

Supporting Information

Part I: Experimental details, Calculations & Discussions

S-1-1: Preparation of NSCN hollow fibers

i) Preparation of the precursor

The precursor was prepared by an electrospinning technique with the coaxial dual-nozzle. Firstly, the polyvinyl pyrrolidone (PVP, MW:1300000, Macklin, China) and nickel acetate tetrahydrate (AR, 99%, Macklin, China) were dissolved in the absolute ethanol (Aladdin, Shanghai, China) at room temperature (23~25 °C) under mild stirring for four hours to achieve a transport solution, which was used as the shell solution. Secondly, the poly(methyl methacrylate) (PMMA, Aladdin, Shanghai, China) was dissolving in the N, N-dimethylformamide (DMF) at room temperature under slowly stirring to form a uniform solution, which was used as the core solution. The dual-nozzle was constructed by two coaxial needles. The core solution was loaded into the syringe connected to the inner channel and the shell solution was loaded into the syringe connected to the outer channel of a dual nozzle. A high voltage of 11~14 kV was applied on the dual nozzle and the distance between the needle and the collector was ~15 cm. After the electrospinning process, the film was peeled off from the collector and the precursor was achieved.

ii) Preparation of the intermediate product

The prepared precursor was firstly stabilized in air. Then the resultant product was placed in a shelf with the abundant amount of poly(methyl methacrylate) particles beneath and

sealed in a glass tube. It was firstly kept at 500 °C and then elevated to 700 °C with the heating rate of 3 °C/min in the nitrogen atmosphere. After the calcinations, it is naturally cooled down to achieve the intermediate product.

iii) Preparation of the NCSN hollow fiber with α -NiS@NCNT heterostructure

Firstly, the sublimed sulfur powder was dissolved into the carbon bisulfide solvent to achieve a mixture. Then, the solution was dropped on as-prepared intermediate product by pipette. After the solvent was evaporating, the film was placed in a shelf and sealed in vacuum glass tubes. It was firstly kept at low temperature of 155 °C to enable the sulfur infiltrate into the intermediate product. Then it was elevated to 500 °C in the nitrogen atmosphere to achieve the final product.

iv) Preparation of the NCSN hollow fiber with NiS₂@NCNT heterostructure

Firstly, the sublimed sulfur powder was dissolved into the carbon bisulfide solvent to achieve a mixture. Then, the solution was dropped on as-prepared intermediate product by pipette. After the solvent was evaporating, the film was placed in a shelf and sealed in vacuum glass tubes. It was firstly kept at low temperature of 155 °C to enable the sulfur infiltrate into the intermediate product. Then it was elevated to 350 °C in the nitrogen atmosphere to achieve the final product.

v) Preparation of the NCSN hollow fiber with β -NiS@NCNT heterostructure

The preparation is a one-step solvothermal process. Firstly, the sulfur and anhydrous ethanediamine were mixed, which followed by the addition of ethylalcohol. Then the mixture was stirred and transferred to a Teflon-lined stainless autoclave. The intermediate product film was immersed into the reaction solution. Then the sealed autoclave was

heated to 160 °C. After cooling down naturally to room temperature, the resultant product was washed with distilled water and dried in oven overnight to achieve the final product.

S-1-2: Preparation of reference samples

i) Preparation of bare α -NiS reference sample

The bare α -NiS reference sample was prepared by two-step process as reported previously.^{S1} Firstly, the precursor was prepared a hydrothermal route. The mixture of nickel sulfide hexahydrate and urea were dissolved in distilled water to gain the pale green solution under vigorous stirring. The trisodium citrate was added into the resultant mixture, which was then transferred into a Teflon-lined stainless autoclave. After kept it at 150 °C for 24 h, the autoclave was cooled to room temperature naturally. The precipitates were collected and washed with distilled water and absolute ethanol several times by centrifugation. After dried at 60 °C overnight, the precursor was obtained. Then, a second hydrothermal route is employed to achieve the final product. The prepared precursor and the thiourea were dispersed into absolute ethanol under stirring. Then it was transferred into the Teflon-lined stainless autoclave and heated at 120 °C. After cooling down to room temperature naturally, the resultant product was collect by centrifugation, washed with distilled water and ethanol several times. After dried at 60 °C overnight, the final product was obtained.

