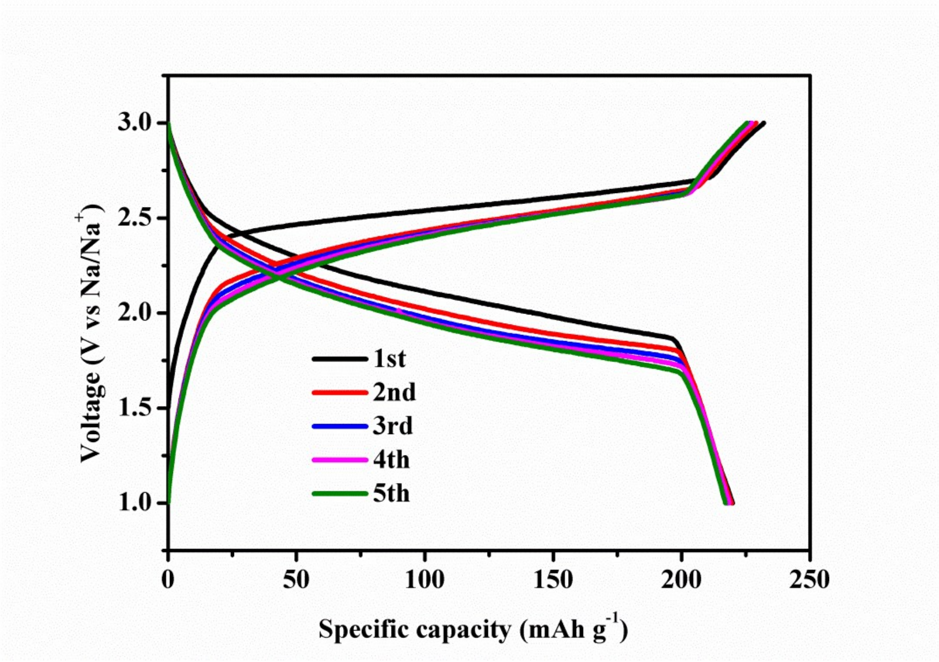

Figure S9. The initial five charge-discharge curves of $FeSe_2$/NC@G // NVP full-cell.

Table S1. Comparison of the Na-storage performance for Iron selenides anodes in the previous literature with our sample

Electrode materials	Rate perfomance	Cycling performance	Ref
$FeSe_2$/NC@G	**331 mAh g^{-1} at 5.0 A g^{-1}**	**323 mAh g^{-1} at 2.0 A g^{-1} after 1000 cycles**	**This work**
$FeSe_2$@rGO	135 mAh g^{-1} at 5.0 A g^{-1}	468.8 mAh/g at 0.1 A g^{-1} after 100 cycles	20
H-$FeSe_2$@GC	417 mAh g^{-1} at 5.0 A g^{-1}	510 mAh g^{-1} at 0.2 A g^{-1} after 200 cycles	21
$FeSe_2$/C	-------------	455 mAh g^{-1} at 0.1 A g^{-1} after 100 cycles	22
$FeSe_2$/N-C	227 mAh g^{-1} at 5.0 A g^{-1}	430.5 mAh g^{-1} at 0.5 A g^{-1} after 100 cycles	28
$FeSe_2$/GNS-300	270 mAh g^{-1} at 4.0 A g^{-1}	230 mAh g^{-1} at 0.1 A g^{-1} after 50 cycles	29
$FeSe_2$/C	316.5 mAh g^{-1} at 5.0 A g^{-1}	380.2 mAh g^{-1} at 1.0 A g^{-1} after 100 cycles	30
$FeSe_2$-HGCNS	361 mAh g^{-1} at 5.0 A g^{-1}	425 mAh g^{-1} at 0.5 A g^{-1} after 100 cycles	32
Fe_7Se_8@C	150 mAh g^{-1} at 3.0 A g^{-1}	219 mAh g^{-1} at 3.0 A g^{-1} after 550 cycles	35
$FeSe_2$ NPs	335 mAh g^{-1} at 5.0 A g^{-1}	450 mAh g^{-1} at 0.8 A g^{-1} after 300 cycles	38
$FeSe_2$/SG	277.5 mAh g^{-1} at 5.0 A	408 mAh g^{-1} at 0.5 A g^{-1} after 100	39

	g^{-1}	cycles	

Table S2. Equivalent circuit parameters of the $FeSe_2$/NC and $FeSe_2$/NC@G electrodes for SIBs.

Sample	R_o/Ohm	R_s/Ohm	R_{ct}/Ohm
$FeSe_2$/NC	13.8	28.3	93.2
$FeSe_2$/NC@G	7.5	21.3	26.0