# Electronic supplementary information

**Boosting reaction kinetics of polycrystalline phase $Fe_7S_8$/$FeS_2$ heterostructures encapsulated in hollow carbon nanofiber for superior fast sodium storage**

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**Experimental**

**Synthesis of Materials**

Preparation of NHCFs-$Fe_2O_3$ precursor: In a typical preparation process, 0.78 g methyl orange was dissolved in 500 mL deionized water, then 3.89 g ferric chloride was added until the mixture was uniform, and 0.94 mL pyrrole monomer was added and stirred for 24 h. Finally, the black solution was centrifuged and washed to obtain hollow polypyrrole (PPy) nanotubes, which were dried in vacuum at 80 °C for use. Then, 0.5 mol $L^{-1}$ $Fe(NO_3)_3$ solution (30 mL) and 0.7 mol $L^{-1}$ $Na_2CO_3$ solution (30 mL) were slowly added to the deionized water (60 mL) of dispersed hollow PPy nanotubes (0.3 g) by a constant flow pump, and slowly stirred during the drip process. After the drip is completed, continue to stir for 2 h, centrifugal collection, and then vacuum drying at 80°C for 24 h to obtain PPy-$Fe_2O_3$. Finally, the NHCFs-$Fe_2O_3$ precursor was obtained by annealing it in an argon atmosphere at 550 °C for 4 h.

Preparation of NHCFs-$Fe_7S_8$ and NHCFs-$FeS_2$ composites: For the preparation of NHCFs-$Fe_7S_8$ composites, the obtained NHCFs-$Fe_2O_3$ was placed in an alumina boat and heated to 550 °C under the atmosphere of argon and $CS_2$ in a tube furnace for 2 h, and the heating rate was 5 °C $min^{-1}$ for sulphuration process to obtain NHCFs-$Fe_7S_8$. For the preparation of NHCFs-$FeS_2$ composites, NHCFs-$Fe_2O_3$ and sulfur powder (mass ratio 1:10) were fully ground and placed on an alumina boat. In an argon atmosphere, the furnace was heated to 550 °C for 2 h and the heating rate was 5 °C $min^{-1}$ for sulphuration process to obtain NHCFs-$FeS_2$.

Preparation of NHCFs-$Fe_7S_8$/$FeS_2$ polycrystalline phase: Briefly, NHCFs-$Fe_7S_8$ above and sulfur powder (mass ratio 1:20) are fully ground, placed on an alumina boat, and then put in the center of the tube furnace. The NHCFs-$Fe_7S_8$/$FeS_2$ polycrystalline phase was obtained by heating up to 550 °C for 2 h at 5 °C $min^{-1}$ in an argon atmosphere.

**Material characterization**

The structure and morphology of samples were observed by field-emission scanning electron microscope (FESEM, Thermo Fisher Scientific Verios 5 UC) and high-resolution transmission electron microscope (HRTEM, Thermo Fisher Scientific Talos F200X). The crystal structure of the composites was studied by X-ray diffraction (XRD, Bruker D8 DISCOVER, Cu-$K_\alpha$). The chemical composition of samples was revealed by raman spectrometer (Renishaw inVia, 532 nm). The elemental composition of the composites was obtained by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Escalab $Xi^+$).

The carbon content of sample has been studied by the thermogravimetric analysis (TGA, TA TGA 5500).

**Electrochemical measurements**

The working electrodes were fabricated through a process of coating a mixture of active samples, sodium alginate, and conductive carbon black in an 8:1:1 ratio using water as a solvent onto copper foil. The resulting slurry was uniformly applied and the electrodes were then vacuum dried at 80°C overnight before being cut into 12 mm diameter discs with a mass loading of approximately 2.0 mg cm$^{-2}$. An electrolyte of 1.0 M NaPF$_6$ in diglyme (DME) was utilized in the assembly of a CR2025 type button cell within a glove box. Constant current discharge/charge tests were conducted using a LAND battery test system across a wide voltage window of 0.005-3.0 V. Additionally, cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) measurements were performed on a Bio-Logic electrochemistry workstation at frequencies ranging from 100 kHz to 10 mHz, over a voltage range of 0.005-3.0 V at various scan rates.

For the preparation of full cell, the as-prepared anode was pre-sodiated via contacting with Na metal for 1 hours. The Na$_3$V$_2$(PO$_4$)$_3$/C on Al foil was employed as the cathode (the electrode diameter is 13 mm), and the n/p ratio of all full-cell defined as the anode areal capacity over cathode areal capacity was set to 1.1. The fabrication process for assembling full cell is same with that for preparing the half cell, which is a button cell. The full cell tests (1C = 110 mA g Na$_3$V$_2$(PO$_4$)$_3$$^{-1}$) were conducted in the potential range of 1.0 - 3.5 V. The full cell at 0.11 A g$^{-1}$ were processed under constant current (CC) mode for charging and discharging.

