Hollow N,C-co-doped carbon-coated ZnS nanospheres derived from metal organic framework (ZIF-8) with improved lithium and sodium storage performance

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Abstract

Transition metal sulfides have been widely used as anode electrodes of lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) due to its high theoretical capacity and low price. However, problems of huge volume expansion and poor conductivity during charging and discharging have been emerged. Herein, we design a N, C-co-doped, nano-sized, and hollow carbon-coated ZnS (ZnS-NC@C) composite using the advantages of metal organic framework (zeolitic imidazolate framework-8) structure and resorcinol-formaldehyde coating. When applied as anodes of LIBs and SIBs, it displays a high reversible capacity of 748 and 150.9 mAh g$^{-1}$ after 500 cycles at the current density of 1.0 A g$^{-1}$, respectively. This work could provide a promising strategy for enhancing the performance of transition metal sulfides for potential applications in LIBs and SIBs.

1. Introduction

With the ever-going supply of global electric energy storage applications and portable electronic devices, like the electric vehicles (EVs) and smart grid drives, are urgently calling for new alternative high-performance electrochemical energy storage. Accordingly, the energy storage devices in the future have become one of the most important devices, so highly power density, long cycle life, eco-friendliness and so forth assurance become more and more urgent in the design of batteries [1, 2]. As we all known, lithium-ion batteries (LIBs) have already devoted to business. Recently, as a potential alternative to LIBs, sodium-ion batteries (SIBs) rely on the advantage of low cost, abundant global resources and the suit oxidation reduction potential, which make it become the large-scale application of portable devices and EVs in the future [3, 4]. However, it is worth noting that along with the process of the society, the demand to the electronic product is more and more high in the information world, which also means the high specific capacity and long cycling stability are most important in our research of the LIBs and SIBs. Moreover, the critical point to develop high performance LIBs and SIBs depends on the electrode materials employed and the reaction mechanisms, which play the key roles in the battery performance. As a consequence, researchers have focused on exploring electrode materials with excellent electrochemical performance for LIBs and SIBs unendingly [5].

During the previous research, the various electrode materials investigated, but notably, metal sulfides attract people's attention due to their excellent physical and chemical properties. For example, metal sulfides perform high capacity and better reversibility because the S element valence is variable which can make M-S bonds more relatively weak, in electrochemical reactions, and further to make kinetically convenient for conversion reactions. As a typical example, zinc sulfide (ZnS) belongs to non-layered metal sulfides, which is very popular because of its nontoxicity, safer and less-expensive compared with the layered metal sulfides, which can be the ideal electrode materials of LIBs and SIBs [6–8]. Unfortunately, one of the most difficult problems to solve is that when ZnS electrode have a conversion reaction with lithium...
(ZnS + 2Li\(^+\) + 2e\(^-\) ⇔ Zn + Li\(_2\)S, Zn + yLi\(^+\) + ye\(^-\) ⇔ Li\(_y\)Zn (0 < y < 1)), the huge volume and structure change. The repeated lithium-ion insertion and extraction is irreversible, and results in structural failure and deteriorated contact of the active material [9, 10]. Considering the similar problems should also happen in SIBs, due to the larger ion radius of sodium, so how to modify the ZnS, improve the poor rate capability and interior cycling stability for SIB applications is needed. Designing the morphologic structure and constructing composite with high capacity conductivity materials, like nitrogen-doped and carbon-doped are proposed [11, 12]. For example, N-doping and C-doping can increase the electronic conductivity, Na\(^+\) ions storage capacities of various carbon materials and enhance the electron transport. Both of the elements co-doping exists the synergetic effect, which can effectively buffer the volume change of ZnS particles and improve the physicochemical properties [13, 14].