ii) Preparation of α -NiS/C reference sample

Firstly, the polyvinyl pyrrolidone (PVP) and nickel acetate tetrahydrate (AR) were dissolved in the absolute ethanol at room temperature under stirring to achieve a transport solution. It was firstly kept at 700 °C in the nitrogen atmosphere to achieve the

intermediate product. Then the intermediate product was mixed with sulfur powder and calcinated at 500 °C in the nitrogen atmosphere to achieve α -NiS/C composite.

iii) Preparation of NiS₂/C reference sample

Firstly, the polyvinyl pyrrolidone (PVP) and nickel acetate tetrahydrate were dissolved in the absolute ethanol at room temperature under stirring to achieve a transport solution. It was firstly kept at 700 °C in the nitrogen atmosphere to achieve the intermediate product. Then the intermediate product was mixed with sulfur powder and calcinated at 350 °C in the nitrogen atmosphere to achieve the NiS₂/C composite.

iv) Preparation of β -NiS/C reference sample

Firstly, the polyvinyl pyrrolidone (PVP) and nickel acetate tetrahydrate were dissolved in the absolute ethanol at room temperature under stirring to achieve a transport solution. It was firstly kept at 700 °C in the nitrogen atmosphere to achieve the intermediate product. Next, the final product is prepared by a one-step solvothermal route. The sulfur powder and anhydrous ethanediamine were mixed, which are followed by the addition of ethylalcohol and the prepared intermediate product. The mixture was stirred and transferred to a Teflon-lined stainless autoclave. Then the autoclave was sealed and heated to 160 °C. After cooling down naturally to room temperature, the resultant product was washed with distilled water and dried in oven overnight to achieve the target product.

v) Preparation of central hollow hierarchical carbon fiber

The intermediate product prepared in S-1-1-ii was etched with acid aqueous solution. After washing with distilled water several times, the product was dried under vacuum.

S-2: Materials characterizations

Powder X-ray diffraction (XRD, Bruker D8/Germany) using Cu K α radiation was employed to identify the crystalline phase of the material. The morphology was observed with a scanning electron microscope (SEM, HITACHIS-4700) and a transmission electron microscope (TEM, JEOS-2010 PHILIPS). The element distribution of the sample was confirmed by energy dispersive X-ray detector (EDX). X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) was employed to measure the chemical or electronic state of each element. Thermogravimetric analysis (TGA, NETZSCH STA 449C) was used to investigate the carbon content of the sample. Nitrogen adsorption-desorption isotherms were measured using a Micromeritics ASAP 2010. Specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method.

S-3: Electrochemical measurements

S-3-1: Electrochemical properties in potassium half cell

The electrochemical characteristics were measured in CR2032 coin cells. The flexible NSCN film was used as the working electrode. The mass loading of the electrode is about 3.92 mg cm⁻². The fresh metal potassium film was used as the counter electrode and the Whatman glass microfiber filters were used as the separator. The electrolytes of 1M KPF₆ dissolved in ethylene carbonate and diethyl carbonate (EC/DEC = 1:1 in volume). The coin cells were assembled in an Ar filled glovebox. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted using a Zivelab electrochemical workstation.

S-3-2: Electrochemical properties in coin-type full PIHC

The full PIHC were assembled by α -NiS-NSCN cathode, CHCF cathode and the glass fiber separator. 1M KPF₆ in a mixture of EC/DEC were used as electrolyte. Before the assembling of full device, the electrodes were activated in a half cell. The cathode/separator/anode was sandwich and put into the coin-type cell. After the electrolytes were injected, the cells were sealed and coin-type PIHC was assembled.

