Ni₃S₂@S-carbon nanotubes synthesized using NiS₂ as sulfur source and precursor for high-performance sodium-ion half/full cells

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ABSTRACT Nickel sulfides are attractive anode materials for sodium-ion batteries (SIBs) due to their rich structures and natural abundance. However, their applications are greatly hindered by the large volume expansion and poor cycling properties. The introduction of hollow structures and heteroatom-doped carbon layers are effective ways to solve these issues. Here, nitrogen, sulfur co-doped carbon coated Ni₃S₂ (abbreviated as, Ni₃S₂@NSC) nanotubes were prepared by a novel templating route. During the annealing process, NiS₂ acts as both a precursor to Ni₃S₂ and an S-doped sulfur source. No additional sulfur source was used during the S-doping procedure, suggesting an atomically economic synthesis process. As anodes for sodium-ion half-cells, Ni₃S₂@NSCs exhibited high discharge capacity of 481 mA h g⁻¹ at 0.1 A g⁻¹ after 100 cycles with exceptional capacity retention of 98.6%. Furthermore, they maintained excellent rate capability of 318 mA h g⁻¹ even at elevated current density of 5 A g⁻¹. Sodium-ion full-cells assembled from the Ni₃S₂@NSC anodes and Na₃V₂(PO₄)₃ (NVP@C) cathodes also presented superior capacities and cyclabilities. These features can be attributed to the N, S co-doped carbon coated hollow structure that provided sufficient contact between the electrode and electrolyte, enhanced surface ion storage performance (capacitive effect), and improved structural stability of electrode materials.

Keywords: hollow structure, N, S co-doped carbon, rate capability, sodium-ion batteries

INTRODUCTION

The rapid development of electric vehicles requires en-

ergy devices with eco-friendly, abundant materials combined with high safety operation, long cycle life, and superior rate capability [1–4]. Lithium-ion batteries (LIBs) have been successfully used as commercial rechargeable batteries due to their relevant cycle stabilities and elevated energy densities [5–7]. However, the high cost and limited lithium resources severely limited the development prospects of LIBs. Sodium-ion batteries (SIBs) are promising alternative to LIBs with environmental benignity and natural abundance of sodium resources [8–11]. Up to now, nanostructured metal sulfides like FeS₂ [12], SnS₂ [13], MoS₂ [14] have been shown to possess rich redox chemistry and elevated electrochemical activities. However, these materials are limited by the serious volume expansion, electrode material degeneration and sluggish dynamics of Na⁺ with large radius, hindering the insertion of Na⁺ into host materials [15–17]. Therefore, the design of advanced electrode materials with suitable structures to meet the reversible storage of Na⁺ is highly desirable.

Nickel sulfides (Ni_xS_y) are promising anode materials for SIBs due to their rich structures, low cost, and low room temperature resistivity [18–20]. However, these materials still suffer from structural instability, poor electrical conductivities, and aggregation of nanomaterials during charge-discharge processes [21,22]. In addition, soluble polysulfide intermediates are formed during Na₂S formation-decomposition processes, leading to irreversible deterioration of the nickel sulfide electrodes [18,23]. An effective way to solve these issues is com-

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binning the nickel sulfides with carbon-based materials to improve the electronic conductivity and inhibit both aggregation of electrode material and dissolution of the polysulfides. For instance, Deng *et al.* [24] used two-dimensional (2D) graphene nanosheets as conductive matrix and spacer to interrupt the self-assembly of Ni_3S_4 nanorods. Li *et al.* [18] showed that *in situ* combination of NiS_2 and nitrogen-doped graphitic carbon might effectively alleviate the dissolution of sulfur component during cycling. Another effective strategy is designing hollow nanostructures to provide relatively large internal space to accommodate volume changes during cycling, as well as increase the electrode/electrolyte contact area. In this respect, $\text{NiS}_{1.03}$ porous hollow spheres with long-term cycling stability and excellent rate properties have been successfully designed by solvothermal route [25]. However, the sodium storage properties of nickel sulfide electrodes are still far from satisfactory despite the tremendous devoted efforts. Hence, the design of reasonable structures for practical applications remains challenging.

Herein, hollow nitrogen, sulfur co-doped carbon coated Ni_3S_2 (abbreviated as, $\text{Ni}_3\text{S}_2@\text{NSC}$) nanotubes were prepared using polyacrylonitrile (PAN) as template. Carbon-coated Ni_3S_2 nanotubes were easily obtained by introducing glucose into the reaction system, and carbon shells not only enhance the conductivity but also accommodate large volume expansion of the metal sulfides. When used as anodes for half/full SIBs, $\text{Ni}_3\text{S}_2@\text{NSC}$ electrodes showed superior capacities and stabilities.

EXPERIMENTAL

Material preparations

Preparation of electrospun PAN nanofibers

Firstly, 0.6 g PAN was added to 8 mL *N,N*-dimethylformamide (DMF) and stirred for 4 h at 60°C. The precursor solution was then poured into 10 mL syringe. PAN nanofibers were prepared by electrospinning. The cathode-anode distance, speed and voltage were fixed at 15 cm, 0.5 mL h⁻¹ and 10 kV, respectively.

