In-situ sulfuration synthesis of sandwiched spherical tin sulfide/sulfur-doped graphene composite with ultra-low sulfur content

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HIGHLIGHTS

- Sandwiched spherical SnS/sulfur-doped graphene (SnS/S-SG) composite is reported.
- An ultra-low sulfur content realizes sulfuration of SnO$_2$ and S-doping of graphene.
- Sandwich sphere structure improves the structural stability during lithium storage.
- High S doping amount enhances the binding force and electrical conductivity.
- Li-Sn alloying and Li$_2$S conversion reactions are highly reversible over 100 cycles.

GRAPHICAL ABSTRACT
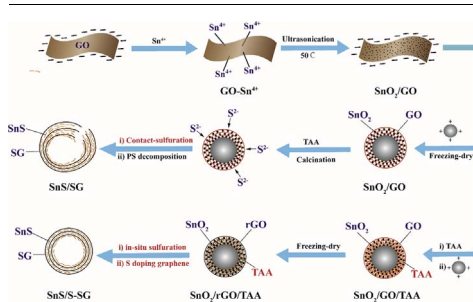
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ABSTRACT

SnS is widely studied as anode materials since of its superior structural stability and physicochemical property comparing with other Sn-based composites. Nevertheless, the inconvenience of phase morphology control and excessive consumption of sulfur sources during synthesis hinder the scalable application of SnS nanocomposites. Herein, we report a facile in-situ sulfuration strategy to synthesize sandwiched spherical SnS/sulfur-doped graphene (SnS/S-SG) composite. An ultra-low sulfur content with approximately stoichiometric ratio of Sn:S can effectively promote the sulfuration reaction of SnO$_2$ to SnS and simultaneous sulfur-doping of graphene. The as-prepared SnS/S-SG composite shows a three-dimensional interconnected spherical structure as a whole, in which SnS nanoparticles are sandwiched between the multilayers of graphene sheets forming a hollow sphere. The sandwiched sphere structure and high S doping amount can improve the binding force between SnS and graphene, as well as the structural stability and electrical conductivity of the composite. Thus, a high reversibility of conversion reaction, promising specific capacity (772 mAh g^{-1} after 100 cycles at 0.1 C) and excellent rate performance (705 and 411 mAh g^{-1} at 1 C and 10 C, respectively) are exhibited in the SnS/S-SG electrode, which are much higher than that of the SnS/spherical graphene synthesized by traditional post-sulfuration method.

1. Introduction

Searching for high-capacity alternative anode materials has attracted wide attention of specialists from material and electrochemical fields [1–3]. To achieve high energy density of 300–350 Wh kg^{-1} for next generation lithium ion batteries (LIBs), silicon (Si) and tin (Sn) based anode materials, with high theoretical capacities of 4212 and 994 mAh g^{-1}, respectively [4,5], are usually added into the composite anode electrodes, with the expectation of enhancing the reversible capacity of the anode to be above 600 mAh g^{-1} or even higher. However, the volume expansion of Li-Si and Li-Sn alloying processes are usually larger than 300%, which would cause cracking and pulverization of the electrode, subsequently, lack of electronic contact between the active materials and the current collector, and thus the continuous capacity loss during cycles. Unfortunately, an effective binder has not been explored to solve the mechanical stress of volumetric expansion during the alloying/de-alloying processes. Based on this, Sn-based oxides (SnO$_2$, SnO) and sulfides (SnS$_2$, SnS) with a moderate specific capacity (660–780 mAh g^{-1} based on the Li-Sn alloying reaction) and intrinsic volume buffer came from the lithiation-generated amorphous Li$_2$O or Li$_2$S matrix may be applicable candidates to meet the pressing energy demand [6–10].

Among all the above-mentioned Sn-based composites, SnO$_2$ and SnS have been widely studied as anode materials for LIBs since of their structural stability and facile synthesis via hydrolysis procedure [11–14]. Even more interesting is that the conversion reactions of these composites have been demonstrated to be partially reversible in our previous research [15] and the currently published literature [16–18], which would prompt the specific capacity increase by a large margin. However, as is all known, the reversibility of Li$_2$O in the SnO$_2$-based composites is much poorer since that the reversion of Sn/LiO needs to overcome a high energy barrier, with a Gibbs free energy change (ΔrGm$^{\theta}$) of about 602.3 kJ mol^{-1} at 298 K [11]. It may be for this reason that the reversibility of conversion reaction continuously decays with cycle number in the SnO$_2$-based hybrids [6,8]. Whereas, the SnS has a superior delivered property, a much lower energy barrier ($\sim$324.8 kJ mol^{-1}) can prompt the reversed conversion reaction of Sn/Li$_2$S to SnS (see Note S1 in the Supporting Information), which means that a higher reaction reversibility and coulombic efficiency can be expected in the SnS-based composites. Considering the combination capacities of the Li-Sn alloying (782.1 mAh g^{-1}) and Sn/Li$_2$S conversion reaction (355.5 mAh g^{-1}), the SnS can deliver a theoretical specific capacity of 1137.6 mAh g^{-1}, which makes it a promising alternative anode material for energy storage.