**Computational methods**

In this work, the simulation is based on density functional theory (DFT) and the Perdew-Burke-Ernzerhof function of generalized gradient approximation. Specifically, the DFT-D3 method was adopted, and the stable crystal structure information of the system was used to analyze the bonding of the polycrystalline phase system by using the electronic iteration algorithm and geometric optimization methods. The cut-off energy used in the expansion of the plane wave is 450 eV, and the self-consistent field energy convergence threshold is set to 10$^{-6}$ eV. Differential charge density is used to analyze the trend of charge movement in the interface. The diffusion barrier of sodium ions in each structure was analyzed by CI-NEB method. Using the VASP algorithm, the force is calculated with an accuracy of 1E-7. All calculations are performed on the basis of structural relaxation.
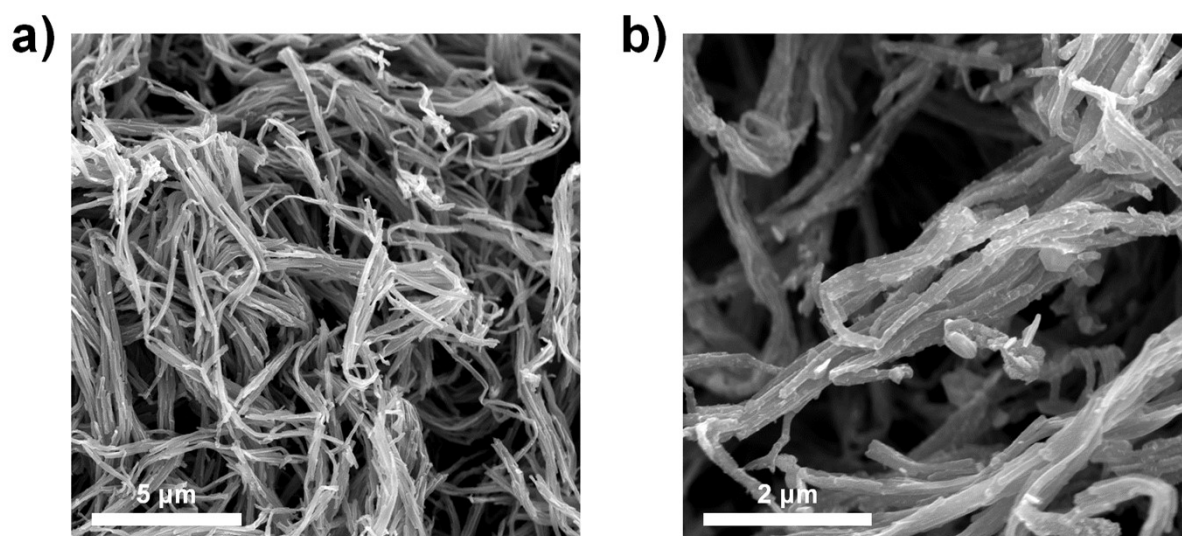
# Supplementary Figures
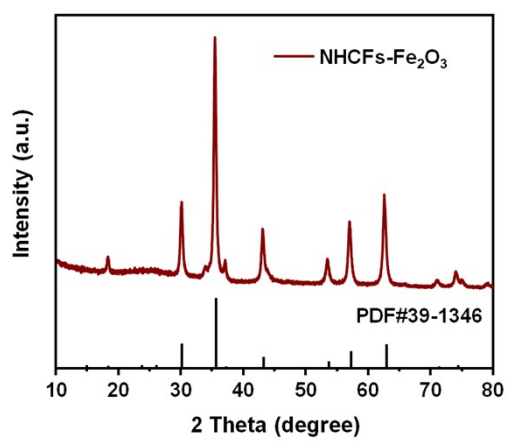


**Fig. S1.** SEM image of a) PPy and b) NHCFs-Fe$_2$O$_3$.



**Fig. S2**. XRD pattern of NHCFs-Fe$_2$O$_3$.

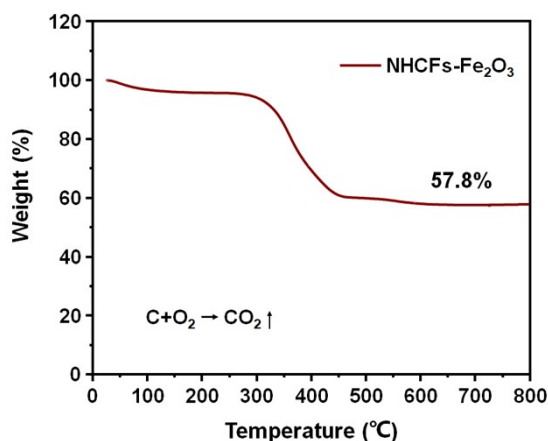**Fig. S3**. The thermogravimetric curves of NHCFs-$Fe_2O_3$.
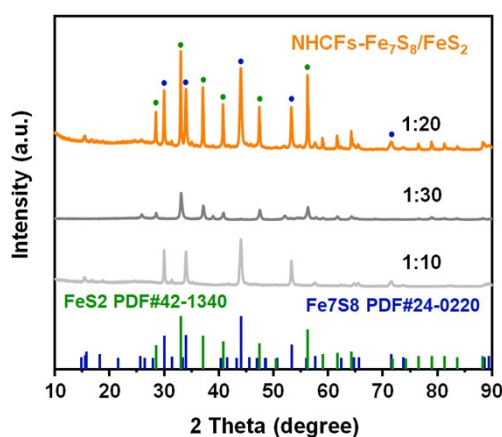


**Fig. S4**. XRD patterns of the composites of polycrystalline heterostructures of $Fe_7S_8$ and $FeS_2$ with different proportions.

Based on the Fe-S phase diagram, the formation temperature of $Fe_7S_8$ phase is at least 800 K (about 550 °C). The higher treatment temperature could cause lower C-S doped in carbon skeleton, which reduces the stability of the product. To obtain a stable $Fe_7S_8$ phase, we adjusted the ratio of S powder to the target product, but pure phase $Fe_7S_8$ could not be obtained only by adjusting the ratio. Thus, we changed the S sources to $CS_2$. Firstly, $CS_2$ contains C atom which is benefited to the formation of C-S bonds, secondly, the $CS_2$ could successful composite the $Fe_7S_8$ phase.
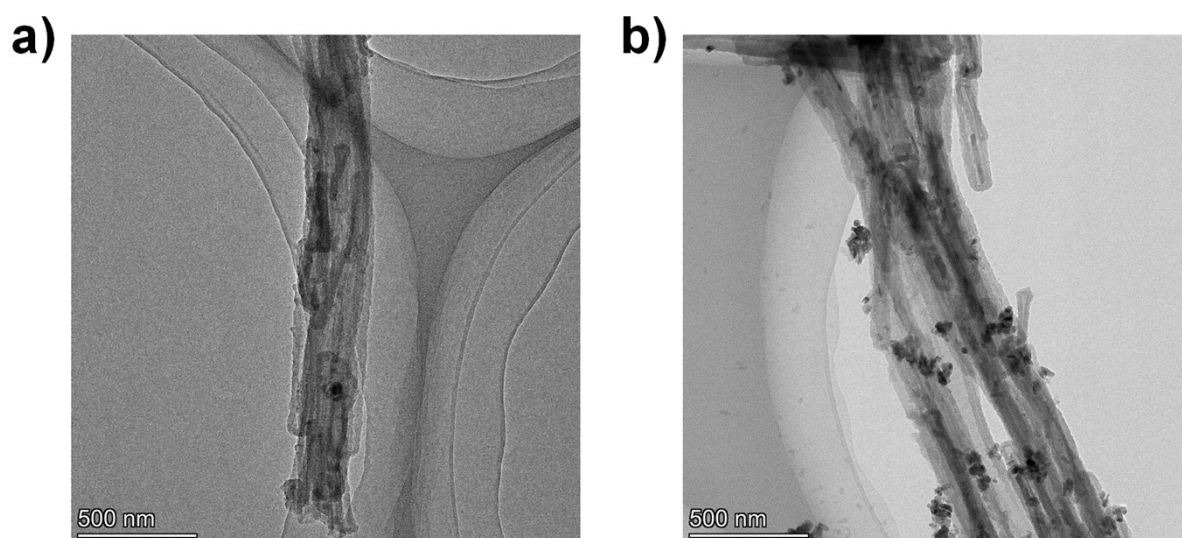
**Fig. S5**. SEM image of a) NHCFs-Fe$_7$S$_8$ and b) NHCFs-FeS$_2$.