S-3-3: Electrochemical properties in flexible PIHC

i) Preparation of the polymer electrolyte

The polymer electrolyte membrane was prepared by a facile method.^{S2} In a typical process, the perfluorinated sulfonic resin power, K form (PFSA-K) was initially prepared by dissolving the PFSA-Li in hot KOH solution. The product was washed and dried in the vacuum over to achieve the PFSA-K powder. Next, obtained PFSA-K power was dissolved in DMF to achieve the homogeneous solution, followed by adding the liquid electrolyte. After homogeneous solution was achieved, the solution blade coating method was employed and the polymer membrane was obtained.

ii) Assembling the flexible PIHC

Firstly, the prepared PFSA-K polymer membrane (S-3-3-i) was wetted by the ethylene carbonate and propylene carbon mixed solution. Next, the modified PIHC device was assembled by α -NiS-NSCN anode, CHCF cathode and the polymer electrolyte. The electrodes were activated in a half cell before assembling the full cell. The flexible cells were assembled in an Ar filled glovebox. Galvanostatic charge/discharge tests were performed using a Land battery testing system (Wuhan, China).

S-4: Calculation of the capacitive contribution

In the CV curves, the current is believed to originate from two independent and distinct parts: the surface-induced capacitive process and the diffusion-controlled process. As described in the following equation,^{S3,S4}

$$i = a \times v^b \quad (1)$$

Where i is the measured current; v is the scan rate. Determined from the slope of the curve between the $\log i$ versus $\log v$, the b values of different peaks can be achieved.

$$\log i = \log a + b \log v \quad (2)$$

To further characterize each contribution to the total properties, the measured current (i) at a fixed potential can be separated into two parts, *i. e.* the contribution from the capacitive and the diffusion processes as described in the following equation,

$$i = k_1 v + k_2 v^{1/2} \quad (3)$$

Where $k_1 v$ and $k_2 v^{1/2}$ correspond to the capacitive and diffusion contributions, respectively. Based on the above equation, the ratios of the capacitive contribution ratios at various scan rates can be quantitatively achieved.

S-5 Computational methods

The theoretical calculations were carried out using the density functional theory and the plane-wave pseudopotential method^{S5}. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) exchange correlation function^{S6} was adopted. All geometric optimizations and energy calculations were performed using periodic boundary conditions with adjacent adsorbents and adsorbents to prevent configurational interactions.

Part II: Supporting Figures

Figure S1

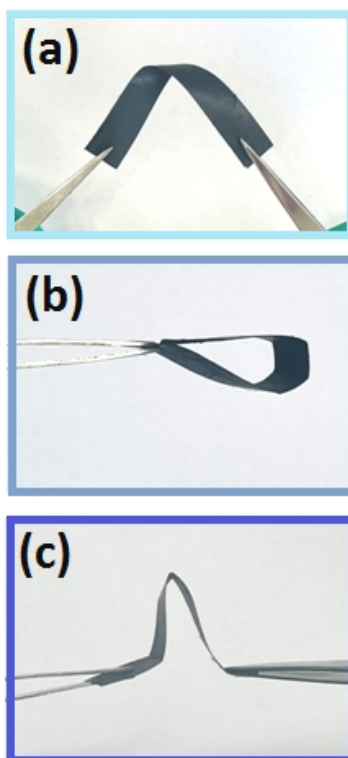


Figure S1 Digital photos of the NSCN hollow fiber based on the engineered phases of α -NiS (a), β -NiS (b) and NiS₂ (c).

Figure S2

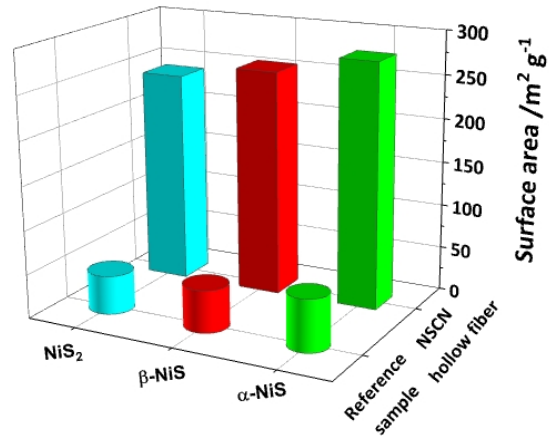


Figure S2 Comparison on the surface areas of the NSCN hollow fiber and the nickel sulfide/C reference samples based on α -NiS, β -NiS and NiS₂.

