



In situ fabrication of nitrogen-doped carbon-coated SnO₂/SnS heterostructures with enhanced performance for lithium storage

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ABSTRACT

Tin-based compounds have incurred tremendous attention due to their higher specific capacities than their analogues for lithium storage. Unfortunately, the undesirable electrical conductivities and huge volume variations during cycling processes coupled with Li⁺ intercalation and de-intercalation will lead to severe capacity fading and poor cycling stability. To address these problems, nitrogen-doped carbon-coated SnO₂/SnS (SnO₂/SnS@N-C) composite was in situ synthesized by virtue of a simple solvothermal reaction and subsequent post-treatment. Herein, the heterostructures between SnO₂ and SnS were designed to accelerate charge transfer by using the effect of internal electric field and improve the dispersion among particles. While coating the nitrogen-doped carbon on heterostructures aimed to improve electrical conductivities and relieve huge volume alterations during the processes of Li⁺ insertion and de-insertion. To our satisfactory, the as-prepared SnO₂/SnS@N-C composite as anodes for lithium-ion batteries can display a high specific capacity (1050 mAh g⁻¹ at 100 mA g⁻¹), enhanced rate capability, and long cycle life (550 mAh g⁻¹ after 100 cycles), which outperforms both SnO₂@N-C and SnS@N-C. The promotion of electrochemical performance demonstrates that Tin-based anode materials with such optimized structures have broad prospects in the applications of energy storage field.

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1. Introduction

The prosperity in electronic products has boosted our demands for lithium-ion batteries (LIBs) to a large extent. How to develop high-performance LIBs, including high gravimetric and volumetric capacity, high power density, and long cycle life to adapt to the development of the electronic industry is a big concern [1–3]. As a necessary component of LIBs, the anode material plays an important part in determining the whole properties of LIBs. Nevertheless, in terms of gravimetric capacity, the currently employed commercial anode material (graphite, theoretically 372 mAh g⁻¹) is insufficient, which makes it difficult to meet our urgent demands. Consequently, it is highly desirable to develop a type of anode material with high specific capacity, excellent rate capability, and long cycling life [4,5].

Recently, tin-based anode materials which were recognized as

promising candidates for LIBs stand out in energy storage system. Particularly, metallic tin (Sn) [6–10], tin oxides (SnO or SnO₂) [11–17], and tin sulfides (SnS or SnS₂) [18–24] have aroused a great interest by virtue of high theoretical specific capacities. Representatively, SnO₂ and SnS are two kinds of important anode materials on the basis of conversion-alloy reaction mechanism, which have attracted special attention. To be specific, SnO₂ has a high theoretical capacity (783 mAh g⁻¹) and layered SnS has a large interlayer spacing (*c* = 0.4330 nm, space group *Pnma*) [25,26]. Tentatively, if their respective merits can be combined to form heterostructures, the designed composite would be expected to possess both high specific capacity and stable cycling lifespan. However, confronting challenges are the large volume expansion and poor intrinsic electrical conductivity, which seriously hampered their practical applications for LIBs.

So far, many efforts have been made to improve the poor intrinsic conductivities of SnO₂ and SnS, such as the introduction of carbon-based materials, including carbon nanocomposites [27,28], carbon coated nanocomposites [29,30], and derived carbon coated nanocomposites [31]. Another effective strategy is to fabricate heterostructures, in which the internal electric field would

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accelerate charge transfer, thus improving the conductivity. Advantageously, the band gaps of SnO₂ and SnS are 3.8 and 1.3 eV, respectively, which would greatly facilitate the fabrication of such heterostructures. However, to the best of our knowledge, most of the preparing processes for SnO₂/SnS heterostructures are always involving the complicated and time-consuming procedures. For examples, Guo's [32] and Li's [33] groups have successfully prepared C@SnS/SnO₂@Gr and C@SnS/SnO₂@CNFs heterostructures, respectively, where multi-steps such as the stepwise preparation of SnS/SnO₂ are both mentioned. These successes encouraged us to design a simple and feasible process for the fabrication of the SnO₂/SnS heterostructures, especially for those whose tin-based precursors can be obtained at the same time. As for volume changes, it has been demonstrated that coating the Tin-based materials with reduced graphene oxide is an effective way, which benefits from its conductive character and elasticity structure. For instance, Feng's group has developed nitrogen-doped carbon-coated SnO₂-SnS/graphene nanosheets with desirable electrochemical performances [34]. However, the synthetic steps are still cumbersome and the production cost of graphene is a handicap. On the other hand, encapsulating tin-based anodes with a carbon layer is a simple and economical way, which can not only improve the electrical conductivity but also buffer the volume variation of the electrode material.