As ideal templates and precursors, metal organic frameworks (MOFs) with its advantages (regular structure and unique combine metal ions with organic linkers) are playing an increasing important role in the electrode materials research. In addition, carbon shell has attracted much attention as ideal structure to synthesize metal sulfide, due to the carbon shell structure can obviously increase the electronic conductivity and alleviate volume change of electrode materials [15–17]. For instance, Fu et al synthesized zinc sulfide/porous carbon composite (ZnS/PC) by virtue of the MOFs strategy which can contain a stable capacity of 438 mA h g\(^{-1}\) after 300 cycles at 100 mA g\(^{-1}\) for LIBs [14]. ZnS nanoparticles wrapped in N-doped mesoporous carbon nanosheets were prepared from MOFs through a simple co-pyrolysis process. Consequently, this material shows its capacity of 160 mAh g\(^{-1}\) at 1 A g\(^{-1}\), and retains 92.9% of initial capacity after cycling for 1000 times at 5 A g\(^{-1}\) [18]. Du et al reported that the synthesis of core–shell structured ZnS-C nanoparticles by a chitosan-assisted hydrothermal method exhibit a specific capacity of 750 mA h g\(^{-1}\) at 200 mA g\(^{-1}\) over 500 cycles [19]. Rational microstructure on the mental sulfide coupling carbon is conductive to enhance the electric conductivity and electrochemical stability of the LIBs and SIBs anodes. So, in our work, it is highly desirable to combine the MOFs as the precursors and carbon shell to build high-performance anodes for LIBs and SIBs. Using a zeolitic imidazolate framework-8 (ZIF-8) and resorcinol formaldehyde (RF) as the precursor and the source of carbon layer, respectively, N, C co-doped ZnS@C (ZnS-NC@C) hybrid nanostructure was synthesized. The carbon layer from RF can be ascribed to the following advantages: (a) facilitating the electrolyte infiltration capacity; (b) reducing the sodium ion or lithium ion or sodium ion diffusion length; (c) preventing the structure pulverization caused by Li\(^+\)/Na\(^+\) insertion/extraction; (d) alleviating the volume changes and stress, which can explain the reasons why to improve the electrochemical reactions in LIBs and SIBs. Therefore, it is of great importance to construct the ZnS-NC@C electrode, benefiting from these particular features, which can exhibit the excellent chemical performances with high specific capacity and long cycles. These results can demonstrate that the ZnS-NC@C composite may become an effective electrode material for LIBs and SIBs in the future.

2. Experimental section

2.1. Materials

The 2-methylimidazole was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd; m-dihydroxybenzene was purchased from Shanghai Macklin Biochemical Co., Ltd; Zn(NO\(_3\))\(_2\) · 6H\(_2\)O, hexadecyltrimethylammonium bromide (CTAB), methanol, ammonium hydroxide (30%), formaldehyde solution (37%) were all acquired from Sinopharm Chemical Reagent Co., Ltd without further purification. Deionized water (DI-water, resistance: >18 MΩ cm) were used as the water source in all experiments.

2.2. Synthesis of ZIF-8 and ZIF-8@RF

Using a facile process [17], in which 2.376 g of Zn(NO\(_3\))\(_2\) · 6H\(_2\)O and 5.256 g of 2-methylimidazole were dissolved in 120 ml of methanol, ZIF-8 was obtained. Then 0.2 g of as-synthesized ZIF-8 was dissolved in the mixture of DI (28 ml) and methanol (12 ml). The mixed solution was treated for 30 min at ambient temperature by using ultrasonic dispersion. Subsequently, 0.23 g of CTAB, 0.07 g of m-dihydroxybenzene and 0.2 ml of ammonium hydroxide (30%) were added to above solution. After 30 min, 0.12 ml of formaldehyde solution was added and the reaction time was up to 8 h. Finally, the pink product was collected by centrifugation, washed with DI, and dried at 60 °C overnight. Finally, ZIF-8@resorcinol-formaldehyde (ZIF-8@RF) was obtained.

2.3. Synthesis of ZnS-NC@C and ZnS-NC

The solution of 0.1 g of ZIF-8@RF and 0.3 g thioacetamide (TAA), as the zinc source and sulfur source, respectively, was transferred into a Teflon-lined stainless autoclave and sealed. The autoclave was kept at 85 °C for 8 h. After cooled naturally, the resulting precipitate was collected by centrifugation, rinsed three times with DI and absolute ethanol, and dried in air at 60 °C for 20 h. The product was annealed under
argon (Ar) atmosphere at 530 °C for 2 h at heating rate of 3 °C min⁻¹, the N, C-co-doped carbon-coated ZnS@C (ZnS-NC@C) composite was obtained.

Compared with the ZnS-NC@C composite, the synthesis of ZnS-NC is briefer. The mixture of 0.1 g of ZIF-8 and 0.3 g of TAA, as the zinc source and sulfur source, respectively, was transferred into a Teflon-lined stainless autoclave and sealed and kept at 85 °C for 8 h. After cooled naturally, the resulting precipitate was collected by centrifugation, washed three times with DI. Then as-prepared product was annealed directly at 530 °C under an argon atmosphere for 2 h (heating rate was 3 °C min⁻¹). After being naturally cooled down to room temperature, the gray product was acquired.

2.4. Material characterization
The morphologies of as-prepared ZnS-NC@C and ZnS-NC composites were observed by field emission scanning electron microscope (JEOL, JSM-7100F), transmission electron microscopy (TEM, TecnaiF20, 200 kV) with an energy dispersive x-ray (EDX) analyzer. The X-ray photoelectron spectroscopy (XPS) experiments were determined the chemical compositions and the structure characteristics of nanocomposite were obtained by x-ray powder diffraction (XRD, Bruker Bruker D8 Advance). The Brunauer–Emmett–Teller tests were carried out on a Micromeritics ASAP 2020 porosimetry system and accelerated surface area.

