Co$_9$S$_8$@carbon nanospheres as high-performance anodes for sodium ion battery

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HIGHLIGHTS

- Co$_9$S$_8$@C nanospheres with 5 nm carbon shell and 50 nm Co$_9$S$_8$ core has been prepared.
- The composite show a specific capacity of 305 mAh g^{-1} at 5 A g^{-1} after 1000 cycles.
- The process can be used for synthesis of other metal sulfides for energy storage.

GRAPHICAL ABSTRACT
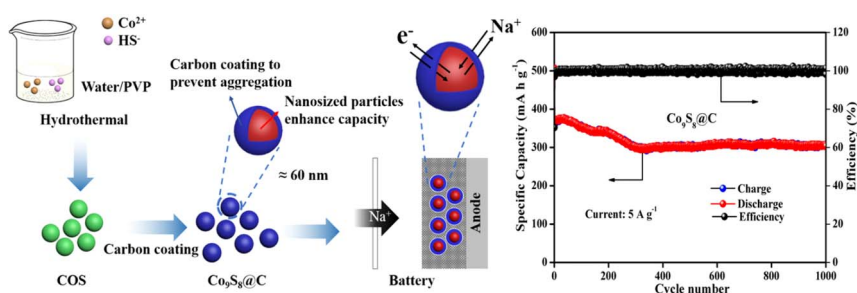
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ABSTRACT

Co$_9$S$_8$@C nanospheres with a 5 nm carbon shell and 50 nm Co$_9$S$_8$ core have been synthesized by a facile hydrothermal method followed by an annealing process. The electrochemical results indicate that the Co$_9$S$_8$@C nanospheres are an excellent anode material for sodium ion batteries. They deliver a specific capacity of 305 mA h g^{-1} after 1000 cycles at current density of 5 A g^{-1} and a high specific capacity of 405 mA h g^{-1} at current density of 500 mA g^{-1}. The good cycling performance and rate capability are attributed to the synergistic effects of the carbon shell and the ultra-small size of Co$_9$S$_8$, which can enhance the electrical conductivity of the composite, as well as resisting the strain caused by repeated charge/discharge processes.

1. Introduction

Room temperature sodium-ion batteries (SIBs) have attracted enormous attention as a prospective replacement of lithium-ion batteries (LIBs) as large-scale energy storage devices because of the practically inexhaustible and low cost of sodium resources [1–8]. The commercial anode for LIBs (graphite), however, cannot effectively enable the insertion of sodium, because of its interlayer spacing smaller than the sodium ion diameter, leading to the thermodynamic inactive of the Na-graphite system [9–10]. It is therefore a matter of great urgency to

develop suitable anodes in order to improve the SIBs system. Various kinds of Na-storage anode materials have been studied for this, such as amorphous carbon materials (soft or hard carbon) [11], phosphorous [12], transition metal oxides/chalcogenides [13], and alloying metals [14]. Among them, transition metal sulfides are of particular interest owing to their higher capacities than common intercalation compounds and higher intrinsic conductivity than transition metal oxides.

Co$_9$S$_8$, as a typical transition metal sulfide, has many advantages over other anode materials, including relatively high theoretical capacity, good electrical conductivity, and superior thermal stability

[15–18]. Its practical application is, however, blocked by the pulverization of this electrode material, which originates from the large volume change during the sodiation/disodiation process [19–23]. In general, encapsulation of Co_9S_8 into highly electrically conductive materials is considered to be an effective route to improve the electrochemical properties of Co_9S_8, because electrically conductive layer not only can suppress the volume variation of Co_9S_8, but also can improve the electrical conductivity of the composite system [24–27]. For example, Liu and co-workers synthesized Co_9S_8/C nanocomposites that delivered a capacity of $\sim 320\,mA\,h\,g^{-1}$ after 30 cycles [28]. Zhou et al. synthesized multi-walled carbon nanotubes (MWCNTs)/Co_9S_8, which displayed a capacity of $300\,mA\,h\,g^{-1}$ after 80 cycles at a current density of $2\,A\,g^{-1}$ [29]. Although improvement has been achieved, the electrochemical performance of Co_9S_8 is still far from practical application as anode for SIBs because of its short cycling life (less than 200 cycles). Therefore, new efforts are still needed to improve the electrochemical properties of Co_9S_8 in order to ameliorate the shortcoming of the SIBs system.

Herein, ultrasmall Co_9S_8@Carbon ($\approx 60\,nm$) nanospheres were synthesized by a two-step method, which combined the hydrothermal method with an annealing process. When used as anode for SIBs, this material has many merits, such as its small particle size, which is beneficial to shorten the diffused distance of sodium ion and resist the strain imposed by volume change in the charge/discharge process. The carbon shells can also facilitate electron transport and effectively accommodate the volume expansion/contraction caused by insertion/extraction of sodium ion. As expected, the Co_9S_8@Carbon nanocomposite delivered an outstanding electrochemical performance including a long-term cycling performance (1000 cycles at a current density of $5\,A\,g^{-1}$) with Coulombic efficiency (higher than 99%), high specific capacity of $550\,mAh\,g^{-1}$ at $500\,mA\,g^{-1}$, and good rate capability.

