Supporting Information

Highly dispersed ultrasmall NiS₂ nanoparticles in porous carbon nanofibersanodes for sodium ion batteries

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EXPERIMENT SECTION

Synthesis

Typically, 1.5 g nickel acetylacetonate ($C_{10}H_{14}NiO_4$, Sigma-Aldrich), 1 g polyacrylonitrile (PAN, Sigma-Aldrich, M_W =150000) and 0.5 g polymethyl methacrylate (PMMA, Sigma-Aldrich) were dissolved in 10 ml N, N-dimethylformamide (DMF, Sigma-Aldrich) for preparing a homogenous solution with stirring assistance. The mixture was then transferred into a syringe for electrospinning under 18 kV voltages with a flow rate of 0.8 mLh⁻¹. The as-obtained polymer textile was stabilized at 300 °C for 2 h with a heating rate of 2 °C min⁻¹ in Air, and then was carbonized under 1200 °C for 2 h with a heating rate of 2 °C min⁻¹ in Air. The NiS₂NP/p-CNF was prepared after the vulcanization by using sulfur powder.

In a typical process, the mixture of 1 g PAN and 0.5 g PMMA in 10 ml DMF was transferred into a syringe for electrospinning. Then, the p-CNF was synthesized after stabilized and carbonized. The preparation of the reference Ni₂S is similar to the NiS₂NP/p-CNF. The mixture of 1 g PAN and 1.5 g nickel acetylacetonate in 10 ml DMF was stirred for a homogenous solution. After the procedure of the electrospinning, stabilization, carbonization and vulcanization, the reference Ni₂S was obtained.

Material characterization

Miniflex 600 powder X-ray diffractometer (XRD, Cu K α radiation) was employed to analyze the crystal phase of prepared samples, which was tested atthe range of 20 from 10 ° to 80 ° at a scan rate of 5 °min⁻¹. The surface morphology and internal microstructure of the samples were carried out by field-emission scanningelectron microscopy (FESEM,Hitachi SU-8020) and high resolution transmission electron microscopy (HRTEM,Tecnai F20). X-ray photoelectronspectroscopy(XPS, ESCALAB 250) measurements were performed for further ensuring the components of the material. The N₂ adsorption-desorption isotherms and Brunauer-Emmett-Teller(BET) surface area of samples were determined by gas sorption analyze (Hiden IGA100B, -195 °C). Thermogravimetric analysis (TGA) was performed with a thermogravimetric analyzer (NETZSCH STA449F3) in flowing air with a heating rate of 10 °C min⁻¹. Raman spectrumwas recorded by Raman microscope (Renishaw, 532 nm laser).

Electrochemical measurements

Electrochemical measurements of NiS₂NP/p-CNF, NiS₂ and NiS₂NP/p-CNF for SIBs were tested by the CR2032 typed coin cells, which are half-batteries assembling in the Ar-filled glove box. Those anode materials were directly employed as the working electrodes, which were fabricated as slurry mixture containing acetylene black (Sigma-Aldrich, 10 wt.%), sodium carboxymethyl cellulose (Sigma-Aldrich, 10 wt.%) and active materials (80 wt.%) on a copper foil, and the loading mass of samples was about 1.2 mg cm⁻². Glass microfiber (Whatman) was applied as the separator, and sodium metal was employed as the counter and reference electrode. The electrolyte used ethylene carbonate and propylene carbonate (EC/PC=1:1, v/v, Sigma-Aldrich) with 5 % fluoroethylene carbonate (FEC, Sigma-Aldrich) containing 1 M NaPF₆ (Sigma-Aldrich). Galvanostatic charge-discharge data was collected by the LAND (Wuhan Kingnuo Electronic Co., China), and the voltage is ranging from 0.01 to 3.0 V. The electrochemical workstation (CHI660E) was utilized to obtain the CV profile at a scan rate of 0.1 mV s⁻¹ and EIS data within the frequency range from 0.01 Hz to 100000 Hz.



Figure S1.The comparison of TGA curve between NiS_2NP/p -CNF and NiS_2 under air in the temperature range of 0 to 850°C.

The general process can be described as:

$$C + O_2 \rightarrow CO_2 \tag{1}$$

$$NiS_2 + O_2 \rightarrow NiO + SO_3 \tag{2}$$

$$NiS_{2}(wt\%) = \frac{\text{molecular weight of NiS}_{2}}{\text{molecular weight of NiO}} \times \text{residual weight (wt\%)}$$
(3)

According to the reaction (1), (2) and Figure S1, we can conclude that the final residual mass percent of NiS₂NP/p-CNF and NiS₂ kept 34.5 % and 39.1 % after being heated to 850 °C, respectively. Then, the mass precent of active material in the NiS₂NP/p-CNF and NiS₂ are 46.4 % and 53.5 % by calculating from equation (3), correspondingly.



Figure S2.a) Low magnification and b) high magnification SEM images of the NiS_2 .



Figure S3.a) Low magnification and b) high magnification SEM images of thepristine carbon nanofiber. c) Low magnification and d) high magnification SEMimagesofthep-CNF.



Figure S4.The galvanostatic discharge/charge profiles of the NiS_2NP/p -CNF electrode at 0.1 A g⁻¹ for SIBs.



Figure S5.a) Low magnification and b) high magnification SEM images of the NiS_2NP/p -CNF electrode after 200 cycle at 0.1 A g⁻¹. c) and d) TEM images of the NiS_2NP/p -CNF electrode after 200 cycle at 0.1 A g⁻¹.



Figure S6.The galvanostatic discharge/charge profiles of a) the NiS₂NP/p-CNF and b) NiS₂ at different current densities (0.05, 0.1, 0.2, 0.5, 1 and 2 A g^{-1}) for SIBs.



Figure S7.a) The capacity retention rate of the NiS_2NP/p -CNF and NiS_2 at different current densities. b) Comparison of the rate performance between NiS_2NP/p -CNF and other typical anode materials of SIBs.

Materials	Voltage range(V)	Specific capacity (mAh g ⁻¹)	Cycle number	Current density(A g ⁻¹)	Reference
NiS ₂ NP/p-CNF	0.01-3.0	375	200	0.1	• This work
		140	1000	2	
NiS/rGO	0.01-3.0	160	10	0.2	S1
Ni ₃ S ₂ -PEDOT	0.5-2.0	280	30	0.6	S2
Ni ₂ P/NiS _{0.66}	0.01-3.0	323	60	0.3	S3
NiS	0.01-3.0	283	50	0.5	S4
Ni ₃ S ₂ /C	0.01-3.0	453	100	0.1	S5
NiS ₂	0.4-2.9	319	1000	0.5	S6
NiS _x /CNT/C	0.01-3.0	340	200	0.1	S7
Co ₂ S/C	0.01-3.0	358	60	0.5	S8
VS ₂ -SNSs	0.4-2.2	245	100	0.2	S9
FeS ₂ /rGO	0.8-2.8	160	800	0.9	S10

Table S1.The comparison of various conversion anode materials for SIBs.

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