**Fig. S6**. TEM image of a) NHCFs-Fe$_7$S$_8$ and b) NHCFs-FeS$_2$.

**Fig. S7**. Size distributions of a) NHCFs-Fe$_7$S$_8$/FeS$_2$, b) NHCFs-Fe$_7$S$_8$ and c) NHCFs-FeS$_2$.



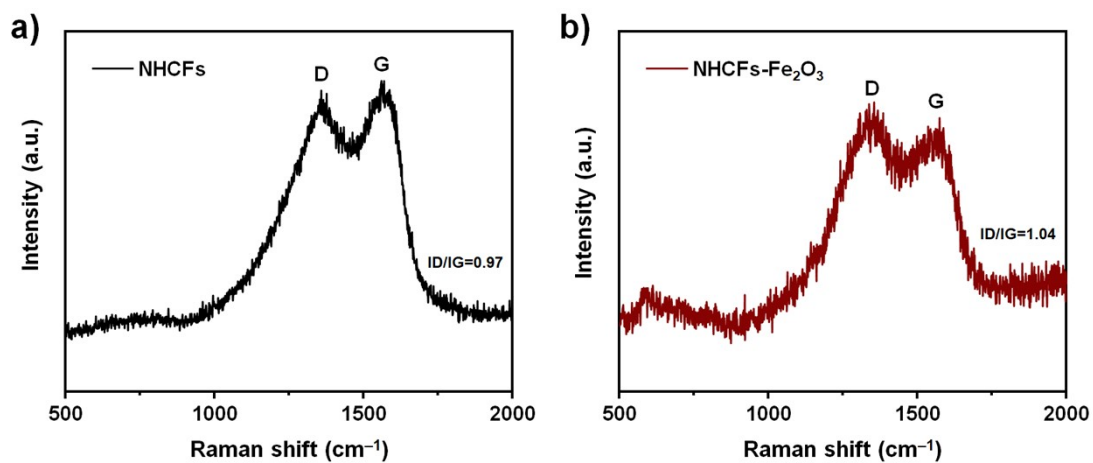**Fig. S8**. a) Nitrogen adsorption–desorption isotherms and b) pore size distributions of NHCFs-Fe$_7$S$_8$/FeS$_2$, NHCFs-Fe$_7$S$_8$ and NHCFs-FeS$_2$.

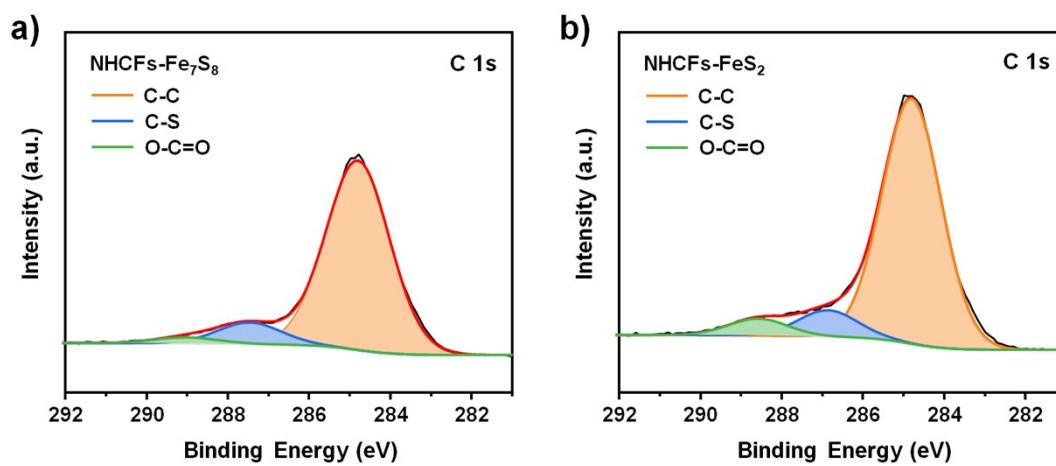**Fig. S9**. Raman spectrum of a) PPy and b) NHCFs-Fe$_2$O$_3$.



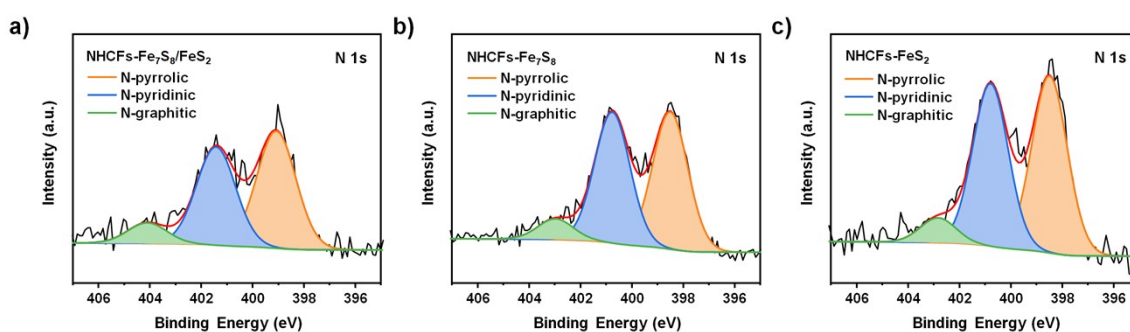**Fig. S10**. The high-resolution XPS spectra C 1s of a) NHCFs-Fe$_7$S$_8$ and b) NHCFs-FeS$_2$.

