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Hierarchical Microboxes Constructed by SnS Nanoplates Coated with Nitrogen-Doped Carbon for Efficient Sodium Storage

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Abstract

We demonstrate the delicate design and synthesis of hierarchical microboxes assembled from SnS nanoplates coated with nitrogen-doped carbon (NC) as an anode material for sodium-ion batteries. The template-engaged multistep synthesis of the SnS@NC microboxes involves sequential phase transformation, polydopamine coating, and thermal annealing in N₂. The SnS@NC composite with two-dimensional nanosized subunits rationally integrates several advantages including shortening the diffusion path of electrons/Na⁺ ions, improving electric conductivity and alleviating volume variation of the electrode material. As a result, the SnS@NC microboxes manifest efficient sodium storage performance with high capacity, good cycling stability, and excellent rate capability.

Keywords: SnS, hollow structures, sodium-ion batteries, nitrogen-doped carbon, microboxes.

In recent years, there has been enormous interest for sodium-ion batteries (SIBs) as a potential technology for large-scale energy storage with merits of the profusion and low cost of sodium resources.^[1-5] However, due to the larger size of Na⁺ ion compared to Li⁺ ion, it is a great challenge to find proper electrode materials for efficient storage, and quick and stable insertion/extraction of Na⁺ ions.^[6-8] Among the examined anode materials, tin-based sulfides (e.g., SnS₂ and SnS) with unique layered structures and large lattice spacings can accommodate Na⁺ ions through combined conversion and alloying mechanisms, thus delivering high capacities.^[9-15] In comparison, SnS is more promising than SnS₂ because of the less phase conversion and the smaller lattice expansion during the sodiation/desodiation processes.^[13-15] Despite these advantages, the direct use of SnS as an anode material for SIBs suffers from large polarization and inferior rate capability owing to the poor electric conductivity.

Compositing the electrode material with carbonaceous species is a typical method to enhance electric conductivity and buffer volume variation of the electrodes.^[16-19] In particular, doping of nitrogen into carbon materials is a reliable approach to further amend the electrical property and thus improve the electrochemical performance.^[20-22] On the other hand, recent studies demonstrate that the realization of efficient sodium storage also strongly depends on the engineering of electrode materials with suitable nanostructures.^[23]

Hierarchical hollow structures constructed by two-dimensional (2D) nanosized building units have shown obvious advantages for SIBs.^[24-26] The hollow configuration with large surface area can not only relax the volume changes for electrodes, but also provide rich active sites and sufficient electrode-electrolyte contact area for electrochemical reactions.^[27-29] Moreover, the hierarchical nanoshells could shorten the diffusion length of electrons/Na⁺ ions to accelerate electrochemical kinetics.^[24-25] On the basis of the above-mentioned considerations, it might be highly desirable to integrate these strategies into the development of new electrode materials to maximize their potential for SIBs.

Herein, we demonstrate the delicate design and fabrication of hierarchical microboxes composed of SnS nanoplates coated with nitrogen-doped carbon (NC) by an effective step-by-step approach as an anode material for SIBs. The multistep production of the complex hollow architecture is schematically illustrated in **Figure 1**. Perovskite hydroxide $\text{ZnSn}(\text{OH})_6$ microboxes are first employed as the precursor to generate hierarchical SnS_2 microboxes assembled from nanoplates through a phase transformation reaction (step I). Then, the surface of SnS_2 nanoplates is coated with a thin layer of polydopamine (PDA) via a sol-gel method to obtain hierarchical $\text{SnS}_2@\text{PDA}$ microboxes (step II). Lastly, the $\text{SnS}_2@\text{PDA}$ microboxes are heated in N_2 to convert the PDA layer to a NC shell and concurrently reduce the SnS_2 to SnS (step III), yielding the hierarchical SnS@NC microboxes. The unique SnS@NC hybrid synergistically combines the electrochemical functions of SnS and NC into a three-dimensional (3D) hierarchical hollow construction with 2D nanoscale subunits. The as-synthesized SnS@NC microboxes show remarkable sodium storage properties with high specific capability, good cycling stability, and excellent rate performance.

Uniform $\text{ZnSn}(\text{OH})_6$ microboxes are synthesized according to a modified co-precipitation method (Figure S1, Supporting Information(SI)).^[30] The successful preparation of $\text{ZnSn}(\text{OH})_6$ is verified by powder X-ray diffraction (XRD) and energy-dispersive X-ray (EDX) tests (Figure S2, SI). The $\text{ZnSn}(\text{OH})_6$ precursor is then transformed to a SnS_2 phase (JCPDS card no. 01-1010) completely through a hydrothermal sulfidation reaction with the assistance of H_4EDTA to extract Zn^{2+} via complexation (Figure S3, SI).^[31] Field-emission scanning electron microscopy (FESEM) images reveal that the SnS_2 particles possess a cubic framework structure with high uniformity (**Figure 2a** and Figure S4a, SI). The closer FESEM examinations clearly show the hierarchical shells of SnS_2 microboxes, which are randomly assembled from nanoplates with the thickness of about 10-20 nm (Figure 2b,c and Figure S4b,c, SI). The well-defined hollow structure of the SnS_2 particles is confirmed by transmission electron microscopy (TEM) studies (Figure 2d and Figure