Figure S3

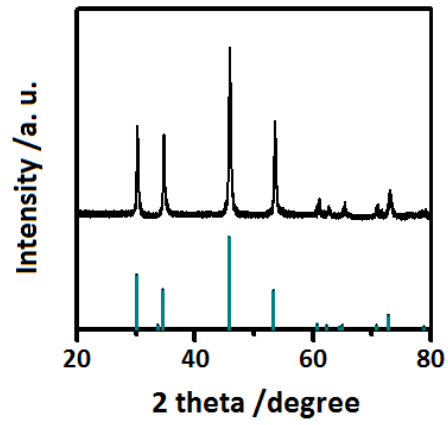


Figure S3 XRD pattern of the bare α -NiS reference sample.

Figure S4

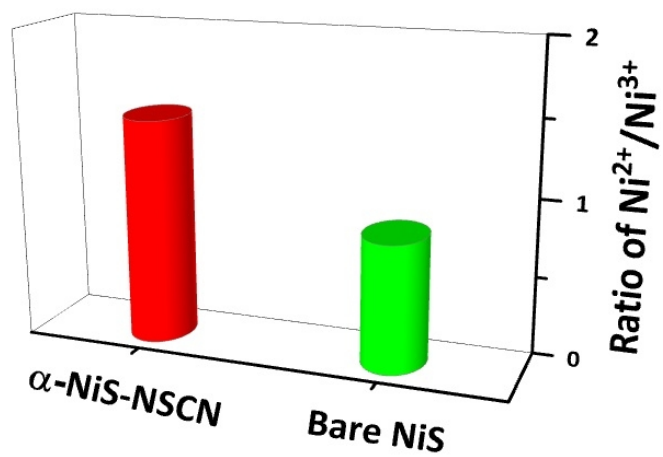


Figure S4 Comparison on the Ni²⁺/Ni³⁺ ratios of α-NiS-NSCN hollow fiber and bare α-NiS reference sample from XPS simulations.

Figure S5

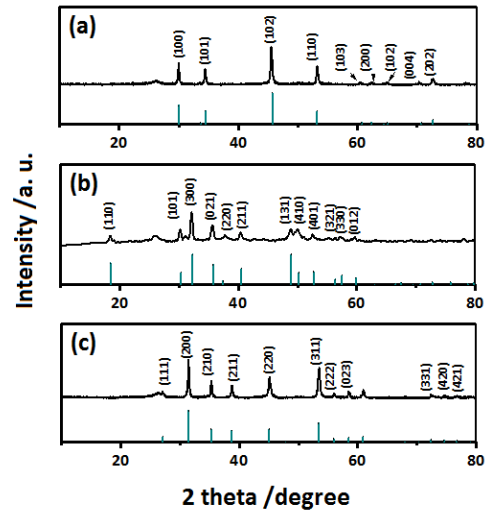


Figure S5 XRD patterns of the nickel sulfide/C reference samples based on α -NiS (a), β -NiS (b) and NiS₂ (c).

Figure S6

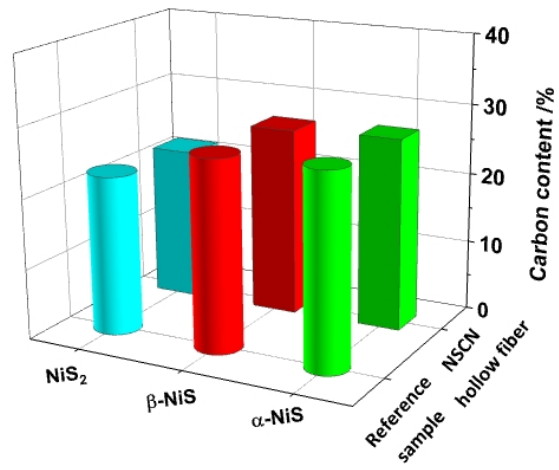


Figure S6 Comparison on the carbon contents of NSCN hollow fiber and nickel sulfide/C reference samples based on α -NiS, β -NiS and NiS₂.