Growth of NiS_2 onto PAN nanofibers

Firstly, 0.5 g nickel acetate tetrahydrate was dissolved in 40 mL ethanol solution, and then 40 mg of pretreated PAN fibers were added to the mixture. After 20 min sonication, the mixture was kept under 80°C heating for 5 h to deposit Ni particles on the nanofibers. The obtained products were then washed with ethanol. The above-prepared nanofibers and 0.3 g thioacetamide (TAA) were

added to 30 mL ethanol. After 30 min stirring, the mixture was placed in a Teflon-lined autoclave (50 mL) at 120°C for 10 h. The obtained core-shell precipitates were then washed with ethanol, and dried under vacuum at 60°C for 12 h.

Preparation of $\text{Ni}_3\text{S}_2@\text{NSC}$ nanotubes

Briefly, 80 mg obtained core-shell nanofibers were added to 40 mL deionized water containing 0.6 g glucose under stirring. The obtained mixture was then transferred into a Teflon-lined autoclave and kept at 200°C for 10 h. The resulting nanotubes were then collected, washed several times with deionized water, and dried at 60°C for 12 h. Finally, the obtained products were further annealed under Ar atmosphere at 700°C for 2 h at rate of 3°C min⁻¹. For comparison, bare Ni_3S_2 nanotubes were synthesized by dissolving PAN in core-shell nanofibers by DMF followed by annealing under Ar atmosphere at 700°C for 2 h. For the solid structure of Ni_3S_2 , 2 g nickel acetate, 0.48 g TAA and 1 g glucose were dissolved in 60 mL of ethanol. The resulting mixture was then transferred into a Teflon-lined autoclave and kept at 150°C for 12 h. The resulting products were then collected, washed several times with ethanol and deionized water, and dried at 60°C for 12 h. Finally, the obtained products were further annealed under Ar atmosphere at 700°C for 2 h.

Electrochemical measurements

For half-cell assembly, the active materials were mixed with carboxyl methylated cellulose and conducting additive carbon black at a mass ratio of 8:1:1. The obtained homogeneous mucus was then coated onto copper foil and dried in vacuum oven at 60°C. The electrodes were then cut into small round pieces with 12 mm in diameter. The loading mass for the anode with the active material ranged from 0.8 to 1.2 mg cm⁻². Half-cells were assembled in a glove box ($\text{H}_2\text{O} < 0.5$ ppm, $\text{O}_2 < 0.5$ ppm) and tested using CR2025 coin cells. Glass-fiber was used as the separator, Na foil as the counter electrodes, and 1 mol L⁻¹ NaClO_4 in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, v/v) containing 5% fluoroethylene carbonate (FEC) as the electrolyte. The charge-discharge measurements were performed by Arbin BT2000 system in the potential range of 0.01–3.00 V for anode materials and 2.0–3.9 V for NVP@C cathode. The cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) profiles were tested on a CHI660E electrochemical station. The full-cells were assembled with CR2032 coin-type cells using $\text{Ni}_3\text{S}_2@\text{NSC}$ as anodes and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP)@C as cathodes at weight ratio of

anodes/cathodes around 1:5. The voltage cut-off used for full-cell ranged from 0.5 to 3 V. The pouch-cells were packaged with Al-plastic film under the glovebox and designed total capacity was around 15 mA h.

RESULTS AND DISCUSSION

The fabrication strategy of hollow Ni_3S_2 @NSC nanotubes is briefly outlined in Fig. 1a. PAN nanofibers were first prepared by electrospinning method, and then used as template for the deposition of NiS_2 . Next, an NiS_2 layer was formed by coating the Ni-containing species onto PAN fibers and followed by sulfidation (abbreviated as, PAN@ NiS_2). The hydrothermal process transmuted the PAN nanofibers into hydrosoluble polyacrylic acid (PAA)

through hydrolysis of CN groups to NH_3 and COOH [26]. Afterward, the hydrosoluble PAA was entirely removed in water solution to create hollow nanotubes, where NH_3 produced a thin layer of N-doped carbon during carbonization of glucose by hydrothermal process [26,27]. The obtained hollow NiS_2 nanotubes (NiS_2 @NC) were annealed at 700°C for 2 h under Ar atmosphere to yield Ni_3S_2 @NSC composite with maintained original tube structure. During the transition of NiS_2 to Ni_3S_2 , some sulfur remained incorporated in the carbon wall. The detailed synthesis procedure is provided in EXPERIMENTAL.

