



Improved sodium-storage performance of stannous sulfide@reduced graphene oxide composite as high capacity anodes for sodium-ion batteries



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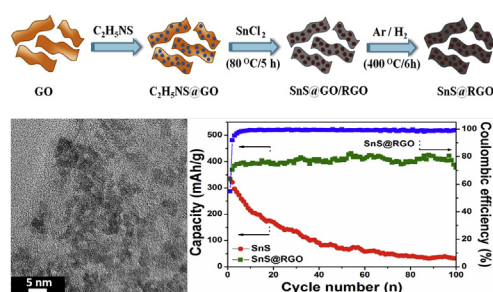
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HIGHLIGHTS

- The SnS@RGO as Na storage anode is synthesized by a simple precipitation method.
- The SnS@RGO can deliver large reversible capacity (457 mAh g⁻¹ at 20 mA g⁻¹).
- The SnS@RGO also shows excellent cycling stability over 100 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Stannous sulfide@reduced graphene oxide (SnS@RGO) composite is successfully synthesized via a facile precipitation route. The structural and morphological characterizations reveal SnS@RGO composites are composed of SnS nanoparticles of the size 5–10 nm, which are uniformly anchored on the surface of RGO. The electrochemical measurements demonstrate the reversible capacity of the SnS@RGO composite – that includes contributions from the conversion reaction of SnS to Sn and Na_xS and the alloying reaction of Sn to Na_xSn. The SnS@RGO electrode exhibits a reversible capacity of 457 mAh g⁻¹ at 20 mA g⁻¹, superior cycling stability (94% capacity retention over 100 cycles at 100 mA g⁻¹) and adequate rate performance. Compared to the neat SnS nanoparticles, the enhanced electrochemical performance of the SnS@RGO composite is primarily due to the incorporation of RGO as a highly conductive, flexible component as well as possessing a large available surface area, which provides desirable properties such as improved electronic contact between active materials, aggregation suppression of intermediate products, and alleviation of the volume change during sodiation and desodiation. Encouraging experimental results suggest that the SnS@RGO composite is a promising material to achieve a high-capacity and stable anode for NIBs.

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1. Introduction

Sodium-ion batteries (NIBs) have attracted an increasing amount of attention in recent years to meet application demands of low-cost energy storage, primarily due to the wide availability of Na

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resources compared to Li [1–6]. However, in contrast to Li ion intercalation chemistry, seldom cathodic materials have been found that enable fast and reversible insertion/deinsertion of the large-sized Na ions yielding and adequate capacity, examples of cathodic materials include, layer and tunnel structured metal oxides [7–11], open-framework ferrocyanides [12], and amorphous FePO_4 [13]. In regard to the anodic component of the NIB, hard carbon [14–17], alloys [18–22] and metal sulfides [23,24] are commonly studied. Hard carbon materials display Na storage capacity in the range of 200–300 mAh g^{-1} [14–17] with limited cyclability, whereas alloy materials (primarily alloys of Sn and Sb) show much higher reversible capacity [18,19,25–32], such as higher than 600 mAh g^{-1} for a Sb–C composite [19] and 550 mAh g^{-1} for a Sn-based materials after 80 cycles [30].

Additionally, Sn(or Sb, W, Mo) oxides [33] and sulfides [23,24,29,30] have also been investigated for their potential as anode materials due to their potentially high capacity offered by both alloying and conversion reactions, such as 667 mAh g^{-1} for SnO_2 , 1227 mAh g^{-1} for Sb_2O_4 , 1136 mAh g^{-1} for SnS_2 , and 1022 mAh g^{-1} for SnS [30,33–35]. Sun et al. reported a Sb_2O_4 thin film electrode demonstrating a reversible capacity of 896 mAh g^{-1} [34]. The Sn–SnS–C and SnS–C nanocomposites, revealed in our previous publications, show reversible capacities of 664 mAh g^{-1} and 568 mAh g^{-1} at 20 mA g^{-1} , respectively [29,30]. However, due to their diminished electron conductivity and large volumetric change during sodiation and desodiation, these Sn/Sb oxides or sulfides suffer from low utilization and poor cycling performance. In order to address said challenges, various methods have been developed, such as designing peculiar nanostructures [19,25,27,36,37] and combining oxides/sulfides with conductive supporters [19,29]. Due to graphene's advantages of high surface area, adequate electronic conductivity, and flexible framework, it is an ideal scaffold for electrochemical reactions [38]. Graphene hybrid nanocomposites have demonstrated a dramatically improved electrochemical performance of electrodes for Na ion storage [26,39,40]. Yu et al. reported a SbS_2 /graphene anode possessing a superior Na storage capacity of 730 mAh g^{-1} at 50 mA g^{-1} [26]. SnO_2 /graphene nanocomposite demonstrates a reversible Na storage capacity of above 700 mAh g^{-1} [39,41,42].