Figure S7

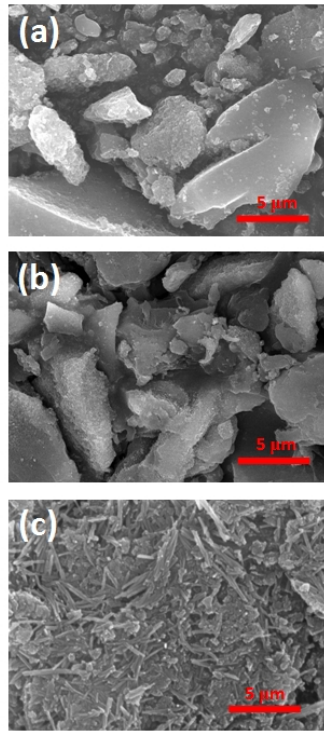


Figure S7 SEM images of the nickel sulfide/C reference samples based on α -NiS (a), NiS_2 (b) and β -NiS (c).

Figure S8

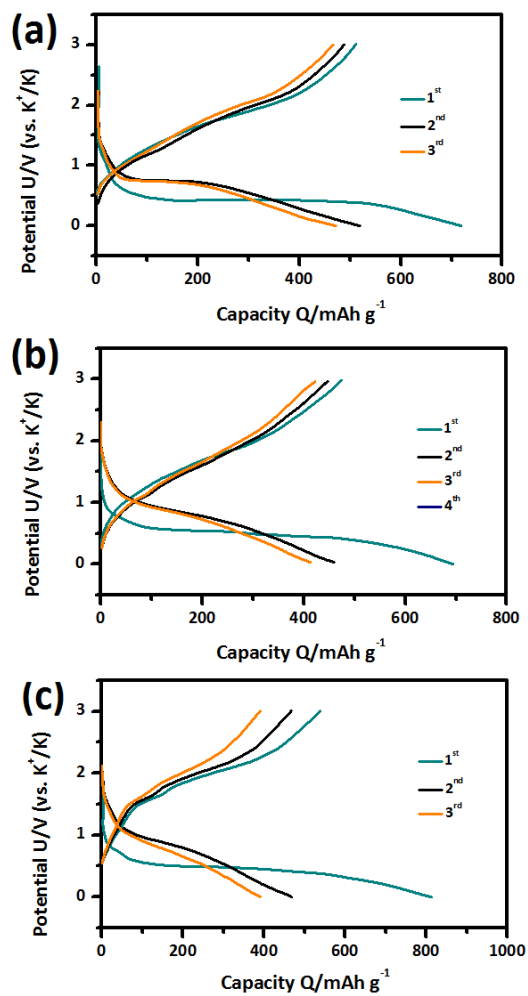


Figure S8 Galvanostatic charge/discharge plots of the nickel sulfide/C reference samples based on α -NiS (a), β -NiS (b) and NiS₂ (c).

Figure S9

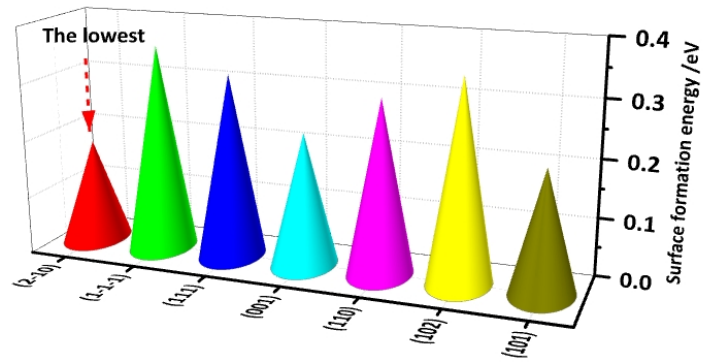


Figure S9 Formation energy of different surfaces for α -NiS based on DFT calculations.

Figure S10

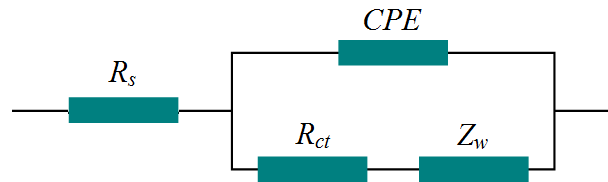


Figure S10 Equivalent circuit of the electrochemical impedance spectra for the samples.

