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Short communication

Highly efficient sol-gel synthesis for ZnS@N, S co-doped carbon nanosheets with embedded heterostructure for sodium ion batteries

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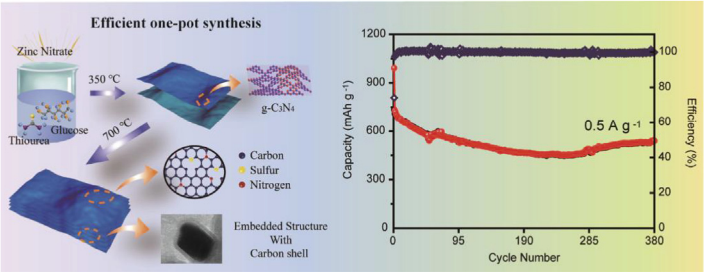
HIGHLIGHTS

- ZnS nanoparticles embedded in N, S codoped carbon framework are prepared for SIBs.
- An efficient one-pot sol-gel synthesis is developed.
- Ultrafine carbon shell is observed on ZnS nanoparticles.
- The as-prepared electrode can last for 380 cycles with 73.6% capacity retention.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein, ZnS nanoparticles on Nitrogen (N) and Sulphur (S) co-doped carbon nanosheets (ZnS@NSC) are prepared through a highly efficient sol-gel synthesis. Interestingly, the ZnS nanoparticles are encapsulated in ultrathin carbon shells, which are crucial to buffer the volume changes of ZnS during sodium ion intercalation/deintercalation. Meanwhile, the nanosheets and ultrafine carbon shells together constitute the N, S co-doped carbon framework, which not only can give rise to abundant active sites for sodium storage but also greatly enhance the electrical conductivity. As a result, the ZnS@NSC achieves a reversible capacity of 734 mAh g^{-1} at 0.5 A g^{-1} and excellent cycling stability (73.6% capacity retention after 380 cycles at 0.5 A g^{-1}).

1. Introduction

Sodium ion batteries (SIBs) are considered as an alternative to Lithium ion batteries (LIBs) due to low cost and widespread distribution of sodium [1–4]. Metal sulfides, with their large theoretical capacity and weak M-S bonds favoring conversion reactions, stand out over other anode materials (hard carbon, Sn, P, etc.) for SIBs [5]. Among them, non-toxic ZnS has been proven as a promising SIB anode with large reversible capacity and low discharge voltage plateau [6,7]. Wang and co-workers reported that ZnS nanospheres with mesopores exhibited a reversible discharge capacity of 774 mAh g^{-1} over 100 cycles at 40 mA g^{-1} in ether-based electrolyte [7]. However, similar to other metal sulfides in SIBs, the intrinsic sluggish kinetics of conversion reactions and large volume expansion during cycling result in limited

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cycle life (50–100 cycles) for ZnS as SIBs anode.

Carbonaceous materials have been proved to be efficient support for loading metal sulfides because they can buffer the volume change, function as "highway" for electrons, and provide sodium ion storage sites by hetero-elements doping [7–14]. Hence, ZnS composited with carbon matrix have been successfully developed and exhibit enhanced cycle performance and rate capability [15–17]. Nevertheless, most of them were synthesized through complex procedures, including the first preparation of carbon matrix, and/or subsequent hetero elements doping, metal sulfides synthesis, *etc*. [11,18–20]. The performance of as-prepared composites is usually limited by the deficient contact between metal sulfides and carbon matrix owing to the complex and inefficient synthesis procedures. Therefore, it is still a great challenge to develop a facile or one-pot method for high-performance ZnS/carbon composites. In this work, we synthesized the uniformly dispersed ZnS nanoparticles on Nitrogen (N) and Sulphur (S) co-doped carbon nanosheets (ZnS@NSC) through a one-pot method. Additionally, an ultrafine carbon shell on ZnS nanoparticles was simultaneously *in situ* formed with the graphene-like carbon nanosheets, which enabled the complete contact between ZnS and carbon matrix. As a result, the ZnS@NSC achieves a reversible capacity of 734 mAh g^{-1} at 0.5 A g^{-1} and excellent cycling stability (73.6% retention after 380 cycles at 0.5 A g^{-1}).

2. Experimental

2.1. Synthesis

The ZnS@NSC composites were synthesized through a sol-gel method, followed by heat treatment. Typically, certain mass of thiourea (10 g), glucose (1 g), and $Zn(NO_3)_2 \cdot 6H_2O$ (0.8, 1.2, or 1.8 g) were dissolved in a mixed solution containing 50 mL of distilled water and 150 mL of ethanol. The solution was stirred continuously in a water bath at 75 °C to form a sol, which was then dried in an oven at 100 °C for 12 h. Subsequently, the as-prepared precursor was preheated at 350 °C for 2 h and then heated at 600, 700 or 800 °C for 5 h in Argon atmosphere to obtain the final product.