The scanning electron microscopy (SEM) image of PAN nanofibers showed smooth surface with diameters

Figure 1 (a) Schematic illustration of Ni_3S_2 @NSC nanotubes using PAN nanofiber as template and nitrogen source; SEM images of (b) PAN nanofibers, (c) PAN@ NiS_2 nanofibers, and (d) hollow Ni_3S_2 @NSC nanotubes after removal of PAN template; (e, f) TEM images of Ni_3S_2 @NSC nanotubes; (g) SEM image of pure Ni_3S_2 nanotubes; (h) corresponding EDS elemental mappings (Ni, S, C, and N) of Ni_3S_2 @NSC.

around 200 nm (Fig. 1b). The SEM image of PAN@NiS₂ nanofibers confirmed preservation of the initial PAN nanofiber structures but the average diameter increased to about 400 nm (Fig. 1c). The composite nanofibers composed of tightly aggregated nanoparticles displayed rougher surfaces than PAN nanofibers, confirming the strong coating of NiS₂ on the PAN nanofibers. After the removal of PAN template, an interesting structural evolution from nanofibers to hollow nanotubes was observed, where nanotube surface showed thin carbon layer (Fig. 1d, e). Almost no difference was noticed between the morphologies of NiS₂@NC nanotubes before annealing (Fig. S1a, d) and Ni₃S₂@NSC after annealing (Fig. S1b, e). In addition, due to the presence of the PAN substrate, the presence of NiSO₄·6H₂O can be found in the X-ray diffraction (XRD) pattern of PAN@NiS₂ (Fig. S2a). After removal of the PAN template, the diffraction peak of NiSO₄·6H₂O no longer appeared in NiS₂@NC (Fig. S2b). The high-resolution transmission electron microscopy (HRTEM) images further demonstrated the formation of carbon walls with thickness around 12 nm (Fig. 1f). The two sets of lattice fringes of 0.18 and 0.28 nm can be attributed to the (113) and (110) planes of Ni₃S₂, respectively. For comparison, pure Ni₃S₂ were also prepared

through dissolution of PAN template by DMF, where pure Ni₃S₂ showed tubular structure similar to that of Ni₃S₂@NSC nanotubes (Fig. 1g). The difference between the two Ni₃S₂ specimens was further observed under low-magnification SEM. In Fig. S1b, e, Ni₃S₂@NSC nanotubes consisted of many interlaced nanotubes while pure Ni₃S₂ nanotubes depicted bad structural integrity with rougher surface (Fig. S1c, f). Hence, introduction of thin carbon layer could effectively encapsulate Ni₃S₂ to inhibit formation of defects on nanotubes' surfaces and prevent Ni₃S₂ nanotubes from breaking upon removal of PAN template. The latter was confirmed by the TEM image in Fig. S3a, b, which clearly revealed nanoparticles randomly assembled on pure Ni₃S₂ nanotubes. On the other hand, the TEM element mappings of Ni₃S₂@NSC nanotubes exhibited uniform distribution of Ni, S, C and N throughout the hollow nanotubes (Fig. 1h). All the above data confirmed the successful rational-design of Ni₃S₂ hollow nanotubes by template route.

Fig. 2a presents the XRD patterns of Ni₃S₂@NSC and pure Ni₃S₂ nanotubes. All diffraction peaks perfectly matched the crystalline Ni₃S₂ (JCPDS No. 44-1418), indicating high phase purity. The presence and composition of carbon layers were examined by Raman spectroscopy.

Figure 2 (a) XRD patterns, (b) Raman spectra, (c) TGA analysis of Ni₃S₂@NSC and pure Ni₃S₂, and (d) nitrogen adsorption-desorption isotherms of Ni₃S₂@NSC nanotubes.

In Fig. 2b, $\text{Ni}_3\text{S}_2\text{@NSC}$ composites showed two typical peaks of carbon materials at 1360 and 1600 cm^{-1} , belonging to the D band (defect-induced amorphous carbon) and G band (graphic carbon), respectively. The intensity ratio of the D band to G band (I_D/I_G) would provide typical index of graphitized degree in graphitic carbon [28,29]. The I_D/I_G ratio of $\text{Ni}_3\text{S}_2\text{@NSC}$ was estimated to be 0.89. For comparison, weak D and G bands were observed in Ni_3S_2 , which may be derived from PAN residues. The thermogravimetric analyses (TGA) of $\text{Ni}_3\text{S}_2\text{@NSC}$ and pure Ni_3S_2 were recorded from room temperature to 800°C under air atmosphere. The obvious weight loss between 400 and 700°C corresponded to transition of Ni_3S_2 to NiO , as well as decomposition of carbonaceous components [23]. In addition, the XRD pattern of the TGA product (Fig. S4) confirms that the product is NiO . In Fig. 2c, approximately 65% and 88.4% of the original mass remained after TGA process under air atmosphere. The Ni_3S_2 contents in the main and comparative materials were estimated to be 69.6% and 94.72%, respectively [30]. The thermogravimetric reaction equation and detailed calculation processes are provided in the Supplementary information online. The pore volumes and specific surface areas of $\text{NiS}_2\text{@NC}$, $\text{Ni}_3\text{S}_2\text{@NSC}$ and pure Ni_3S_2 nanotubes were investigated by nitrogen adsorption/desorption measurements and the