S4d,e, SI). In the high-resolution TEM (HRTEM) image, the clear lattice fringes with spacing of 0.59 nm are indexed to the (001) crystal planes of hexagonal SnS₂ (Figure 2e). Afterward, the SnS₂ microboxes are coated with a thin layer of PDA to acquire the SnS₂@PDA microboxes.^[32] FESEM images display that SnS₂@PDA well maintains the hierarchical cubic morphology with an increased thickness in the nanoplate building blocks (Figure 2f,g and Figure S5a,b, SI). XRD pattern confirms that the SnS₂ phase is unchanged and EDX spectrum reflects the presence of PDA after the coating (Figure S6, SI). The hierarchical hollow construction of SnS₂@PDA and the core-shell structure of the building units are evidenced by TEM observation (Figure 2h and Figure S5c,d, SI). HRTEM image of an individual SnS₂@PDA nanoplate reveals that the SnS₂ core is tightly covered by a uniform PDA layer with thickness of about 5 nm (Figure 2i).

The hierarchical SnS₂@PDA microboxes can withstand an annealing treatment under a N₂ atmosphere at 600 °C for 2 h. After that, the PDA layer is converted to a NC shell and simultaneously the SnS₂ core is reduced to SnS by the derived NC, forming the SnS@NC hybrid structure. The phase purity of SnS (JCPDS card no. 39-0354) is validated by XRD (Figure S7a, SI), and the EDX spectrum indicates the existence of NC in SnS@NC with a nitrogen content of about 2.5 wt.% (Figure S7b, SI). FESEM and TEM images clearly show the hierarchical hollow configuration of SnS@NC microboxes organized by nanoplates (**Figure 3a-e**, and Figure S8a,b, SI). Further TEM investigations reveal the intimate core-shell structure of the SnS@NC nanoplates made of crystallized particles (Figure S8c,d, SI). HRTEM image of a single SnS@NC nanoplate exhibits visible lattice fringes with an interlayer distance of 0.28 nm identified as the (111) planes of orthorhombic SnS, and discerns the outer NC shell with a thickness of about 4 nm (Figure 3f). The valence states of elements in SnS@NC are determined by X-ray photoelectron spectroscopy (XPS, Figure S9, SI). In virtue of the 3D hierarchical hollow structure and the 2D secondary units, SnS@NC possesses the porous characteristics with a high specific surface area of 75 m² g⁻¹ (Figure S10, SI), which might be favorable for facilitating ion/electrolyte transport and at the same time

endow abundant active sites for electrochemical reactions. For comparison, some bare SnS material without carbon coating is also synthesized (Figures S11 and S12, SI).

The electrochemical properties of the hierarchical SnS@NC microboxes are evaluated as an anode material for SIBs. The Na⁺ ion storage behavior of the SnS@NC electrode is first investigated by cyclic voltammetry (CV) (Figure S13, SI). In the first cathodic scan, the small reduction peak at around 0.92 V should be assigned to the conversion of SnS to Sn and Na₂S,^[15] while the strong peak located at 0.55 V is attributed to the subsequent alloying reaction between Sn and Na, and the formation of solid-electrolyte interface (SEI) film.^[15, 24, 33] From the second cathodic scan onward, two peaks at about 1.05 and 0.67 V are observed, which are associated with the conversion reaction of SnS^[15] and the multistep alloying reaction between Sn and Na,^[13, 15, 18] respectively. In the anodic scans, the oxidation peaks at around 0.35 and 0.70 V correspond to the multistep dealloying reaction of Na_xSn to Sn,^[13-15] and the two peaks at around 1.07 and 1.35 V represent the reverse conversion reaction from Sn to SnS_x.^[12-13, 24] The small shoulder peak at ~1.75 V might be related to the de-intercalation of Na⁺ ions from layered SnS_x materials.

Figure 4a shows the representative galvanostatic discharge-charge voltage profiles in a cutoff voltage range of 0.01-3.0 V versus Na/Na⁺ at a current density of 0.1 A g⁻¹. The SnS@NC electrode delivers high initial discharge and charge capacities of 759 and 581 mAh g⁻¹, respectively, corresponding to a Coulombic efficiency (CE) of 76.5 %. The relatively low initial CE mainly results from the decomposition of electrolyte and the formation of SEI film in the initial cycle.^[24] The first discharge curve is different from the ones in the subsequent cycles, suggesting that the electrode material experiences large structural and compositional changes during the first cycle.^[14, 16] After the first cycle, the capacity quickly stabilizes and the discharge-charge curves almost overlap with each other, indicating the electrochemical reactions are highly reversible and stable in the SnS@NC electrode. At a higher current density of 0.5 A g⁻¹, the discharge-charge voltage profiles are also very similar up to 100 cycles (Figure S14, SI).