2.5. Electrochemical characterization
The as-prepared ZnS-NC@C working electrode was obtained by pasting the mixed homogeneous slurry consisted of active materials, super-P and polyvinylidene fluoride binder with a weight ratio of 7:2:1, and then coated onto the current collect copper foils, dried at 120 °C for 12 h in a vacuum oven. The dried foil sheet was directly cut into circular disks about 1 mg and diameter about 0.8 cm as anode. LIBs and SIBs were assembled in an argon-filled glove box. For LIBs, lithium foil was used as the counter electrode and reference electrode, the glass fiber was used as the separator. The electrolyte was consisted of a solution of 1 mol 1⁻¹ LiPF₆ in ethylene carbonate/diethyl carbonate (1:1 v/v). For SIBs, microporous polypropylene membrane was used as the separator. Sodium foil was used as the counter electrode and reference electrode. The electrolyte was 1 mol 1⁻¹ NaPF₆ in EC/DEC (1:1 v/v)). The cells were assembled into CR2035 coin cells in an Ar glove box to prepare half-cells.

The galvanostatic charge and discharge cycles were tested by using automatic battery testing system (Neware, China) within the voltage range from 0.01 to 3.0 V (vs. Li⁺/Li, Na⁺/Na). Cyclic voltammetry (CV) was recorded using an electrochemical workstation (CHI660E). CV measurements were conducted from 0.01 to 3.0 V at a scan rate of 0.1–0.5 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was recorded by applying an AC voltage of 0.1 mV in a frequency range of 0.01 Hz to 100 kHz at the open circuit potential of the cells.

3. Results and discussion
Figure 1 illustrates the synthetic strategy of ZnS-NC@C and ZnS-NC composites. Firstly, using Zn(NO₃)₂ and 2-methylimidazole as the source of Zn²⁺ ions and organic linkers, respectively, the well-structured ZIF-8 polyhedron was synthesized by the precipitation method. Next, due to the existence of terminal N-H functional group, the interior of ZIF-8 nanocrystals are strongly hydrophobic and exterior surfaces are hydrophilic. So, utilizing the hydrophilic nature and capacity for H-bonding from ZIF-8 and the hydroxyl groups from the RF, the ZIF-8@RF can be obtained. RF shell was transformed into carbon layers during the annealing process under Ar atmosphere, which can coat on or be within the ZnS particles to keep the high electric conductivity and structural stability of the composite during the electrochemical reaction.

Figure 2(a) is the XRD pattern of the as-prepared ZnS-NC@C and ZnS-NC composites. Three diffraction peaks at around 28.5°, 47.6°, and 56.3° can be indexed to the (111), (220), and (311) plane of hexagonal ZnS (ICPD cards No:12-0088). The diffraction peaks become broader, indicating their small size and amorphous structure. Additionally, because of the amorphous nature of the nitrogen-doped carbon, there is no obvious diffraction of C. In figure 2(b), Raman spectrum peaks in the ZnS-NC@C hybrid can be detected at about 1358 and 1600 cm⁻¹, which can be ascribed to the graphite edges (D band) and the graphitic lattice (G band) of the carbon host, respectively. The calculated intensity ratio of the D band to the G band (I_D/I_G) is about 1.18, which can further evidence the amorphous features of the nitrogen-doped carbon polyhedral.

X-ray photoelectron spectroscopy (XPS) is an effective way to confirm the elemental composition and chemical bonding state of materials, as shown in figure 2(c). Zn, O, N, C and S can be easily confirmed in the XPS spectrum of as-prepared ZnS-NC@C composite, which can characterize the presence of ZnS-NC@C. The two peaks at 1021.51 and 1044.61 eV correspond to Zn 2p₉/₂ and Zn 2p₇/₂, respectively, shown in figure 2(d). The high-resolution C 1s spectra (figure 3(e)) shows four peaks related to O=C=O at 288.1 eV,
Figure 1. The synthesis procedure of ZnS-NC@c and ZnS-NC composites.