**Fig. S11**. The high-resolution XPS spectra N 1s of a) NHCFs-Fe$_7$S$_8$/FeS$_2$, b) NHCFs-Fe$_7$S$_8$ and c) NHCFs-FeS$_2$.
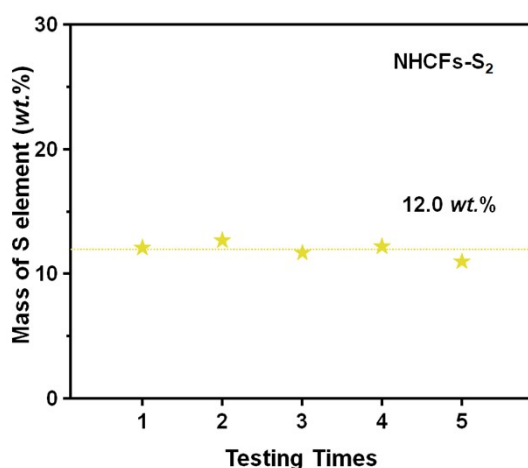


**Fig. S12**. The mass ratio of S element in the carbon tube after a two-step sulphuration method which tested by Elemental Analysis. (NHCFs-S$_2$).

In the thermogravimetric curve of polycrystalline NHCFs-Fe$_7$S$_8$/FeS$_2$ composites, the first weight loss before 300 °C is mainly due to the loss of absorbed water and the combustion of sulfur atom in the carbon skeleton. Later, the apparent weight loss was attributed to the combustion of the carbon skeleton and the subsequent oxidation of the Fe$_7$S$_8$/FeS$_2$ nanoparticles.

We assume the weight percentage of Fe$_7$S$_8$ is $x$, and the weight percentage of FeS$_2$ is $y$, then the percentage of the final product Fe$_2$O$_3$ is as follows:

$Fe_2O_3(wt.\%) =$

$$\left(\frac{14 \times molecular\ weight\ of\ Fe_2O_3 \times weight\ of\ Fe_7S_8}{4 \times molecular\ weight\ of\ Fe_7S_8} + \frac{2 \times molecular\ weight\ of\ Fe_2O_3 \times weight\ of\ FeS_2}{4 \times molecular\ weight\ of\ FeS_2}\right) \times$$

$$100\% = \left(\frac{14 \times 159.7 \times x}{4 \times 647.4} + \frac{2 \times 159.7 \times y}{4 \times 120}\right) \times 100\% = 41.3\ wt.\%$$

As shown in Fig. S12, on the carbon skeleton without in-situ growth of iron particles, elemental analysis was performed after sulphuration steps under the same conditions as that of synthetic NHCFs-Fe$_7$S$_8$/FeS$_2$, the mass ratio of S element in carbon skeleton was about 12.0 *wt.%*. According to the 41.3 *wt.%* Fe$_2$O$_3$ remaining after the complete reaction of NHCFs-Fe$_7$S$_8$/FeS$_2$, the content of Fe element in the composites is calculated to be 28.9 *wt.%*. Since the mass ratio of Fe element to pure carbon skeleton is not changed during the sulphuration process, the mass ratio of pure carbon skeleton of polycrystalline phase NHCFs-Fe$_7$S$_8$/FeS$_2$ composites is 30.2 *wt.%*.

$NHCFs(wt.\%) =$

$$\frac{weight\ of\ Fe\ element\ of\ NHCFs - Fe_7S_8/FeS_2 \times weight\ of\ pure\ carbon\ skeleton\ of\ NHCFs - Fe_2O_3}{weight\ of\ Fe\ element\ of\ NHCFs - Fe_2O_3} \times$$

$$100\% = \frac{\frac{28.9 \times 42.2}{40.4}}{} \times 100\% = 30.2\ wt.\%$$

Thus, the mass ratio of Fe$_7$S$_8$/FeS$_2$ in the NHCFs-Fe$_7$S$_8$/FeS$_2$ is 57.8 *wt.%*.

$x + y = 57.8\ wt.\%$ $\qquad\qquad$ $x = 13.4\ wt.\%,\ y = 44.5\ wt.\%$

Thus, the mass ratio of Fe$_7$S$_8$ is 13.4 *wt.%*, and the mass ratio of FeS$_2$ is 44.5 *wt.%*. The molar ratio between Fe$_7$S$_8$ and FeS$_2$ in the NHCFs-Fe$_7$S$_8$/FeS$_2$ is about 1:18.