Figure S11

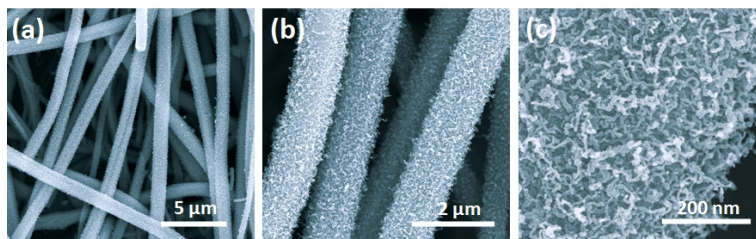


Figure S11 SEM images of the α -NiS-NSCN hollow fibers after repeated charging/discharging cycles. .

Figure S12

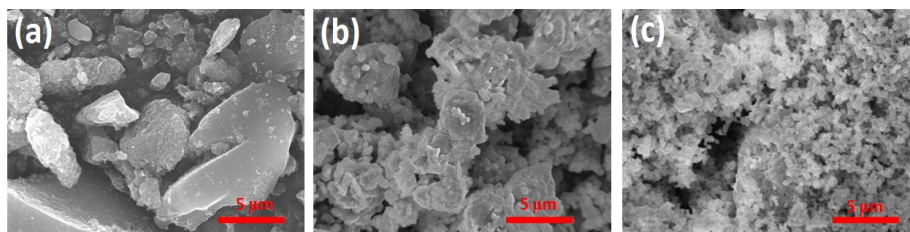


Figure S12 SEM images of the original α -NiS/C reference sample (a), after the initial potassiation (b) and after extensive charging/discharging cycles (c).

Figure S13

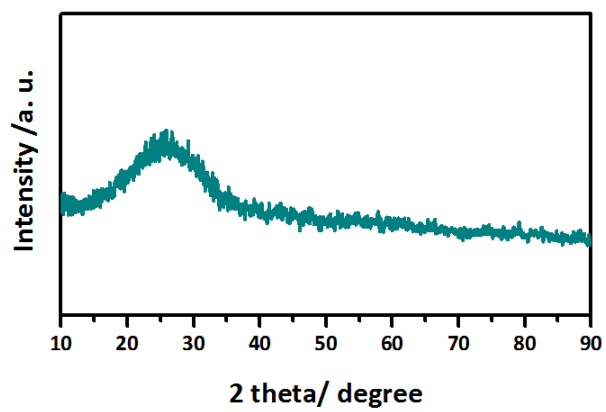


Figure S13 XRD pattern of the CHCF fiber.

Figure S14

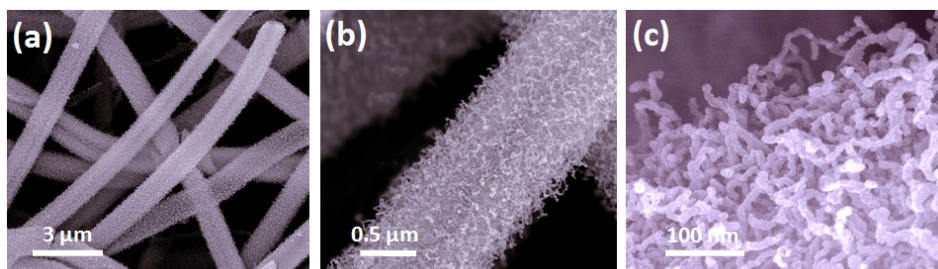


Figure S14 SEM images of the CHCF fiber.

Figure S15

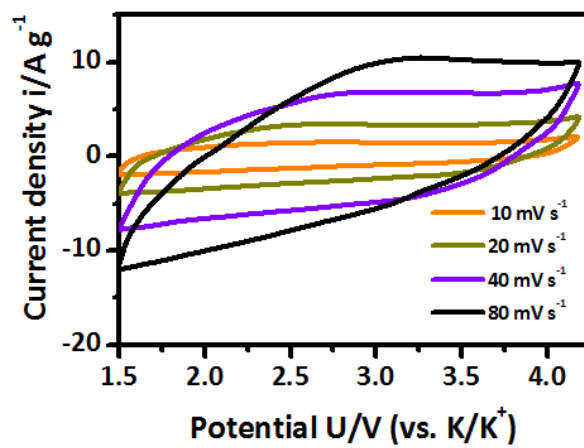


Figure S15 CV profiles of the CHCF cathode in different scan rates.