C–N at 286.2 eV, C= C at 284.6 eV and C– C at 284.1 eV [19]; Moreover, figure 2(f) displays the S 2p spectra and the two major peaks at 161.6 and 163.6 eV indicate the S 2p3/2 and S 2p1/2 in ZnS phase. Figure 2(g) shows that the N 1s spectrum can be deconvoluted into three peaks, pyridinic N (N-6, 397.7 eV), pyrrolic or pyridonic N (N-5, 398.8 eV) and quaternary N (400 eV) [20]. N-5 represents pyrrolic N in a five-membered ring and contributes two electrons to the p system. N-6 is pyridinic N because the N atom substitutes a carbon atom in the C6 ring and bonds with two sp2 carbon atoms. Quaternary N is graphitic N, which is located inside the graphitic carbon plane and bonds with three sp2 carbon atoms. The fitting results for the N 1s spectra of the as-prepared N-doped graphene analogous particles. The N-5 and N-6 species are the dominant N-containing functional groups in all of the MOF-derived N-doped graphene analogous particles. Moreover, the N2 adsorption/desorption isotherms performed on ZnS-NC@c composite belong to type IV with a hysteresis loop of type H4 (figure 4(h)). The pore volumes of the Zns-NC@c and ZnS-NC composites are 0.38 and 0.09 cm3 g−1, respectively. The ZnS-NC@c composite has a specific surface area of 196.1 m2 g−1, which is much higher than that of ZnS-NC composite (2.8 m2 g−1). The ZnS-NC@c composite behaves a narrow pore size distribution of below 10 nm, which is maybe due to the internal hollow structure (the inset of figure 4(h)). The high specific surface area combination with large pore volume is beneficial for a large interface to enhance the contact between electrolyte and active material, and improve lithium and sodium storage performance.

FESEM can characterize the morphologies of the materials, as shown in figure 3. As shown in figure 3(a), ZIF-8 takes on the uniform polyhedron with the size of 100–120 nm. The SEM image of the ZIF-8@RF, shown in figure 3(b), shows the uniform dodecahedrons pile up together with an average diameter of 150 nm, which is larger than that of ZIF-8 due to the RF shell. In the further processing by sulfurizing and calcining for ZIF-8@RF, the as-obtained ZnS-NC@c particles show uniform spheres or polyhedrons with bumpy surfaces, shown in figures 3(c) and (d). N, C-co-doped part could act as a buffer to alleviate the further structure change during sulfidation under the annealing process from the ZIF-8 organic structure, so the as-obtained ZnS-NC@c composite can almost maintain the dodecahedral morphology of precursor. Some hollow spheres or polyhedrons can be obviously seen. In contrast, the ZnS-NC composite shows irregular and broken particles, as indicated in figures 3(e) and (f). The morphology of the ZnS-NC composite changes obviously after sulfuration and annealing processes without the encapsulation of RF shells [16–26].

As shown in figures 4(a) and (b), the synthetic ZnS-NC@c composite behaves hollow spheres with an average diameter size of 170 nm, which is close to the size and morphology of SEM observation. The size of hole is about 20–50 nm. Rough particles are found on the surface of composite particles. In addition, for a single sphere, a shell at the edge of the particle and hollow nanostructure can be observed, shown in figure 4(b). It shows a typical coexistence of micropores and mesopores. Some small holes with the size of about 5–10 nm and an obvious large hole with the size of about 20–50 nm can be seen, which is probably resulted from the water release during the carbonization process. In figure 4(c), the high-resolution TEM (HRTEM) image shows the lattice fringes of 0.31 nm, which match well with the (111) crystal plane of ZnS. The selected-area electron diffraction (SAED) pattern of ZnS-NC@c is shown in figure 4(d), indicating its amorphous nature. The clear diffraction rings correspond to the (111), (220), and (311) crystal planes of the ZnS phase. Besides, the images of elemental mapping of ZnS-NC@c indicate the uniform existence and
Figure 2. (a) XRD patterns of the as-obtained ZnS-NC@C and ZnS-NC composites; (b) Raman spectra of ZnS-NC@C and ZnS-NC composites; (c) XPS survey spectrum; High-resolution XPS spectrum of (d) Zn 2p; (e) C 1s; (f) S 2p; (g) N 1s. Black curves are experimental data and colored curves are deconvolution fits; (h) N$_2$ adsorption/desorption isotherm curves of the ZnS-NC@C and ZnS-NC composites, the inset in (h) shows the corresponding pore size distribution curve.

distribution of C, N, Zn, S elements, shown in figure 4(e). The atomic fraction and mass fraction of C, Zn, S, N determined by EDX measurements of the particles of ZnS-NC@C are shown in table 1 and figure 4(f). The mass fraction of S is 25.54% and the atomic ratio of Zn and S is close to 1:1, which is consistent with the ZnS phase. These results prove that the ZnS-NC@C composite has been obtained, which is consistent with XRD pattern [18, 19, 21–23].