Herein, as mentioned above, the SnO₂/SnS@N-C composite was designed and synthesized via a facile solvothermal process and followed by a simple post-treatment. Two kinds of active components in SnO₂/SnS heterostructures generate a synergistic enhanced effect at heterointerfaces [35], combined with the N-doped C, the electrical conductivity was further enhanced. In addition, the layered SnS and N-doped C collectively buffer the volume change during cycling. Expectantly, when evaluated as anodes for LIBs, the as-prepared SnO₂/SnS@N-C composite delivered a high specific capacity of up to 1050 mAh g⁻¹ at a current density of 100 mA g⁻¹, as well as much improved rate capability and cycle stability, which validates their great promise for electrochemical applications in LIBs. More meaningfully, obtaining SnO₂/SnS@N-C composite with such simple in-situ preparation method not only enriches the fabrication strategies but also widens their applications as electrode materials for LIBs.

2. Experimental sections

2.1. Materials and reagent

Tin chloride pentahydrate (SnCl₄·5H₂O), thioacetamide (TAA), and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Dopamine hydrochloride and tris(hydroxymethyl)amino-methane were obtained from Aladdin Co., Ltd. All of these chemicals were used directly.

2.2. Preparation of SnO₂@N-C

Firstly, SnO₂ was synthesized via a facile solvothermal method. In a typical process, 1 mmol (0.35 g) SnCl₄·5H₂O was dissolved in 30 mL ethanol under magnetic stirring for 1 h. After that, the solution was transferred to a 50 mL autoclave, sealed and kept in an oven at 180 °C for 12 h. When the temperature cooled to room temperature, the resulting milky suspension was centrifuged and washed three times with distilled water and ethanol to obtain SnO₂. Subsequently, the product was dispersed in 50 mM Tris-HCl buffer solution (pH = 8.5) containing 50 mL deionized water by ultrasonication. After that, equal amount of dopamine hydrochloride was added into the solution and the mixture was kept stirring at room temperature for 24 h. Finally, after washing several times

with water and ethanol and drying at 80 °C overnight, the resultant composite was heated in a tube furnace under argon atmosphere at 500 °C for 2 h, yielding N-doped carbon-coated SnO₂ (SnO₂@N-C).

2.3. Preparation of SnS@N-C

Above all, the sheet-like SnS₂ was synthesized via a simple solvothermal method. In a typical process, 1 mmol (0.35 g) SnCl₄·5H₂O and 4 mmol TAA (0.30 g) were dissolved in 30 mL ethanol under magnetic stirring for 1 h. Afterwards, the mixed solution was moved to a 50 mL autoclave, which was kept in an oven at 180 °C for 12 h. When the temperature cooled down, the resulting brown suspension was washed by centrifugation with deionized water and ethanol to obtain SnS₂. Ultimately, a smooth carbon layer was covered under the same procedure as that used for SnO₂ mentioned above. Differently, during the calcining process, SnS₂ was decomposed to SnS. Thus, the final product was N-doped carbon-coated SnS (SnS@N-C).

2.4. Preparation of SnO₂/SnS@N-C composite

Firstly, 1 mmol (0.35 g) SnCl₄·5H₂O and 1 mmol TAA (0.075 g) were dissolved in 30 mL ethanol under magnetic stirring for 1 h. After that, the mixed solution was transferred to a 50 mL autoclave, sealed and kept in an oven at 180 °C for 12 h. After cooling down to room temperature, the resulting yellow suspension was centrifuged and washed three times with distilled water and ethanol. After being dried at 80 °C overnight, SnO₂/SnS₂ precursor can be obtained. Secondly, similarly to the preparation processes of SnS@N-C, the final product was N-doped carbon-coated SnO₂/SnS (SnO₂/SnS @N-C).

2.5. Characterization

Powder X-ray diffraction (XRD) measurements were conducted by a D8 ADVANCE X-ray diffractometer with Cu-K_α radiation operated at 40 kV and 30 mA from 10 to 80°. The morphologies of the samples were investigated by JSM-6701F field-emission scanning electron microscopy (FESEM) when the voltage accelerated to 5.0 kV. Transmission electron microscopy (TEM) was performed by a JEM-2100F electron microscope operated with an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA) was tested on a TGA 4000 Thermogravimetry Analyzer from 80 to 700 °C at a ramp rate of 10 °C min⁻¹ in air. Raman spectrum was taken on a SENTERRA Raman spectrometer. X-ray photoelectron spectroscopy (XPS) experiment was carried out on ESCALAB250Xi system from ThermoFisher with Al K_α radiation as the X-ray radiation source.

2.6. Electrochemical measurement

The electrochemical performance was measured by CR2032 coin cells. In detail, the active material, acetylene black, and polytetrafluoroethylene (PTFE) binder were mixed in a mass ratio of 85:10:15, forming homogeneous slurry. Next, the obtained slurry was casted on a piece of Cu mesh and dried in vacuum at 60 °C for 12 h. The coin cells were assembled in glove box full of argon. Various samples were employed as working electrodes and pure Li foils were simultaneously employed as reference and counter electrodes. 1 M LiPF₆ in mixed solvent of ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume) and microporous polypropylene membrane (Celgard 2400) was respectively adopted as the electrolyte and separator. Attentively, the loading mass of work electrode can affect the electrochemical performance due to the fact that the polarization increases with the loading mass increasing [36,37]. Herein, the loading mass of all working

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