Figure S16

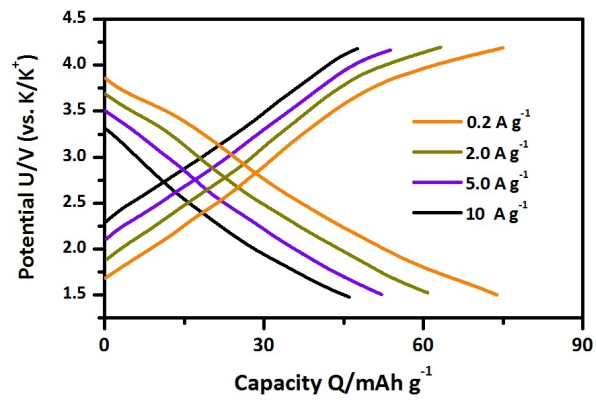


Figure S16 Galvanostatic charge/discharge profiles of the CHCF cathode in different current densities.

Part II: Supporting Tables

Table S1 Elemental contents of nickel sulfides based NSCN hollow fibers based on the EDS results

| Samples | Carbon/wt.% | Nitrogen/wt.% | Nickel/wt.% | Sulfur/wt.% |
|------------------------|-------------|---------------|-------------|-------------|
| α -NiS-NSCN | 26.3 | 12.0 | 40.1 | 21.6 |
| β -NiS-NSCN | 25.9 | 11.5 | 40.7 | 21.9 |
| NiS ₂ -NSCN | 23.2 | 11.6 | 31.2 | 34.0 |

Table S2 High-rate long-term cycling properties of α -NiS-NSCN hollow fiber and the transition metal composites in recent publications

| Materials | Current density $i/ \text{A g}^{-1}$ | Cycling number n | Capacity retention /% | Ref |
|---------------------------------------|---|---------------------|--------------------------|-----------|
| h-NiS@N-C | 1 | 1000 | 74.2 | 58 |
| NiS/S-rGO | 4 | 2000 | 68.7 | 47 |
| NiS/rGO | 0.5 | 500 | 87.9 | 52 |
| T-Co ₃ Se ₄ /GO | 1 | 500 | 86 | 59 |
| NiSe@C/rGO | 0.2 | 700 | 78.6 | 55 |
| Co ₃ O ₄ @N-C | 0.5 | 740 | 80 | 20 |
| α -NiS-NSCN hollow fiber | 1 | 1000 | 89 | This work |

Part III: Supporting references

[S1] B. Guan, Y. Li, B. Y. Yin, K. F. Liu, D. W. Wang, H. H. Zhang, C. J. Cheng, Synthesis of hierarchical NiS microflowers for high performance asymmetric supercapacitor. *Chem. Eng. J.* 2017, *308*, 1165-1173.

[S2] G. Y. Du, M. L. Tao, D. Y. Liu, M. K. Aslam, Y. R. Qi, J. Jiang, Y. T. Li, S. J. Bao, M. W. Xu, *J. Colloid Interf. Sci.* 2021, *582*, 932-939.

[S3] J. G. Wang, H. Y. Liu, R. Zhou, X. R. Liu, B. Q. Wei, *J. Power Sources* 2019, *413*, 327-333.

[S4] H. H. Sun, J. G. Wang, Y. Zhang, W. Hua, Y. Y. Li, H. Y. Liu, *J. Mater. Chem. A* 2018, *6*, 13419-13427.

[S5] J. Wang, J. Polleux, J. Lim, B. Dunn, *J. Phys. Chem. C* **2007**, *111*, 14925-14931.

[S6] B. K. Lesel, J. S. Ko, B. Dunn, S. H. Tolbert, *ACS Nano* **2016**, *10*, 7572-7581.