The ZnS-NC@C composite was prepared as anode for LIBs and SIBs. The cycle voltammetry (CV) test was first applied to evaluate the lithium storage mechanism. In the voltage range of 0.01 ~ 3.0 V (vs Li$^+$/Li), figure 5(a) shows the voltammetry (CV) curves for first to five cycles, which are revealed the lithiation/delithiation electrochemical reaction process at a scan rate of 0.1 mV s$^{-1}$. For the first cathodic scan, several reduction peaks appear below 0.9 V, which can be attributed to reduction of ZnS to metallic Zn, the further formation of Zn-Li alloys with multiple steps and the formation of solid–electrolyte interface...
Figure 3. FESEM images: (a) ZIF-8; (b) ZIF-8@RF; (c), (d) ZnS-NC@C composite; and (e), (f) ZnS-NC composite.

Table 1. Atomic fraction and mass fraction of C, Zn, S, N determined by EDX measurements of the particle.

| Element | Atomic fraction (%) | Mass fraction (%) |
|---------|---------------------|------------------|
| C       | 72.38               | 43.28            |
| S       | 9.92                | 15.83            |
| Zn      | 9.95                | 32.39            |
| N       | 7.75                | 5.4              |

(SEI) films due to the decomposition of electrolyte. The basic reactions during positive scan are elucidated by the equations (1) and (2). In the first charging process, the broad anodic peak from 0.25 to 0.7 V can be contributed to the delithiation process of LiZn alloy, demonstrating the multi-step processes of de-alloying of LiZn. Another anodic peak at around 1.39 V in the oxidation scan can be assigned to the regeneration of ZnS from the back-conversion of Zn and Li$_2$S:

\[
\text{ZnS} + 2\text{Li}^+ + 2e^- \leftrightarrow \text{Zn} + \text{Li}_2\text{S} \tag{1}
\]

\[
\text{Zn} + \text{Li}^+ + \text{x}e^- \leftrightarrow \text{Li}_x\text{Zn}. \tag{2}
\]

For the subsequent four CV curves, the well-overlapped reduction/oxidation peaks can be demonstrated the good reversibility towards lithiation/delithiation and excellent electrochemical stability [20, 26, 27]. Figure 5(b) shows the galvanostatic charge/discharge curves of the as-prepared ZnS-NC@C electrode at a current density of 0.1 A g$^{-1}$ in the voltage range from 0.01 to 3.0 V versus Li$^+$/Li. The first discharge and charge specific capacities are around 1500 and 925 mAh g$^{-1}$, which corresponds to a Coulombic efficiency (CE) of about 61.67%. The irreversible capacity loss might be contributed to the formation of SEI layer from the decomposition of electrolyte during the first scanning process [27]. In addition, the slope of the discharge curve ranged from 0.9 to 0.01 V and the plateau at 1.39 V in the charge curve, which correspond to the similar features show in the CV curves of the as-prepared ZnS-NC@C, indicating their similar
Figure 4. (a), (b) TEM images; (c) HRTEM image; (d) SAED pattern; and (e) Elemental mapping of ZnS-NC@C composite; (f) EDX results of ZnS-NC@C composite.

electrochemical behaviors. The profiles of the 2nd, 3rd cycles are nearly overlapped, showing an excellent cycling stability of ZnS-NC@C electrode.

The specific discharge capacities of ZnS-NC@C electrode are 880, 730, 660 mAh g$^{-1}$ at current densities of 100, 200 and 500 mA g$^{-1}$, respectively, shown in figure 5(c). And more remarkable, at the high current densities of 1000 and 2000 mA g$^{-1}$, the specific capacities can still reach up to 600 and 470 mAh g$^{-1}$, even after ten cycles, which can still maintain at 590 and 450 mAh g$^{-1}$, respectively. Additionally, when the current density is returned back to 100 mA g$^{-1}$, the specific capacity of ZnS-NC@C electrode can quickly recover to 910 mAh g$^{-1}$ and extend to 960 mAh g$^{-1}$ after ten cycles, suggesting the high reversibility and
Figure 5. Electrochemical tests of ZnS-NC@C electrode for LIBs: (a) CV curves at a scan rate of 0.1 mV s\(^{-1}\) in the voltage range of 0.01–3.0 V; (b) galvanostatic discharge/charge curves at 0.1 A g\(^{-1}\); (c) rate performance; (d) cycling performance at 0.1 A g\(^{-1}\); (e) long-term cycling stability at current density of 1 A g\(^{-1}\); (f) Nyquist plots of ZnS-NC@C before and after cycling and corresponding equivalent circuit model (inset); (g), (h) FESEM images of ZnS-NC@C electrode after 50 cycles in LIBs.