results are depicted in Fig. 2d and Fig. S5a, b. The surface area and microporous area of pure Ni_3S_2 were estimated to be 12.57 and 8.51 $\text{m}^2 \text{g}^{-1}$, respectively (Table S1). For comparison, $\text{NiS}_2\text{@NC}$ coated with N-doped carbon layer showed specific surface area of 22.87 $\text{m}^2 \text{g}^{-1}$ and microporous area of 13.75 $\text{m}^2 \text{g}^{-1}$. After high-temperature annealing, the microporous area and surface area of $\text{Ni}_3\text{S}_2\text{@NSC}$ both increased to 100.3 and 104.1 $\text{m}^2 \text{g}^{-1}$, respectively. In addition, the total pore volume of $\text{Ni}_3\text{S}_2\text{@NSC}$ (0.059 $\text{cm}^3 \text{g}^{-1}$) was superior to those of pure Ni_3S_2 (0.02 $\text{cm}^3 \text{g}^{-1}$) and $\text{NiS}_2\text{@NC}$ (0.058 $\text{cm}^3 \text{g}^{-1}$). This indicated that the introduction of carbon layer and sulfur doping during high temperature annealing can effectively increase the specific surface area and the pore volume, especially within the microporous volume. During Na^+ insertion-extraction process, enlarged pore volume and high surface area would be advantageous for electrolyte immersion and adaptation of volume expansion of Ni_3S_2 electrode [30].

In Fig. 3a, the signals of Ni, N, S, C and O were detected in the survey X-ray photoelectron spectroscopy (XPS) spectrum. The comparison of XPS spectra of $\text{Ni}_3\text{S}_2\text{@NSC}$ and pure Ni_3S_2 materials showed relatively weak peak signals of $\text{Ni}_3\text{S}_2\text{@NSC}$ nanomaterial, especially the Ni peak that may be attributed to limited detection depth of the XPS equipment. Hence, this XPS equipment would be

Figure 3 XPS spectra of Ni_3S_2 nanotubes. (a) Survey spectrum of $\text{Ni}_3\text{S}_2\text{@NSC}$ and pure Ni_3S_2 ; (b) C 1s spectrum of $\text{Ni}_3\text{S}_2\text{@NSC}$ before annealing, (d) FTIR spectra of $\text{Ni}_3\text{S}_2\text{@NSC}$ before and after annealing; (c) S 2p, (e) C 1s, and (f) N 1s spectra of $\text{Ni}_3\text{S}_2\text{@NSC}$ after annealing.

unable of collecting signals below the carbon layer. In other words, most Ni_3S_2 nanoparticles in $\text{Ni}_3\text{S}_2@\text{NSC}$ should have been encapsulated with N, S co-doped carbon nanotubes [31]. For Ni 2p XPS (Fig. S6), two peaks at 854.5 and 872.8 eV were noticed and assigned to Ni^{3+} . The peaks at 852.2 and 869.6 eV would be attributed to Ni^{2+} . The other two peaks corresponded to shake-up satellites (marked as "Sat.") [30,32]. The comparison of C 1s of the products before and after annealing revealed that C 1s peak of $\text{NiS}_2@\text{NC}$ can be decomposed into four components at 284.6, 285.2, 286.5 and 288.9 eV, assigned to C–C bond, C–N bond, C–O bond, and O=C–O bond, respectively (Fig. 3b) [23]. After 2 h annealing at 700°C, O=C–O bond vanished and new peak at 283.8 eV appeared in the C 1s spectrum of $\text{Ni}_3\text{S}_2@\text{NSC}$, attributed to C–S–C bond (Fig. 3e) [33,34]. Thus, incorporation of S atoms in the carbon matrix during high-temperature annealing recombined the carbon atoms, resulting in changes in binding energies. The latter could be confirmed by the relative content of Ni and S listed in Table S2. As for $\text{NiS}_2@\text{NC}$, the XPS contents of Ni and S were recorded as 2.72 at% and 5.71 at%, consistent with the atomic ratio of NiS_2 . After annealing, the Ni and S contents in $\text{Ni}_3\text{S}_2@\text{NSC}$ changed to 1.95 at% and 5.52 at%. The additional ratio of S also indicated its successful incorporation in the carbon wall while avoiding the waste of S element. Combining the results of elemental analysis and inductively coupled plasma (ICP) in Table S3, the doping amounts of N and S are 0.92 wt% and 0.89 wt%, respectively. For the high-resolution S 2p XPS in $\text{Ni}_3\text{S}_2@\text{NSC}$ (Fig. 3c), the two peaks at 161.2 and 163 eV were attributed to S $2p_{3/2}$ and S $2p_{1/2}$ regions of metal-sulfur bonds, while that at 164.3 eV indicated the presence of C–S–C covalent bond, consistent with the C 1s results [35]. In Fig. 3f, three N 1s peaks at 403.3, 399.9 and 397.5 eV were noticed, and derived from graphitic N, pyrrolic N and pyridinic N, respectively. The presence of nitrogen was linked to decomposition of PAN [36]. Meaningfully, the existence of nitrogen-doped carbon layer would effectively increase the electronic conductivity and create more extrinsic defects, benefiting insertion-extraction of Na^+ in the carbon layer [37,38].