Generally, the sulfides exhibit better electrochemical performance than the oxides for sodium ion storage [29,39]. It is possibly because that M–S bonds in metal sulfides are weaker than the corresponding M–O bonds in metal oxides, which would be kinetically favorable for the conversion reactions. In this publication, the synthesis of SnS@RGO (reduced graphene oxide) hybrid structure with SnS nanocrystals uniformly anchored onto RGO nanosheets via a simple precipitation method (Fig. 1). The as-prepared SnS@RGO nanocomposite demonstrated a high reversible capacity of 457 mAh g^{-1} at 20 mA g^{-1} and an excellent cycling stability in a Na-ion battery. To the best of our knowledge, said material is the first demonstration of Na ion storage performance using a SnS@RGO-based material.

2. Experimental

The SnS@RGO composite was prepared by a simple precipitation

method described as follows. 40 mL of GO (Graphene Oxide, 98.5% purity, Sinocarbon Graphene Marketing Center, Shanxi, China) dispersion (2 mg mL^{-1}) was dispersed in 40 mL of 0.05 mol L^{-1} thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, 99% purity, National Medicine Co., Ltd, Shanghai, China) solution under sonication for 0.5 h, and then 80 mL of 0.05 mol L^{-1} SnCl_2 ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 98% purity, National Medicine Co., Ltd, Shanghai, China) solution was added into the above mixture under stirring at 80 °C for 5 h. After cooling to room temperature, the solid product was recovered by centrifugation, washed with deionized water and absolute alcohol thrice, and vacuum dried at 60 °C overnight. The dried product was then heated in Ar (92 vol. %)/ H_2 (8 vol. %) at 400 °C for 6 h to reduce GO completely to RGO. Neat SnS nanoparticle was synthesized under the same conditions mentioned above without the presence of GO.

Morphological and structural features of the SnS@RGO composite before and after sodium insertion were performed by scanning electron microscopy (SEM, ULTRA/PLUS, ZEISS) and by transmission electron microscopy (TEM, JEOL, JEM-2010-FEF and JEM-2100 (HR)). The crystalline structures of the as-prepared composite were characterized by X-ray diffraction (XRD, Shimadzu XRD-6000, Cu–K α radiation). The composition analysis of the SnS@RGO composite was performed with TGA, the temperature ramping rate in the TGA measurement is 5 °C min^{-1} (Diamond TG/DTA6300). Raman spectroscopy was performed with a laser micro-Raman spectrometer (Renishaw in Via, Renishaw, 532 nm excitation wavelength).

The SnS@RGO anodes were prepared by mixing 80 wt% SnS@RGO composite, 10 wt% super P, and 10 wt% Polyacrylic acid (PAA, 25 wt%) to form a slurry, which was then coated onto a copper (Cu) foil and dried at 60 °C overnight under vacuum. The mass loading of the electrode is about 3 mg. The charge–discharge performance of the electrode were examined by 2016 coin-type cells using the SnS@RGO anode as working electrode and Na disk as counter electrode, 1 M NaPF_6 dissolved in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume) with 5% fluoroethylene carbonate (FEC) as the electrolyte, and microporous membrane (Celgard 2400) as separator. The Na disks were home-made by rolling sodium lumps into thin plate, and then cutting the thin plate into circulated disks. All the cells were assembled in a glove box with water/oxygen content lower than 1 ppm and tested at room temperature. The galvanostatic charge–discharge test was conducted on a LAND cyler (Wuhan Kingnuo Electronic Co., China). The Na storage capability of the SnS@RGO electrode was calculated solely based on the contribution from SnS by deducting the capacity contributions from the RGO (30 mAh g^{-1}) and Super P (90 mAh g^{-1}) [19,40]. Cyclic voltammetric measurements were carried out with the coin cells at a scan rate of 0.1 mV s^{-1} using a CHI 660 c electrochemical workstation (ChenHua Instruments Co., China). Electrochemical impedance spectra were recorded by the Impedance Measuring Unit (IM 6e, Zahner) with oscillation amplitude of 5 mV at the frequency range from 10 m Hz to 100 k Hz.

3. Results and discussion

The SnS@RGO composite was prepared by a simple precipitation method. The scheme of the synthetic reactions is shown in Fig. 1.

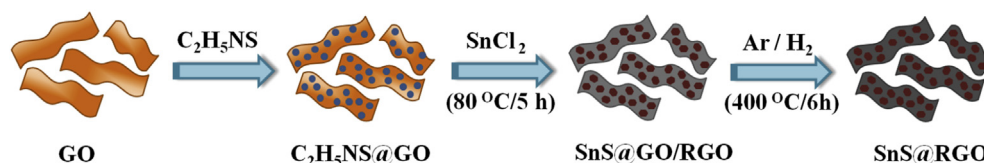


Fig. 1. Schematic illustration of the formation process of the SnS@RGO composite.

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