The rate capability of the hierarchical SnS@NC microboxes for sodium storage is evaluated by galvanostatic tests at various current densities. As presented in Figure 4b, the SnS@NC electrode delivers average specific capacities of 607, 567, 502, and 456 mAh g⁻¹ at the current densities of 0.1, 0.2, 0.5, and 1.0 A g⁻¹, respectively. Of note, the capacities at all the current densities are very stable except the initial cycle. Importantly, when the current density is abruptly returned back from 1.0 to 0.1 A g⁻¹, the discharge capacity quickly recovers and the voltage plateaus can fully resume (Figure S15, SI), suggesting the good reversibility of SnS@NC for sodium storage.^[15] Furthermore, the outstanding rate performance of the SnS@NC electrode is also revealed by the discharge-charge voltage profiles at various current densities (Figure S16, SI). In sharp contrast, the specific capacities of the bare SnS electrode decline fast with the increase in current density (Figure S17, SI).

The cycling performance of the SnS@NC electrode at a current density of 0.5 A g⁻¹ is shown in Figure 4c. A high discharge capacity of 443 mAh g⁻¹ is obtained over 100 cycles without apparent capacity fading. During the cycling tests, the CE is close to 100 % except for the first few cycles. For comparison, the SnS electrode manifests poor cycling performance with substantial capacity loss. As an anode material for SIBs, the performance of SnS@NC microboxes is comparable to those of other SnS-based materials (Table S1, SI). Electrochemical impedance spectra indicate that the charge-transfer resistance of the SnS@NC electrode is much smaller than that of the SnS electrode (Figure S18, SI).^[16] Control experiments reveal that the coated amount of NC shows some effect on the sodium storage performance of the final SnS@NC materials (Figures S19 and S20, SI). After the cycling tests, the morphological and compositional changes in the SnS@NC electrode are examined by FESEM, XRD and EDX (Figures S21-23, SI). All the above results highlight the efficient sodium storage properties of the SnS@NC microboxes, which may be attributed to their distinct hierarchically hollow hybrid structure. More specifically, the overall hollow configuration can buffer the mechanical strain induced by the insertion/extraction of Na⁺ ions during cycling. Besides, the nanoplate building blocks could reduce the diffusion length of

electrons/Na⁺ ions to promote the electrochemical kinetics.^[13-14, 24] The outer NC shell would enhance the electric conductivity to accelerate the charge transfer process and more importantly buffer the volume change during repeated insertion/extraction of Na⁺ ions hence improving the stability of the electrode material.

In summary, hierarchical microboxes assembled from nitrogen-doped carbon (NC) coated SnS nanoplates are synthesized as an anode material for sodium-ion batteries (SIBs). The designed synthesis involves sequential phase transformation, polydopamine coating and thermal annealing in N₂. The hierarchical SnS@NC microboxes hold several structural and compositional advantages including improved electric conductivity, reduced diffusion distance for electrons/Na⁺ ions, ameliorated volume variation, and more active sites for electrochemical reactions. The SnS@NC microboxes show efficient sodium storage properties in terms of high capacity, good cycling stability and outstanding rate performance. This work may inspire the design and construction of advanced anode materials for sodium-ion batteries.

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Figures and Captions

Figure 1. Schematic illustration of the synthetic process of hierarchical SnS@NC microboxes: (I) phase transformation, (II) PDA coating, and (III) thermal annealing in N_2 .

Figure 2. (a-c) FESEM images and (d) TEM image of hierarchical SnS₂ microboxes. (e) HRTEM image of a SnS₂ nanoplate. (f,g) FESEM images and (h) TEM image of hierarchical SnS₂@PDA microboxes. (i) HRTEM image of an individual SnS₂@PDA nanoplate.

Figure 3. (a-c) FESEM images and (d,e) TEM images of hierarchical SnS@NC microboxes. (f) HRTEM image of a single SnS@NC nanoplate.

Figure 4. Electrochemical performance of hierarchical SnS@NC microboxes for sodium storage. (a) Discharge-charge voltage profiles for the 1st, 2nd, 3rd, 4th, 5th and 10th cycles at a current density of 0.1 A g⁻¹. (b) Rate performance at various current densities. (c) Cycling performance of SnS@NC and SnS at a current density of 0.5 A g⁻¹ and the corresponding Coulombic efficiency of SnS@NC.

for Table of Content Entry

Hierarchical microboxes constructed by SnS nanoplates coated with N-doped carbon (NC) are synthesized as an anode material for sodium-ion batteries. Benefiting from the unique structural and compositional advantages, the SnS@NC microboxes show efficient sodium storage performance with high capacity, long cycling stability and superior rate capability.