...good rate performance of the ZnS-NC@C electrode. Figure 5(d) displays the cycling performance of ZnS-NC@C electrode at a current density of 100 mA g\(^{-1}\), the initial 20 cycles shows stable capacity at 880 mAh g\(^{-1}\) and to the subsequent cycles exhibit a typical increasing slope. To further verify the high-rate cycling stability, ZnS-NC@C electrode is tested at a high current density of 1 A g\(^{-1}\). A reversible capacity of 748.32 mAh g\(^{-1}\) still maintains after 500 cycles with the Coulombic efficiency of about 100%, shown in figure 5(e). After 100 cycles, it is accompanied by obvious capacity increasing, which can be ascribed to the following points: (a) the reversible formation/dissolution of gel-like polymer layer formed at the interface between electrode and electrolyte can provide extra capacity; (b) the repeated processes of reversible reaction could facilitate Li-diffusion kinetics; (c) the defects generated upon multiple cycles provide extra lithium storage sites [28]. Figure 5(f) shows the Nyquist plots of ZnS-NC@C electrode before and after 50 cycles. The semicircle in the high frequency region corresponds to the charge transfer resistance (\(R_{ct}\)) on the interface between electrolyte and electrode, while the slop line at low frequency is related to lithium-ion diffusion process in the electrode. Fitted by the equivalent electrical circuit, the \(R_{ct}\) decreases to 93.35 \(\Omega\) after 50 cycles, in comparison, the \(R_{ct}\) is 99.92 \(\Omega\) before 50 cycles, which should be ascribed to activation process during lithium-ion insertion and extraction. The ZnS-NC@C electrode maintains mostly sphere-like morphology after 50 cycles in LIBs, shown in figures 5(g) and (h). It can be seen that this strategy of synthetic ZnS-NC@C
Figure 6. Electrochemical tests of ZnS-NC@C for SIBs: (a) CV curves at a scan rate of 0.1 mV s$^{-1}$ in the voltage range of 0.01–3.0 V; (b) galvanostatic discharge/charge curves at 0.1 A g$^{-1}$; (c) Rate performance at different current densities (100, 200, 500, 1000, 2000 mA g$^{-1}$); (d) cycling performance at 0.1 A g$^{-1}$; (e) cycling performance at 1.0 A g$^{-1}$; (f) Nyquist plots of the ZnS-NC@C and ZnS-NC electrodes (inset) corresponding equivalent circuit model (inset); (g), (h) FESEM images of ZnS-NC@C electrode after cycling in SIBs.

is effective for improving the performance in comparison to bare ZnS, which might benefit from rational hybridization of ZnS and N, C-co-doped and C-coated structure.

The electrochemical performance of ZnS-NC@C composite in SIBs is not as expected performance in LIBs because the larger radius of sodium ion than lithium ion and the sluggish kinetics, making Na$^+$ ions much more difficult to insert/extract into/from the active materials. That is the reason why lots of electrode materials with good performance for LIBs, but for SIBs they exhibit limited specific capacity and poor cycle life. However, based on the hollow structure and rational combination of N, C-doping and carbon coating, the as-prepared ZnS-NC@C composite exhibits excellent sodium storage performance.

Sodium storage behavior of as-prepared ZnS-NC@C was accessed through both CV and galvanostatic cycling measurement. Similar to the CV curve in LIB, the open circuit voltage and cycling from 0.01 to 3.0 V (vs Na/Na$^+$) at the constant rate of 0.1 mV s$^{-1}$, shown in figure 6(a). At the first cathodic scan, the broad peak below 0.5 V is recorded, corresponding to the initial insertion of sodium ions into ZnS-NC@C electrode (equations (3) and (4)) and the formation of SEI layer [28–30]. The anodic peaks in the corresponding reverse scan at 0.9 V can be assigned to the extraction of sodium ions and the reformation of ZnS:

Conversion reaction: $\text{ZnS + 2Na}^+ + 2e^- \leftrightarrow \text{Zn + Na}_2\text{S}$  \hspace{1cm} (3)