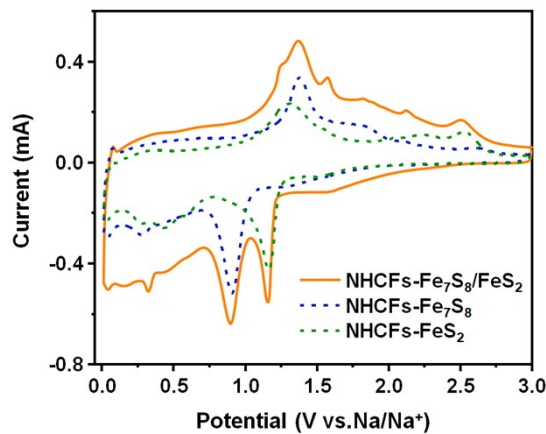**Fig. S13**. Comparison of the first CV curves at 0.2 mV s$^{-1}$ of NHCFs-Fe$_7$S$_8$/FeS$_2$, NHCFs-Fe$_7$S$_8$ and NHCFs-FeS$_2$.
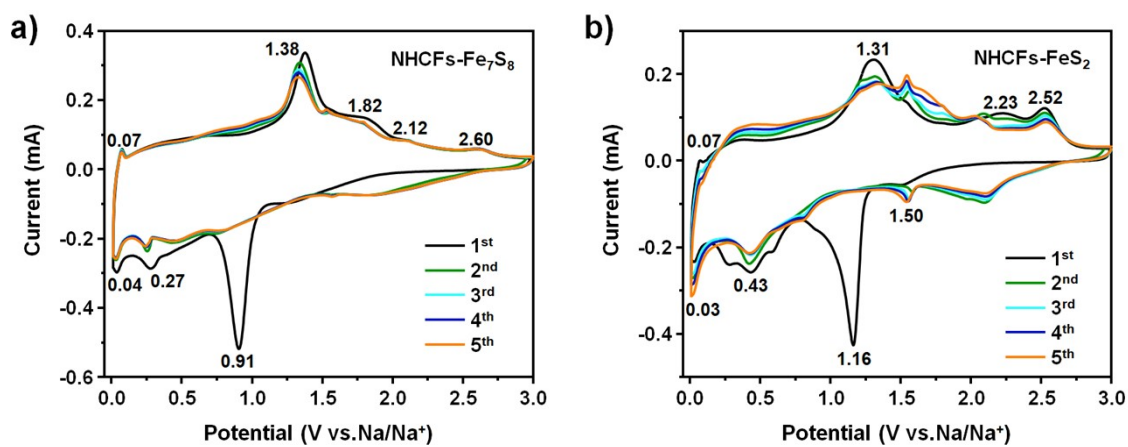
**Fig. S14**. The CV curves of a) NHCFs-Fe$_7$S$_8$ and b) NHCFs-FeS$_2$ at a scan rate of 0.2 mV s$^{-1}$.



**Fig. S15**. The corresponding galvanostatic discharge/charge profiles of a) NHCFs-Fe$_7$S$_8$/FeS$_2$, b) NHCFs-Fe$_7$S$_8$ and c) NHCFs-FeS$_2$.

**Fig. S16.** The capacity-voltage curves increasing from 0.2 to 50 A g$^{-1}$ of a) NHCFs-Fe$_7$S$_8$ and b) NHCFs-FeS$_2$.
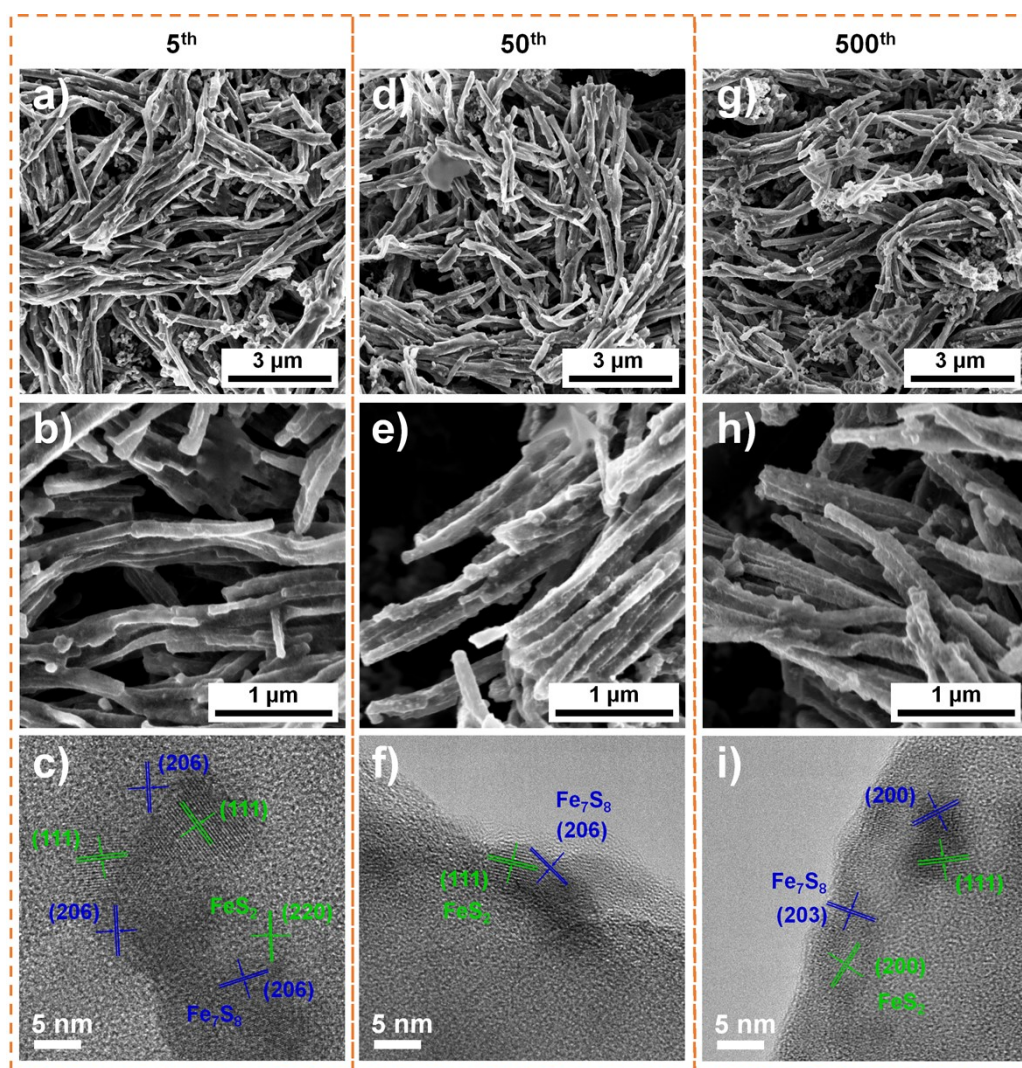


**Fig. S17.** SEM images and HRTEM images of NHCFs-Fe$_7$S$_8$/FeS$_2$ electrode anode for the (a, b, c) 5, (d, e, f) 50 and (g, h, i) 500 cycles of sodium storage.