2. Experimental

2.1. Synthesis of Co_9S_8

The Co_9S_8 nanospheres were synthesized through a facile hydrothermal method and followed by an annealing process. Typically, 2 mmol $Co(NO_3)_2\cdot6H_2O$ (0.58 g), 0.2 g poly(vinylpyrrolidone) (PVP) (M = 360,000), and 2 mmol thioacetamide (TAA) (0.15 g) were sequentially dissolved in 50 mL distilled water to generate a pink solution. After vigorous stirring for 10 min, 0.2 mL of ammonia solution was added into the above solution, immediately resulting in a blue suspension. Subsequently, the suspension was transferred into an autoclave and kept at 150 °C for 40 min. The product (denoted as COS) was harvested by centrifugation and washed with water and ethanol, then dried at 60 °C for 12 h. Afterwards, the Co_9S_8 was synthesized by annealing the as-prepared COS, by heating it at 2 °C/min to 350 °C, keeping it at that temperature for 2.5 h, and then heating it at a rate of 5 °C/min up to 600 °C for a 3 h dwell time in flowing N_2.

2.2. Synthesis of Co_9S_8@C

For the preparation of Co_9S_8@C, 0.2 g of COS, was dispersed in 40 mL deionized water by ultrasound, which was followed by the addition of 0.06 g of L-cysteine, 0.125 g of resorcinol, 17.5 mL of ethanol, and 0.1 mL of ammonia solution in turn. After stirring at 40 °C for 30 min, 0.15 mL of formaldehyde solution was injected into the dispersion drop by drop. After vigorous stirring for 6 h, the product was obtained by filtration and washed with deionized water and ethanol, before being dried at 60 °C for 12 h. The product was treated by the same procedure as for the synthesis of Co_9S_8, and then the final product, Co_9S_8@C, was obtained.

2.3. Characterization

The synthesized products were examined by scanning electron microscopy (SEM, JEOL JSM-7600F Field Emission), transmission electron microscopy (TEM, JEOL JEM, 1011), X-ray powder difference with Cu Kα radiation (λ = 1.5418 Å) (XRD, Bruker D8 Adv, Germany), and high resolution transmission electron microscope (HRTEM, JEOL-2100F) at an accelerating voltage of 200 kV. XPS measurements were performed on a Thermo Scientific K-Alpha using an Al Kα X-ray source. Thermal gravimetric analysis (TGA) was conducted on a thermal analyzer (Mettler Toledo TGA/SDTA 851, Switzerland) in air at a heating rate of 10 °C min^{-1}.

2.4. Electrochemical measurements

The Co_9S_8@C electrodes were prepared by mixing the active material (70 wt%), acetylene black (20 wt%) and polyvinylidene fluoride (PVDF; 10 wt%) binder in 1-methy 1–2-pyrrolidinone (NMP) solvent to obtain a homogeneous slurry. The slurry was uniformly coated on copper foil substrates, and then the coated electrodes were pressed after being dried at 60 °C for 12 h in a vacuum oven. The mass of active material loading on the copper foil discs (12 mm diameter) was about 1–1.5 mg. CR2032 coin cell was assembled in an argon-filled glove box with the working electrodes as prepared, sodium metal as counter/reference electrode, and glass fiber as separator. The electrolyte solution was 1 M $NaPF_6$ dissolved in diethyleneglycol -dimethylether (DEG-DME). Galvanostatic discharge/charge tests were carried out on a LAND battery-test instrument (CT2001A) in the voltage range of 0.01 V–3.0 V. Cyclic voltammetry (CV) was conducted on a CHI-760 electrochemical workstation at a scan rate of $0.1\,mV\,s^{-1}$ within a potential window of 0.01–3.0 V. Electrochemical impedance spectroscopy (EIS) curves were collected on a CHI-760 electrochemical workstation with a frequency range of 100 kHz to 0.01 Hz.

3. Result and discussion

Fig. 1 displays a schematic illustration for the fabrication process of ultra-small Co_9S_8 and Co_9S_8@ nanospheres. Firstly, the $Co(NO_3)_2\cdot6H_2O$, TAA, and PVP were dissolved in distilled water to obtain a homogeneous solution. Subsequently, a moderate amount of ammonium hydroxide was added into the above solution to achieve alkaline condition. Then, the mixture was treated through a hydrothermal reaction to produce the precursor (COS). The XRD pattern and XPS survey spectrum of the COS was tested as shown in Fig. S1 (Supporting Information). In Fig. S1(a), the dominant diffraction peaks can be indexed to cubic CoS_2 phase (JCPDS 41-1471). Combined with XPS survey spectrum of the COS, the sample of COS can be identified as CoS_2. It should be noted that the existence of PVP is crucial to the formation of COS nanospheres, because it functions as a surfactant in the solution (Fig. S2 in Supporting Information). Two different processes were carried out on the COS precursor. Firstly, Co_9S_8 nanospheres was obtained by a single calcination process in N_2. Severe aggregation of particles occurred in this process, however, which will make the material less electrochemical reactive and then lead to bad electrochemical performance. To avoid this situation, a thin carbon layer was coated on the surface of the precursor to form a protective layer, which not only can protect the nanoparticle from aggregation during the annealing, but also can enhance the electronic conductivity of the composite, subsequently resulting in improved electrochemical properties. Well dispersed Co_9S_8@C nanospheres are, therefore, obtained after the heat treatment.

Fig. 2a shows XRD patterns of Co_9S_8@C and Co_9S_8. All the reflection peaks were clearly indexed to cubic Co_9S_8 phase (JCPDS No. 75-2023) with the Fm$\bar{3}$m (2 2 5) space group. The peaks of both samples are strong and sharp, indicating the high crystallinity of Co_9S_8. The peaks of carbon are not detected in the Co_9S_8@C sample, which may be because