Alloying/dealloying reaction: $13\text{Zn} + 3\text{Na}^+ + 3e^- \leftrightarrow 3\text{Na}_2\text{Zn}_{13}$, \hspace{1cm} (4)
Notably, after 1st cycle, the CV curves are almost well overlapped, indicating the good reversibility and electrochemical stability of the as-prepared ZnS-NC@C composite. The discharge/charge profiles of the ZnS-NC@C electrode are shown in figure 6(b). The first cycles charge and discharge capacities of as-prepared ZnS-NC@C are 484.37 and 677.23 mAh g\(^{-1}\), and the Coulombic efficiency is 71.5%. The low initial Coulombic efficiency can be ascribed to the consumption of Na\(^+\) ions for the formation of SEI. In figure 6(c), the ZnS-NC@C electrode can deliver remarkably high reversible specific discharge capacities of 475.4, 419.2, 310.5, 245.4 and 188.6 mAh g\(^{-1}\) at the current densities of 100, 200, 500, 1000 and 2000 mA g\(^{-1}\), respectively. Though the capacity of the ZnS-NC@C fades during the initial cycles, the capacity quickly recovers to as high as 472.2 mAh g\(^{-1}\) when the current density is finally returned back to 100 mA g\(^{-1}\), demonstrating the excellent robustness of the electrode. In figure 6(d), the ZnS-NC@C behaves a reversible capacity of 476.5 mAh g\(^{-1}\) at the current density of 100 mA g\(^{-1}\) after 140 cycles and the CE is increased rapidly to almost 100%, except the initial a few cycles. In addition, the electrochemical performance of ZnS-NC@C in SIBs is evaluated at a high current density of 1 A g\(^{-1}\), as shown in figure 6(e). The discharge capacity is 625.7 mAh g\(^{-1}\) in first cycle with the CE of 75.6%. After 500 cycles, a reversible capacity of 150.9 mAh g\(^{-1}\) can be retained and about 98.5% retention rate, and there is a steady trend of capacity. These results suggest that the ZnS-NC@C composite exhibits good electrochemical performance and long-term cycling performance. In order to study the reaction kinetics of the electrode materials and to have a better insight into the superior performance of composites, EIS was measured. Figure 6(f) shows the Nyquist plots related to the ZnS-NC@C and ZnS-NC electrodes. The Nyquist plots of both electrodes are composed of a depressed semicircle in the high frequency region, a large semicircle in the medium frequency region, and a sloped straight line in the low frequency region. Apparently, the two electrodes show much difference in the charge transfer resistance. The \(R_{ct}\) of the ZnS-NC@C is below 30 \(\Omega\), in comparison, the \(R_{ct}\) of the ZnS-NC is above 400 \(\Omega\) (the inset of figure 6(f)), suggesting carbon shell from RF is an effective strategy to enhance the conductivity of ZnS. The FESEM images (figures 6(g) and (h)), show that the ZnS-NC@C electrode still maintains sphere-like morphology after cycling in SIBs.

The above results strongly suggest that the remarkable electrochemical performance of ZnS-NC@C is due to the N, C co-doping, carbon coating and hollow structure. These are further confirmed by additional studies in the following. CV tests of the ZnS-NC@C at different sweep rates were performed to help us better understand the kinetic effects and rate capability of the ZnS-NC@C structure. As shown in figure 7(a), the CV curves at different scan rates ranging from 0.1 to 0.5 mV s\(^{-1}\), which can be seen that both the cathodic and anodic become broad and the current increase as the sweep rates increase. These CV curves display similar peaks. The total stored charge can be separated into three components: the faradaic contribution from the Na\(^+\) ions insertion process, the faradaic contribution from the charge-transfer process with surface atoms (pseudocapacitance), and the nonfaradaic contribution from the double layer effect. These capacitive effects can be distinguished by analyzing the relationship between the current \((i)\) and the scan rate \((v)\) at various scan rates, which can be expressed as the equation (5):

\[
i = av^b\tag{5}
\]

where \(i\) and \(v\) are the peak current and scan rate, respectively, \(a\) and \(b\) are adjustable parameters. For \(b = 0.5\), the current response is diffusion controlled, which is indicative of a faradaic intercalation process. For \(b = 1.0\), which is representative of ideal capacitive behavior. When the values of \(b\) located in the range of 0.8–1.0, indicating that the current is predominantly capacitive. Equation (5) can be transformed to

\[
\log i = b \log v + \log a. \tag{6}
\]

By plotting \(\log i\) vs. \(\log v\) according to the equation (6), the \(b\)-values of these peaks can be determined, as shown in figure 7(b). The \(b\)-values of peaks 1, 2 and 3 are 0.803, 0.932 and 0.544, respectively. According to the previous report, the current at a fixed voltage consists of two independent mechanisms: the current contributions from the surface capacitive effects \((k_1v)\) and the diffusion-controlled Na\(^+\) intercalation process \((k_2v^{1/2})\):

\[
i = k_1v + k_2v^{1/2}. \tag{7}
\]

Because the CV curves at different scan rates are similar, the values of \(k_1\) and \(k_2\) are the same to each other. To determine the value of \(k_1\) and \(k_2\), equation (7) can be transformed to
Figure 7. (a) CV curves for SIBs at different scan rates ranging from 0.1 to 0.5 mV s\(^{-1}\). (b) Capacitance-controlled current (shaded region) as a share of total current at a scan rate of 0.5 mV s\(^{-1}\). (c) Log–Log plots of peak current vs. sweep rate for each peak and the slopes of the fitted lines; capacitance-controlled current (shaded region) as a share of total current at a scan rate of 0.5 mV s\(^{-1}\). (d) Contribution ratio of capacitive and diffusion controlled capacities at different scan rates.