Fourier-transform infra-red (FTIR) spectroscopy of $\text{NiS}_2@\text{NC}$ and $\text{Ni}_3\text{S}_2@\text{NSC}$ were employed to further determine the interactions between N, S and carbon layer. $\text{NiS}_2@\text{NC}$ showed absorption peaks of pure NiS_2 at 630 and 1099 cm^{-1} (Fig. 3d) [39]. The peaks at 1615 and 1699 cm^{-1} were attributed to formation of $\text{C}_6\text{H}_5\text{--C=O}$ after glucose hydrothermal process [40]. The NiS_2 absorption peak vanished from the FTIR pattern of

$\text{Ni}_3\text{S}_2@\text{NSC}$ but the absorption peak of C–S–C appeared at 614 cm^{-1} [35], indicating the successful sulfur doping after annealing. The presence of C–N peak at 2383 cm^{-1} indicated the combination of N element with the carbon layer during the hydrothermal process [26,41]. These FTIR results demonstrated the successful doping of sulfur into the carbon skeleton during high-temperature calcination. Note that doping with S atoms can increase the carbon layer distance [42,43], which would not only enhance the electron conductivity through formation of strong C–S–C bonds [43], but also enhance the migration rate of Na^+ for the rapid charge-discharge performance [44].

The electrochemical performances of the products in SIBs were tested in coin-type half-cells. Fig. 4a and Fig. S7a show the CV curves of the initial five cycles at scan rate of 0.1 mV s^{-1} and voltage window of 0.01–3.0 V (vs. Na/Na^+). During the first cathodic scan, one broad and intense reduction peak was observed at 0.67 V for $\text{Ni}_3\text{S}_2@\text{NSC}$ and 0.52 V for pure Ni_3S_2 , which could be attributed to the reduction process ($\text{Ni}_3\text{S}_2 + 4\text{Na}^+ + 4\text{e}^- \rightarrow 3\text{Ni} + 2\text{Na}_2\text{S}$) and formation of solid electrolyte interphase (SEI) layer, respectively [32]. In the anodic scan, the oxidation peaks at 1.66 V for $\text{Ni}_3\text{S}_2@\text{NSC}$ and 1.76 V for pure Ni_3S_2 might be assigned to the recovery of Ni_3S_2 [23]. No significant changes were observed in the reduction and oxidation peaks of $\text{Ni}_3\text{S}_2@\text{NSC}$ composite during subsequent cycles. For comparison, the peak intensity and area of pure Ni_3S_2 significantly reduced, consistent with previous reports [19]. In addition, *ex-situ* XRD measurement of $\text{Ni}_3\text{S}_2@\text{NSC}$ under fully charged state was performed, as shown in Fig. S8. When charged to 3.0 V, diffraction peaks around 21.6°, 30.7° and 37.6° corresponding to the (101), (110) and (003) faces of Ni_3S_2 were observed, which is consistent with the initial XRD, indicating the re-formation of Ni_3S_2 . Hence, the electrochemical reversibility would improve by introduction of N, S co-doped carbon into the composite.

Fig. 4b presents the typical galvanostatic discharge-charge profile of $\text{Ni}_3\text{S}_2@\text{NSC}$ as anode for SIBs at current density of 0.1 A g^{-1} . Initial discharge-charge capacities of 568.8 and 444.11 mA h g^{-1} were obtained during the first cycle, corresponding to coulombic efficiency of 78.1%. The initial coulombic efficiency is low because the large specific surface area will increase the irreversible consumption of the electrolyte when the SEI film is formed. However, the charge and discharge plateaus of pure Ni_3S_2 electrode gradually vanished after cycling due to lack of protection of the carbon layer (Fig. S7b). This could be attributed to collapse of the microstructure during cycling

Figure 4 Electrochemical properties of composites as anodes of SIBs. (a) CV curves of $\text{Ni}_3\text{S}_2@\text{NSC}$ at scan rate of 0.1 mV s^{-1} ; (b) galvanostatic charge-discharge profile of $\text{Ni}_3\text{S}_2@\text{NSC}$ for the 1st, 2nd, 50th, and 100th cycles at current density of 0.1 A g^{-1} ; (c) cycling performance of $\text{Ni}_3\text{S}_2@\text{NSC}$ and pure Ni_3S_2 anode materials at 0.1 A g^{-1} ; (d) rate properties of $\text{Ni}_3\text{S}_2@\text{NSC}$ and pure Ni_3S_2 from 0.1 to 5 A g^{-1} ; (e) cycling properties and coulombic efficiency of $\text{Ni}_3\text{S}_2@\text{NSC}$ at current density of 0.2 A g^{-1} .