**Fig. S18**. a) CV curves of NHCFs-Fe$_7$S$_8$ electrode at different scan rates. b) The plots of peak current versus scan rate for NHCFs-Fe$_7$S$_8$ electrode.
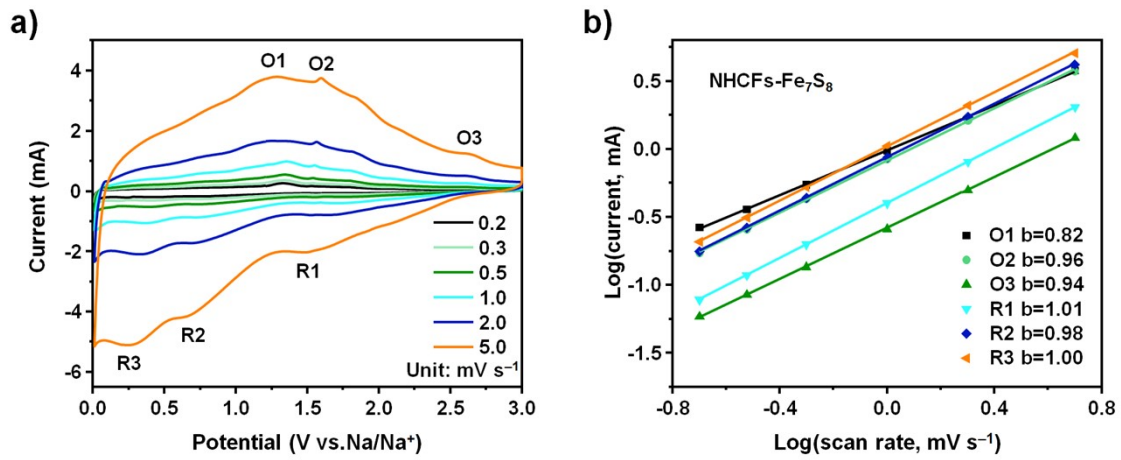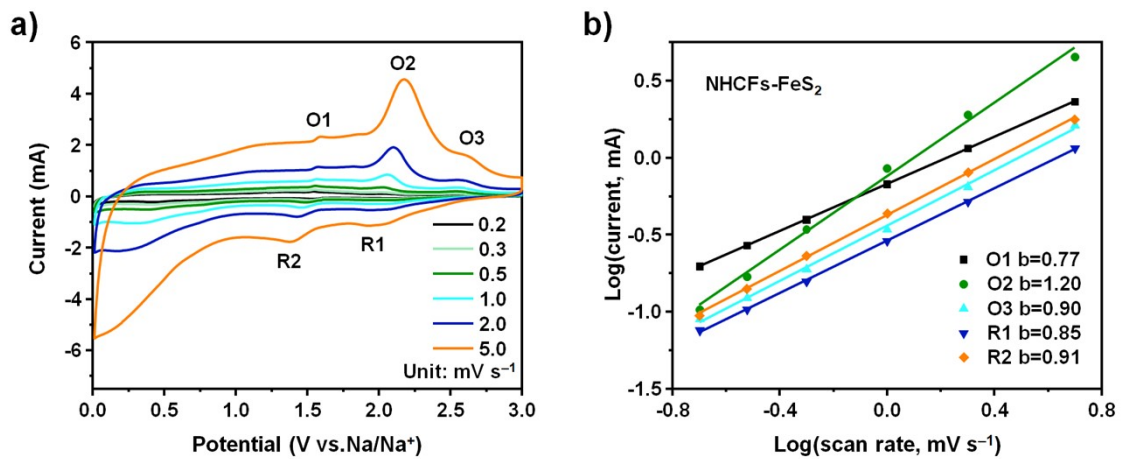


**Fig. S19**. a) CV curves of NHCFs-FeS$_2$ electrode at different scan rates. b) The plots of peak current versus scan rate for NHCFs-FeS$_2$ electrode.

**Fig. S20**. The diffusion and capacitive contributions of sodium storage for NHCFs-Fe$_7$S$_8$/FeS$_2$ at the scan rate of 1.0 mV s$^{-1}$.