\[ i/v^{1/2} = k_1 v^{1/2} + k_2. \]  

(8)

Separate curves are obtained at the scan rates of 0.5 mV s\(^{-1}\) for fixed potentials according to equation (8). As shown in figure 7(c), the shaded part corresponds to the capacitive contribution to the current, which is 59.41% of the total capacity at a scan rate of 0.5 mV s\(^{-1}\). As the scan rate increases from 0.1 to 0.5 mV s\(^{-1}\), the capacity contributions are calculated to be 37.68, 43.11, 46.97, 50.84 and 59.41%, respectively, shown in figure 7(d), suggesting that the kinetics of interfacial Na\(^+\) ion storage is sufficient while the kinetic of Na\(^+\) ion diffusion is limited at high rates [31]. All the CV analyses indicate the effect of the hollow structure of ZnS-NC@C with capacity dominated behavior to further prove that the high capacity, good rate capability and long cycle life at the same time.

Table 2 shows the specific capacities of this work and some previously reported ZnS-based anodes at various current densities for LIBs and SIBs. As anode material in LIBs, the as-prepared ZnS-NC@C composite behaves the highest discharge capacity among these ZnS-based composites. As anode material in SIBs, though the ZnS-NC@C composite exhibits good electrochemical performance, its discharge capacity needs to be improved at the large rate.

All these factors, which are helpful to the improvement of high-specific capacity, good rate capability and long-term cyclic stability for LIBs and SIBs, are as follows: the ZIF-8 precursor, unique hollow structure, the rational hybridization of ZnS with the carbon shell. These factors promote the hybrid turn into one of the promising electrochemical materials in LIBs and SIBs [32]. It is worth mentioning that the hollow structure of ZnS hybrid with carbon shell can not only promote the diffusion of electrolyte and Li\(^+\) and Na\(^+\) ions movement, but also can act as a buffer to alleviate the volume variations. Consequently, the ZnS-NC@C electrode can be used as a high-performance SIB anode with high specific capacity and good rate capability, and cycling stability.
Table 2. The specific discharge capacities of ZnS-NC@C and reported ZnS-based electrodes in LIBs and SIBs.

| Materials       | Current density (A g⁻¹) | Reversible capacity (mA hg⁻¹) | Battery | Reference |
|-----------------|-------------------------|-------------------------------|---------|-----------|
| ZnS-NC@C        | 1.0                     | 783 (450 cycles)              | LIB     | This work |
| ZnS-NC@C        | 0.1                     | 476.5 (500 cycles)            | SIB     | This work |
| ZnS@HPC         | 1.0                     | 408 (200 cycles)              | LIB     | [32]      |
| ZnS/C           | 0.4                     | 304.4 (300 cycles)            | LIB     | [7]       |
| ZnS@NC          | 1.0                     | 520 (200 cycles)              | LIB     | [31]      |
| ZnS/PCNFs       | 0.2                     | 718 (150 cycles)              | LIB     | [8]       |
| ZnS@graphite    | 0.1                     | 444 (300 cycles)              | LIB     | [33]      |
| Core–shell ZnS/C| 0.2                     | 750 (500 cycles)              | LIB     | [19]      |
| Hollow ZnS@C    | 0.1                     | 760 (240 cycles)              | LIB     | [34]      |
| ZnO@NC@CNTs     | 1.0                     | 300 (100 cycles)              | LIB     | [35]      |
| ZnS-RGO         | 0.1                     | 481 (50 cycles)               | SIB     | [13]      |
| ZnS/GAs         | 1.0                     | 362 (300 cycles)              | SIB     | [17]      |

4. Conclusions

In summary, hollow ZnS-NC@C hybrid derived from ZIF-8@RF was obtained after sulfidation and carbonization, which features carbon shell, N, C co-doping, and nanoscale. With the benefits of hollow structure and high carbon content, the ZnS-NC@C composite exhibits great electrochemical performance. As anode materials in LIBs and SIBs, the ZnS-NC@C composite behaves the reversible capacity of 748.3 and 150.9 mA h g⁻¹ at a current density of 1.0 A g⁻¹ after 500 cycles, respectively. The ZnS composite based on MOFs can enhance obviously the specific capacity, rate capability, and cycling stability. This kind of synthesis strategy can be extended to preparation and modification of the other metal sulfides.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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