[18]. Fig. 4d gathers the rate performance values of the electrodes. Though pure Ni_3S_2 showed higher capacity than $\text{Ni}_3\text{S}_2@\text{NSC}$ at low current densities ($< 0.1 \text{ A g}^{-1}$), $\text{Ni}_3\text{S}_2@\text{NSC}$ was advantageous when current density further rose. Therefore, the nitrogen-doped carbon layer might enhance the electrical conductivity of Ni_3S_2 for ultra-fast electron transport rates [18]. In order to compare the volumetric energy density of the hollow structure and the solid structure, we measured the tap density of the hollow structure and the solid structure to be 0.833 and 1.667 g cm^{-3} , respectively. The volumetric specific capacity was converted by tap density (Fig. S9). Although the solid structure Ni_3S_2 showed a higher capacity than the hollow $\text{Ni}_3\text{S}_2@\text{NSC}$ at the initial 30 cycles, $\text{Ni}_3\text{S}_2@\text{NSC}$ was advantageous when the number of cycles was further increased. Therefore, we think that although the hollow structure we design will sacrifice a part of the volumetric capacity, it is helpful for the cycle stability of the electrode. In addition, $\text{Ni}_3\text{S}_2@\text{NSC}$ restored its initial capacity upon return of current to 0.1 A g^{-1} , reflecting good reversibility. Improved electrodes should not only have good rate performances but also good stability. After subsequent 100 cycles at 0.1 A g^{-1} (Fig. 4c), the capacity was maintained at $481.5 \text{ mA h g}^{-1}$ with retention rate of

98.6%. This remarkable stability might be attributed to N, S co-doped carbon coated hierarchical hollow structure, which can effectively buffer the volume changes during cycling. In Fig. 4e and Fig. S10, $\text{Ni}_3\text{S}_2@\text{NSC}$ electrode exhibited reversible capacities of 442 and 351 mA h g^{-1} after 200 cycles at high discharge-charge currents of 0.2 and 0.5 A g^{-1} , respectively. Besides, $\text{Ni}_3\text{S}_2@\text{NSC}$ showed better cycling and stability performances than reported Ni_3S_2 -based materials (Table 1) [19,23,30,32,45–50].

EIS was used to analyze the sodium storage kinetics of the as-prepared $\text{Ni}_3\text{S}_2@\text{NSC}$ materials. All Nyquist plots depicted high-frequency semicircles assigned to charge-transfer resistance (R_{ct}) between the electrode and electrolyte, as well as Warburg impedance in low-frequency region due to diffusion of Na^+ into the electrode materials [25]. After 10 cycles at 0.1 A g^{-1} (Fig. 5a), $\text{Ni}_3\text{S}_2@\text{NSC}$ and pure Ni_3S_2 showed low R_{ct} values of 54 and 62Ω , respectively. Obvious differences started to be noticed after 100 cycles (Fig. 5b). In high-frequency region and compared to $\text{Ni}_3\text{S}_2@\text{NSC}$ ($R_{\text{ct}}=147 \Omega$), pure Ni_3S_2 ($R_{\text{ct}}=359 \Omega$) displayed larger semicircle, suggesting that the added carbon layer can stabilize the charge-transfer impedance and promote fast electrochemical reaction kinetics. The electrode material was analyzed by SEM after 100 cycles

Table 1 Electrochemical performances of reported Ni_3S_2 anodes for SIBs

Material	Initial coulombic efficiency	Capacity (mA h g^{-1})/current density (A g^{-1})/cycle number	Rate capacity (mA h g^{-1})/current density (A g^{-1})	Capacity retention	Ref.
0D Ni_3S_2 nanoparticles	59% at 0.1 A g^{-1}	453/0.1/100 430/0.4/100	583/0.1; 529/0.2; 491/0.4; 459/0.8; 421/1.6; 408/2	85%/0.1/100 87%/0.4/100	[23]
Ni_3S_2 on Ni foam	~85% at 0.05 A g^{-1}	315.3/0.05/100	~320/0.05; 290/0.1; 275/0.2; 250/0.4; 230/0.8	90.6% at 0.05 A g^{-1} after 100 cycles	[46]
RGO/ Ni_3S_2 /Ni	83.2% at 0.05 A g^{-1}	433/0.05/100	~390/0.05; 370/0.1; 330/0.2; 300/0.4; 263.1/0.8	96.5% at 0.05 A g^{-1} after 100 cycles	[47]
Hollow Ni_3S_2 / Ni_9S_8 /RGO nanospheres	71% at 0.3 A g^{-1}	449/0.3/150	504/0.2; 468/0.5; 442/1; 411/2; 377/3	100%/0.3/150	[32]
Ni_3S_2 -Ni nanoarrays	89% at 0.15 A g^{-1}	350.6/0.15/200	395.5/0.15; 362.5/0.3; 290.5/0.75; 224/1.5; 188.5/3		[48]
RGO/ Ni_3S_2	77.1% at 0.1 A g^{-1}	391.6/0.1/50	513/0.1; 443/0.25; 404/0.5; 346/1	76.4%/0.1/50	[19]
Ni_3S_2 nanoparticles	78.8% at 0.1 A g^{-1}	458.1/0.1/100 392.6/0.5/300	~450/0.1; 400/0.5; 380/1; 323.3/2	\	[30]
Carbon nanotubes encapsulating Ni_3S_2	93% at 0.2 A g^{-1}	340/0.2/300	~463/0.2; 360/0.5; 320/1; 290/2; 260/3; 220/5	\	[49]
Ni_3S_2 /Ni	~85% at 0.05 A g^{-1}	320/0.05/200	~300/0.05; 280/0.1; 250/0.2; 230/0.4; 210/0.8	86.6% at 0.05 A g^{-1} after 200 cycles	[45]
Ni_3S_2 nanosheets	51.9% at 0.2 A g^{-1}	432.8/0.2/100	~650/0.1; 580/0.2; 520/0.4; 460/1.6; 371/6.4	\	[50]
Ni_3S_2 @NSC hollow nanotube	78.1% at 0.1 A g^{-1} 77.95% at 0.2 A g^{-1}	481/0.1/100; 442/0.2/200	473/0.1; 443/0.2; 403/0.5; 389/1; 366/2; 321/5	98.6% at 0.1 A g^{-1} after 100 cycles; 93.6% at 0.2 A g^{-1} after 200 cycles	This work