**Fig. S21**. a) The diffusion and capacitive contributions of sodium storage for NHCFs-Fe$_7$S$_8$ at the scan rate of 1.0 mV s$^{-1}$, and b) The percentage for capacitance contribution of NHCFs-Fe$_7$S$_8$ at different scan rates.
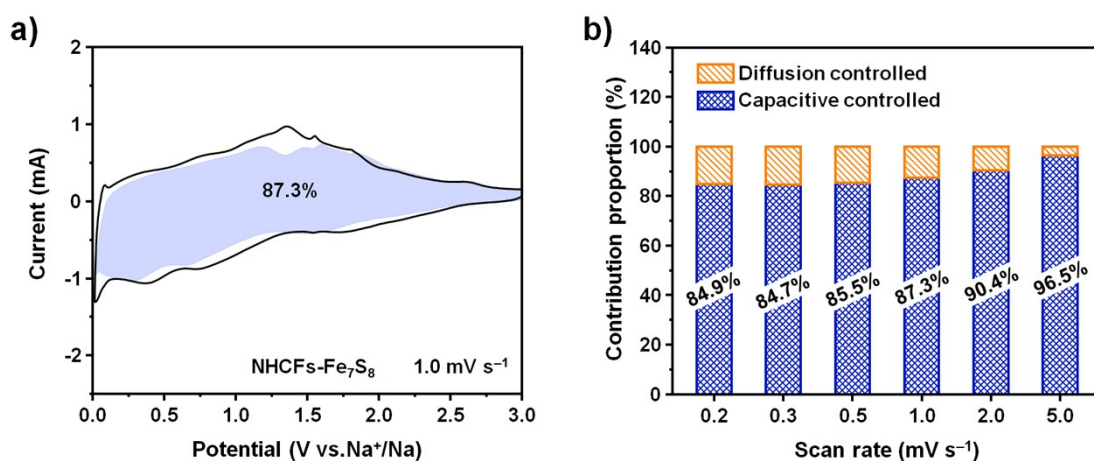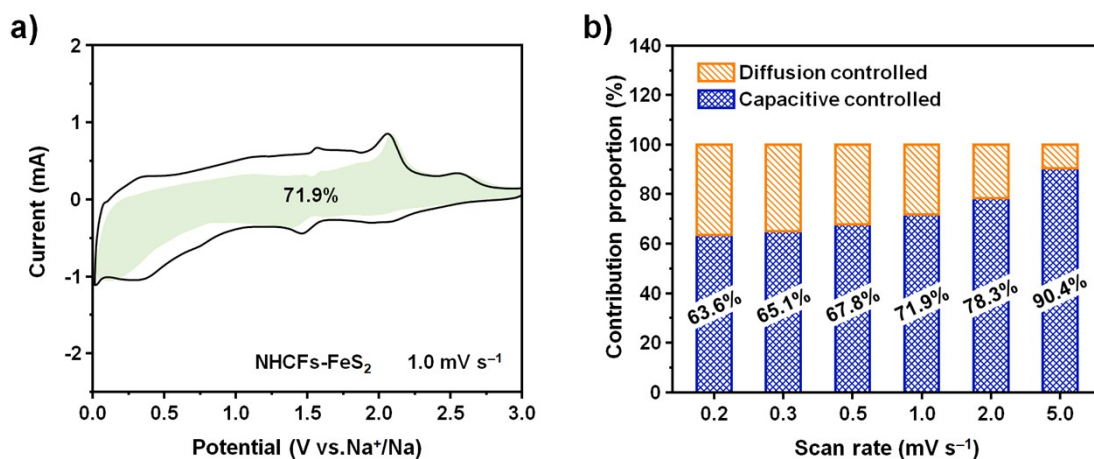
**Fig. S22**. a) The diffusion and capacitive contributions of sodium storage for NHCFs-FeS$_2$ at the scan rate of 1.0 mV s$^{-1}$, and b) The percentage for capacitance contribution of NHCFs-FeS$_2$ at different scan rates.
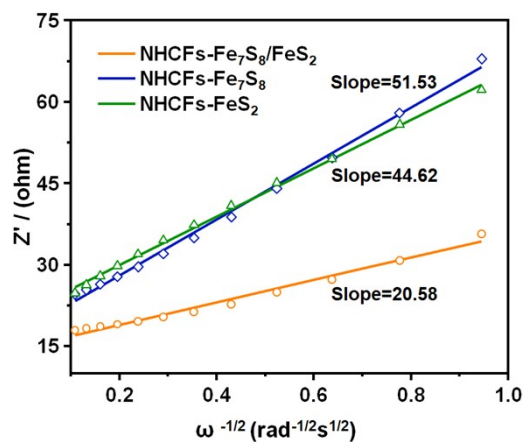


**Fig. S23**. The plots of $\omega^{1/2}$ versus Z' curves in the low-frequency area of NHCFs-Fe$_7$S$_8$/FeS$_2$, NHCFs-Fe$_7$S$_8$ and NHCFs-FeS$_2$ before cycling.

**Fig. S24**. The GITT curves of NHCFs-Fe$_7$S$_8$/FeS$_2$, NHCFs-Fe$_7$S$_8$ and NHCFs-FeS$_2$.

The sodium-ion diffusion coefficient $D_{Na+}$ (cm$^2$ s$^{-1}$) was determined through Galvanostatic Intermittent Titration Technique (GITT) results. The value of $D_{Na+}$ was calculated using the Fick's second law:
$$D = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left(\frac{\Delta E_s}{\Delta E_t}\right)^2$$
. In the Equation, $M_B$ represents the molar mass of active material, S means the electrode area, $V_M$ equals to the molar volume of the active materials, $m_B$ describes the mass of active material, and $\tau$ denotes the current time.
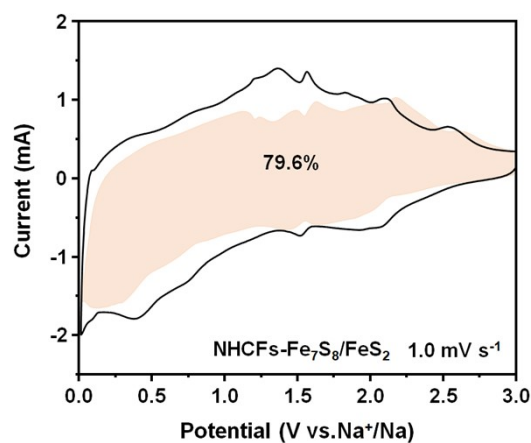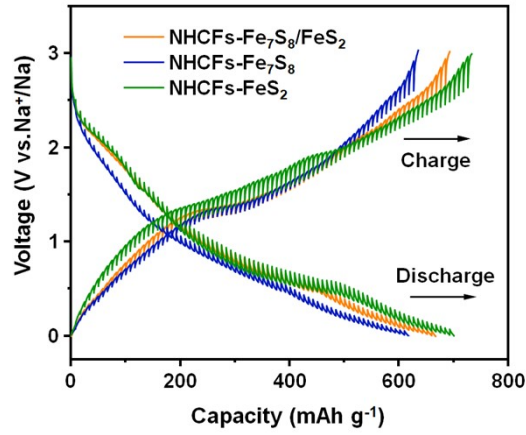