3. Results and discussion

Thiourea is known as an active molecular precursor under thermal treatment, in which self-polymerization and condensation will be triggered to form the two-dimensional layered graphitic carbon nitride (g-C_3N_4) networks [21]. As schematically illustrated in Fig. 1a, the precursor containing zinc nitrate, glucose and thiourea was first heated at 350 °C to generate the g-C_3N_4 anchored with ZnS nanoparticles [22]. In the meantime, the aromatic carbon intermediates originated from the decomposition of glucose at 250–350 °C adhere on the surface of sulphur doped g-C_3N_4 nanosheets and the *in situ* formed ZnS nanoparticles. Subsequently, the g-C_3N_4 was then adopted as a self-sacrificing template because of its complete pyrolysis at temperature > 700 °C [23]. Simultaneously, the carbonization of aromatic carbon intermediates at 600–800 °C results in the formation of graphene-like carbon nanosheets and ultrafine carbon shells on ZnS nanoparticles. Notably, the decomposition of thiourea provided N and S sources for N and S co-doping in carbon nanosheets. The scanning electron microscopy (SEM) images in Fig. 1b–d shows the crumpling nanosheet morphology of ZnS@NSC-x-700 samples (x is the starting material mass of zinc nitrate: 0.8, 1.2, and 1.8 g), indicating the graphene-like carbon framework has been successfully obtained. The crumples can significantly improve the specific surface area. As shown in Fig. S1 in Supporting Information (SI), the specific surface area of ZnS@NSC-1.2-700 sample is determined to be 33.64 $m^2\,g^{-1}$, which is higher than recently reported ZnS nanoparticles on N, S co-doped carbon composites (13.5 $m^2\,g^{-1}$) [15]. Notably, no obvious ZnS nanoparticles can be observed on the nanosheets of ZnS@NSC-x-700 samples.

X-ray diffraction (XRD) patterns of ZnS@NSC-x-700 samples in Fig. 2a exhibit strong pattern diffraction peaks corresponding to wurtzite ZnS (JCPDS card: 36–1450). A small weak peak can also be observed at around 26°, which can be assigned to the (002) reflection of graphitic carbon. Fig. 2b presents the thermogravimetric analysis (TGA) of ZnS@NSC-1.2-700 sample. The final mass retention of 42% at 800 °C can be attributed to the formed ZnO. Consequently, the content of ZnS in ZnS@NSC-1.2-700 was calculated to be 53.5%.

Fig. 2c reveals the C1s core-level XPS spectrum of ZnS@NSC-1.2-700, from which four peaks can be deconvoluted by the fitting analysis. The four peaks at 284.2 eV, 284.9 eV, 286.2 eV, and 288.4 eV can be attributed to C—C/C=C, C—S, C—N and C=O bonds, respectively [22,24,25], indicating the successful modification of heteroatoms in the carbon matrix. The S 2p core-level spectrum shown in Fig. 2d presents multiple peaks, including two Zn—S peaks at 161.2eV and 162.2 eV [16], a broad C-SO_x-C peak at 168.5 eV, and a broad C—S—C covalent peak at 164.4 eV [15]. Notably, the ratio between Zn—S $2p_{1/2}$ and Zn—S $2p_{3/2}$ is much higher than 1:2 for pure ZnS, which can be ascribed to the occurrence of C—S—Zn bonds [11,15]. The C—S—Zn bonds in the composites enable good structural stability for ZnS particles to pin on the 3D carbon framework. Its conductivity can also be improved with free electrons flowing directly between C, S, and Zn atoms due to the

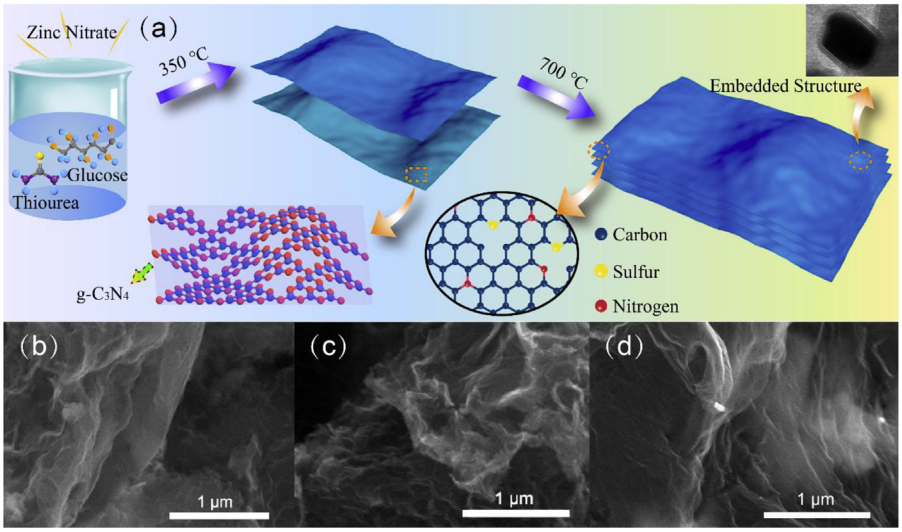

Fig. 1. (a) Schematic illustration for the synthesis of ZnS@NSC-x-700. (b–d) SEM images of ZnS@NSC-x-700.