and the results are depicted in Fig. 5c, d. Note that the original tubular structure of Ni_3S_2 @NSC was well maintained in Fig. 5c, while pure Ni_3S_2 electrode deteriorated after cycling with formation of agglomerates (Fig. 5d). Hence, carbon coating effectively retained the structural integrity of Ni_3S_2 nanotubes during cycling, as well as accommodated volume expansion and limited aggregation of the nanoparticles. In addition, the rationally designed hollow structure enhanced the structure stability of the electrodes.

Previous reports indicated that heteroatom-doped carbon materials should promote surface ion storage properties (capacitance effects) for additional capacity [34,51]. In addition, nitrogen adsorption/desorption analysis showed that the surface area and micropore volume of Ni_3S_2 @NSC were significantly higher than pure Ni_3S_2 . As a result, these features provide a rich site for ion adsorption storage. Thus, the fundamental kinetics of Ni_3S_2 @NSC and pure Ni_3S_2 electrodes were analyzed by CV. Fig. 6a exhibits typical CV tests of the electrodes at different scan rates from 0.2 to 1 mV s^{-1} . The relationship between the peak current (i) and scan rate (ν) could be expressed according to the equation as follow [52]:

$$i = a\nu^b, \quad (1)$$

where a and b are adjustable parameters and their values

can be determined by the intercept and slope of $\log(\nu)$ - $\log(i)$ plots (Fig. 6b and Fig. S11b), respectively.

Note that b value of 0.5 would represent diffusion-controlled behavior, whereas a value of 1 would indicate an ideal pseudocapacitive effect. Ni_3S_2 @NSC electrode showed higher b values when compared with pure Ni_3S_2 electrode at both cathodic and anodic peaks (0.84 vs. 0.68 and 0.65 vs. 0.55, respectively). The latter revealed more surface capacitance-dominated processes, implying that nitrogen and sulfur co-doped carbon layer of Ni_3S_2 @NSC could effectively enhance the surface-controlled pseudocapacitive behaviors. Fig. 6d summarizes the pseudocapacitive contributions at various scan rates calculated as the following [52,53]:

$$i(V) = k_1\nu + k_2\nu^{1/2}, \quad (2)$$

where i is the current associated with capacitance and diffusion control processes at fixed voltage and ν is the scan rate of CV tests.

The capacitive and diffusion-controlled currents can be dissociated through $k_1\nu$ and $k_2\nu^{1/2}$, respectively. Fig. 6c and Fig. S11c show that the current divided into the diffusion-controlled (blank area) and capacitive (shadow area) processes at the scan rate of 0.6 mV s^{-1} . The capacitive contribution ratio of Ni_3S_2 @NSC electrode was recorded as 71.1%, which was superior to that of pure

Figure 5 Nyquist plots of Ni_3S_2 @NSC and pure Ni_3S_2 for SIBs after (a) 10 and (b) 100 cycles; SEM of (c) disassembled electrode of Ni_3S_2 @NSC, and (d) pure Ni_3S_2 after 100 cycles.

Figure 6 Capacitance effect arising from Ni_3S_2 @NSC and separation between the capacitive and diffusion-controlled processes. (a) CV tests at various scan rates from 0.2 to 1 mV s^{-1} ; (b) illustration of b -value issued from the relationship between peak current and scan rate; (c) current separation of capacitive (shadow area) and diffusion-controlled (white space) processes; (d) determination of total charge contribution ratio of the capacitive and diffusion-controlled processes at different scan rates.

Ni_3S_2 (59.3%). The higher capacitive contribution of $\text{Ni}_3\text{S}_2@\text{NSC}$ matched well with the previously calculated b value, revealing the superior rate capability of $\text{Ni}_3\text{S}_2@\text{NSC}$ electrode material when compared with pure Ni_3S_2 . This might be due to the pseudo-capacitance effect and improved electrical conductivity. According to blank region, the charge of diffusion control was mainly generated near the peak voltage, causing deviation of the peak current from the capacitive effect. As scan rate rose, the capacitive contribution increased gradually (Fig. 6d and Fig. S11d), implying that large rate of Na-storage capability was mainly dominated by surface-capacitive behaviors.