**Fig. S25**. SEM image of Na$_3$V$_2$(PO$_4$)$_3$ (NVP).

**Fig. S26**. a) The cycling performance and b) the corresponding galvanostatic discharge/charge profiles of NVP at the current density of 1.0 C.
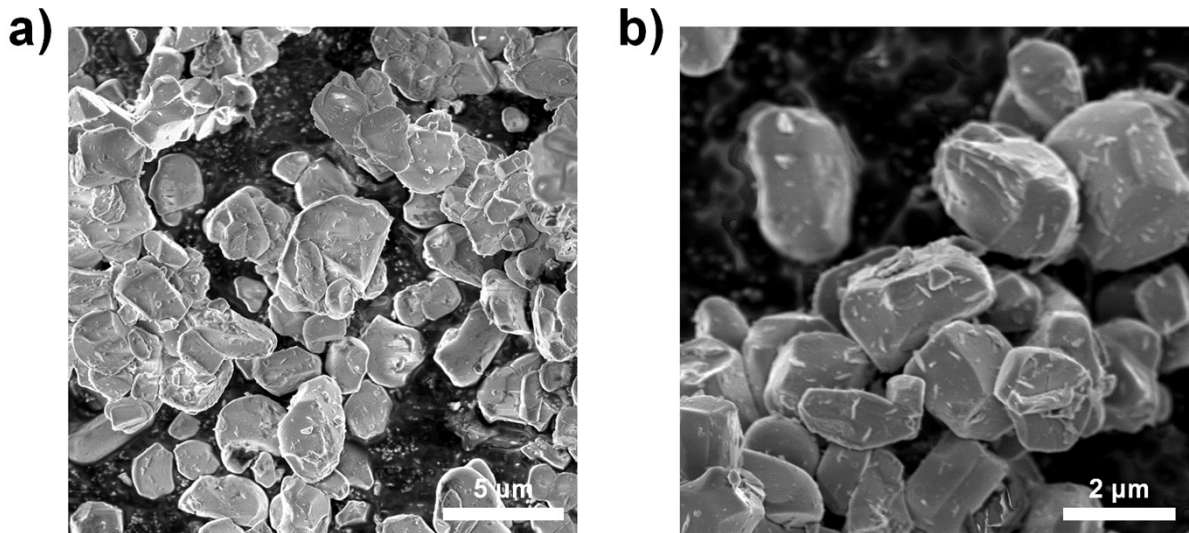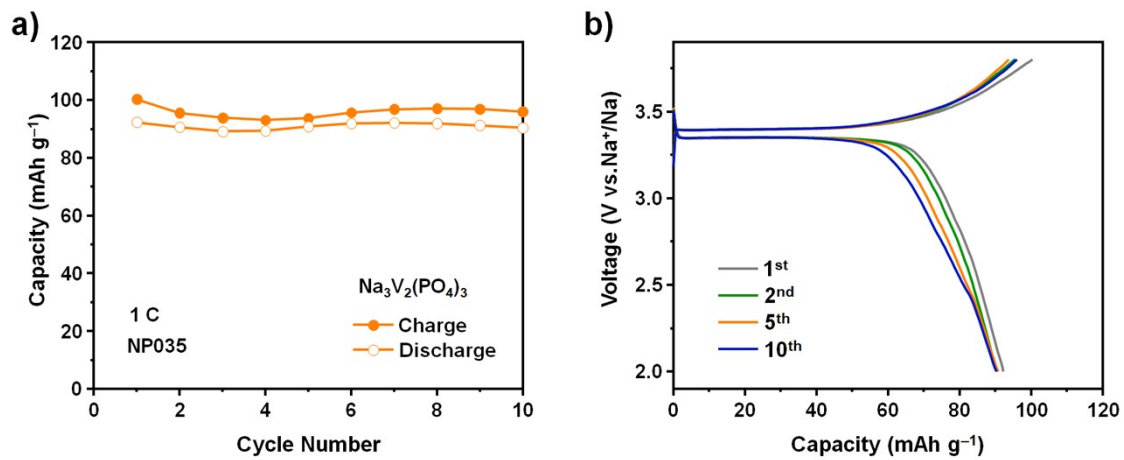
**Table S1**. Comparison of electrochemical data of NHCFs-$Fe_7S_8$/$FeS_2$ in this work with recently reported transition mental sulfide-based heterojunction anode materials for sodium ion batteries.

| Sample | Cut-off voltage (V) | ICE (%) | Cycling stability | | | Rate capability | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | Current density (A g$^{-1}$) | Cycle number | Capacity retention (mAh g$^{-1}$) | Current density (A g$^{-1}$) | Capacity retention (mAh g$^{-1}$) | |
| **NHCFs-$Fe_7S_8$/$FeS_2$** | **0.005-3.0** | **85.3** | **1** | **1000** | **596** | **50/100** | **269/107** | **This work** |
| ZnS/$Fe_9S_{10}$@C | 0.005-3.0 | 85.3 | 1 | 200 | 485 | 50 | 235 | [1] |
| SnS/$MoS_2$/NS-CNs | 0.01-3.0 | 69.8 | 1 | 800 | 287.2 | 5 | 372.9 | [2] |
| (SnCo)$S_2$/SG | 0.01-3.0 | 78.6 | 5 | 5000 | 487 | 10 | 469 | [3] |
| L-$Sb_2S_3$/$Ti_3C_2$ | 0.005-3.0 | 65.7 | 1 | 100 | 358.2 | 2 | 339.5 | [4] |
| SnS/$Fe_{1-x}$S@SC | 0.01-3.0 | 74.3 | 2 | 2900 | 310 | 1 | 491 | [5] |
| ZnS/$Sb_2S_3$@NC | 0.01-3.0 | 68.0 | 2 | 450 | 511.4 | 10 | 400.4 | [6] |
| $Bi_2S_3$-CuS/C | 0.01-3.0 | 97.2 | 8 | 1000 | 592.2 | 20 | 459.9 | [7] |
| $Sb_2S_3$/$MoS_2$@C | 0.1-3.0 | 75.9 | 5 | 650 | 411.5 | 10 | 408.7 | [8] |
| $Fe_9S_{10}$@$MoS_2$@C | 0.005-3.0 | 80.1 | 2 | 1000 | 355 | 30/50 | 197/132 | [9] |
| $MoO_2$/$MoS_2$/C | 0-3.0 | / | 1 | 1000 | 324 | 5 | 273 | [10] |
| $Fe_7S_8$/$FeS_2$/NCNT | 0.01-3.0 | 73.4 | 5 | 1000 | 466.7 | 20 | 536.5 | [11] |

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