The successful assembly of half-cells based on $\text{Ni}_3\text{S}_2@\text{NSC}$ anodes demonstrated promising features for energy storage. However, the practical application of $\text{Ni}_3\text{S}_2@\text{NSC}$ should be tested in full-cells, which was evaluated with respect to NVP@C cathode prepared as previously reported [36]. The SEM images, XRD patterns and electrochemical performances of NVP@C cathode are shown in Figs S12–S14. NVP@C provided a reversible capacity of $100.5 \text{ mA h g}^{-1}$ after 100 cycles in the voltage range of 2–3.9 V at 100 mA g^{-1} , with charge-discharge plateau

characteristics. To match the cathode/anode capacity and ensure outstanding electrochemical properties of NVP|| Ni_3S_2 full-cell, the cathode/anode mass ratio was controlled to about 5:1. Fig. 7a shows a scheme of Na^+ full-cell coupled with NVP|| Ni_3S_2 . Na^+ deintercalated from NVP electrode and reacted with Ni_3S_2 through the electrolyte during charging process. Fig. 7b illustrates the galvanostatic charge-discharge voltage profiles of NVP|| Ni_3S_2 full-cell. An initial discharge capacity of $329.3 \text{ mA h g}^{-1}$ (based on mass of Ni_3S_2 anode) was obtained in the voltage range of 0.5–3 V at 500 mA g^{-1} , with discharge voltage plateau varying from 1.7 to 2.0 V. Fig. 7c displays the cycle performance of NVP|| Ni_3S_2 cell, showing large discharge capacity of $265.5 \text{ mA h g}^{-1}$ at 500 mA g^{-1} after 50 cycles. The initial coulombic efficiency was estimated to be 97.3% and remained at about 99% in the following cycles.

Furthermore, full-cells were used to light up commercial light emitting diode (LED) bulbs. The “HNU” logo could easily be lightened using full charged pouch-type cell (Fig. 7d) or coin-cell (Fig. S15). Surprisingly, the pouch-type cells could even drive miniature electro-

Figure 7 Electrochemical measurements of NVP|| Ni_3S_2 full-cells. (a) Schematic illustration of Na-ion full-cell coupled with NVP|| Ni_3S_2 ; (b) galvanostatic charge and discharge profiles; (c) cycling performance of NVP|| Ni_3S_2 full-cells tested in the voltage range of 0.5–3 V at 500 mA g^{-1} ; (d) digital picture of “HNU” logo light by the pouch-type NVP|| Ni_3S_2 full-cells.

motors for more than 2 min (Video S1, Supplementary information). The good performances of the full-cells were attributed to the unique structures and stable charge-discharge platforms, confirming the potential practical applications of these materials.

CONCLUSIONS

A simple and economical template strategy was successfully developed for the rational design and synthesis of hollow $\text{Ni}_3\text{S}_2@\text{NSC}$ nanotubes, in which NiS_2 served as both the precursor of Ni_3S_2 and sulfur source for doping carbon. The N, S co-doped carbon layer did not only limit the aggregation of nanoparticles during cycling but enhanced the surface ion storage (capacitive effect) of the material. The hollow nanostructures with well-defined internal voids improved the mechanical stability of metal sulfides. As a result, $\text{Ni}_3\text{S}_2@\text{NSC}$ showed excellent cycling stability (481 mA h g^{-1} at 0.1 A g^{-1}) and rate capability (318 mA h g^{-1} at 5 A g^{-1}) in sodium-ion half cells. For practical applications, sodium-ion full-cells were assembled by matching $\text{Ni}_3\text{S}_2@\text{NSC}$ with NVP, and the resulting devices delivered an average reversible capacity of $323.6 \text{ mA h g}^{-1}$ after 50 cycles. Overall, rational design of nanomaterials could lead to materials with great electrochemical performances of SIBs.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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使用 NiS_2 作为硫源和前驱体合成 $\text{Ni}_3\text{S}_2@\text{S}$ 纳米管用于高性能钠离子半/全电池

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摘要 由于结构的多样性和丰富的自然储量, 硫化镍是钠离子电池极具潜力的负极材料. 然而, 大体积膨胀和差的循环性能阻碍了它们的应用. 引入中空结构和杂原子掺杂碳层是解决这些问题的有效方法. 本文通过新颖的模板法制备了氮、硫共掺杂碳层包覆的 Ni_3S_2 纳米管($\text{Ni}_3\text{S}_2@\text{NSCs}$). 在退火过程中, NiS_2 既作为形成 Ni_3S_2 的前体又作为S掺杂的硫源. 在S掺杂过程中没有使用额外的硫源, 这表明合成过程具有原子经济性. 作为钠离子半电池的阳极, $\text{Ni}_3\text{S}_2@\text{NSCs}$ 在 0.1 A g^{-1} 的电流密度下循环100次后表现出 481 mA h g^{-1} 的高放电容量, 具有98.6%的优异容量保持率. 此外, 即使在 5 A g^{-1} 的高电流密度下, 它们仍保持 318 mA h g^{-1} 的优异倍率性能. 由 $\text{Ni}_3\text{S}_2@\text{NSC}$ 阳极和 $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP@C)阴极组装的钠离子全电池也具有优异的容量和循环稳定性. 这些特征可归因于N, S共掺杂碳涂覆的中空结构. 此结构可使电极和电解质之间充分接触, 增强表面离子存储性能(电容效应), 并改善电极材料的结构稳定性.