Recently, various structures of SnS, including SnS nanoplatelets [19], SnS nanorods [20], SnS hollow nanostructures [21], SnS nanoflowers [22], core-shell SnS/C nanorods [23], SnS$_x$-graphene nanocomposite [18], sandwich structured SnS/polypyrrole [24] and three-dimensional porous interconnected SnS/C composite [17] etc., have been extensively investigated. Many of them deliver a high specific capacity exceeding the theoretical value, demonstrating the important value as alternative anode material. However, it should be noted that almost all of them have low initial coulombic efficiency (less than 70%) and continuously decayed capacity upon cycling. On one hand, similar to other Sn-based compounds, the coarsening of metallic Sn may be the main cause of Sn inactivation and conversion irreversibility of Sn/Li$_2$S in SnS-based composites, since that the active materials SnS are directly exposed on the surface of conductive substrates. Without the effective confinement effect, the generated Sn would gradually transform into amorphous structure and its migration would further induce the aggregation of Li$_x$Sn alloy during lithiation, thus deteriorating the lithium storage performances. On the other hand, all previously reported sulfur source contents during SnS preparation are much higher. For instance, the hydrothermal synthesis of SnS usually required SnCl$_2$·2H$_2$O and thiourea at the molar ratio range of 1:3–4 [18,20], thermal decomposition phase transformation of SnS consumed K$_2$SnO$_3$·3H$_2$O and L-

cysteine at molar ratio of 1:4 [13], while SnCl$_2$ and L-cysteine with molar ratio of 1:10 were needed for electrostatic spray deposition (ESD) of SnS/C nanocomposites [17]. Especially, the calcination-sulfuration [25,26] and chemical vapor deposition method [27–29] usually required ten times of sulfur containing compounds comparing to the stoichiometric ratio, and the final products, without exception, were found to be tin disulfides (SnS$_2$). Given the above, most of the sulfur contents used during SnS synthesis procedure are three-fold over the stoichiometric ratio, which means that most of the sulfur sources are dissolved in the solution (expelling with the waste water) or thermally decomposed into toxic H$_2$S (as one composition of exhaust gases), and eventually become the ones of the main causes of acid rain. Therefore, preparation of SnS with well-designed confinement nanostructure by a sulfur-complete utilization method is vital for the large-scale industrial production from an environmental point of view and has important reference value for new energy and new materials industries.

Herein, we report a novel in-situ sulfuration approach to synthesize sandwiched spherical SnS/sulfur-doped graphene (SnS/S-SG) composite. An ultra-low sulfur content with approximately Sn:S molar ratio of 1:1 can effectively promote the sulfuration reaction of SnO$_2$ and simultaneous sulfur-doping of graphene. The possible sulfuration mechanism is discussed in detail by investigating the phase structure and morphology evolution of the products in different stages, and by comparing with that of the traditional post-sulfuration samples. The microstructural characterization indicates that the as-prepared SnS/S-SG composite shows a three-dimensional interconnected spherical structure as a whole, in which SnS nanoparticles are inserted between the multilayers of graphene sheets forming a sandwiched hollow sphere. The SnS/S-SG electrode exhibits a high specific capacity, and the reversible capacity retains 772 mAh g^{-1} after 100 cycles at 0.1 C, which is much stable and higher than that of the SnS/spherical graphene composite synthesized by post-sulfuration method.

2. Experimental

2.1. Materials synthesis

2.1.1. Synthesis of SnS/S-SG composite

Firstly, amino-polystyrene spheres (PS) with diameter of 200–300 nm were synthesized by the continuous addition of water-soluble cationic initiators in emulsifier-free emulsion polymerization system reported elsewhere [15]. Graphene oxide (GO) was prepared by a modified Hummers method [30,31]. Then, 10 mL of 0.2 M SnCl$_4$·5H$_2$O solution was added dropwise into 50 mL of GO suspension (2 mg mL^{-1}) under stirring for 2 h with the following sonication at 50 °C for 2 h. Subsequently, 10 mL of 0.2 M thioacetamide (TAA, Sn/S molar ratio = 1:1) solution was added and stirred for 2 h, then 10 mL of PS dispersion (30 mg L^{-1}) was added into the above solution under magnetic stirring. The mixed solution was stirred for 12 h and freeze-dried at -55 °C to obtain the SnO$_2$/GO/TAA/PS precursor. After that, the precursor was calcined at 500 °C for 2 h in a N$_2$ gas atmosphere. During the annealing process, the PS sphere was decomposed and the GO was thermally reduced to graphene with numerous SnS nanoparticles inserted between the adjacent layers. Thus the sandwich-structured SnS/S-SG composite was obtained.

2.1.2. Synthesis of SnS/SG composite by post-sulfuration method

Firstly, the SnO$_2$/GO/PS precursor was synthesized by the similar procedure of SnO$_2$/GO/TAA/PS without addition of thioacetamide (sulfur sources). Then the SnO$_2$/GO/PS precursor was physically mixed with 8.0 mmol TAA (Sn/S molar ratio = 1:4) and heated at 500 °C for 2 h under N$_2$ atmosphere. During the annealing process, the SnO$_2$ was controllably sulfurized to SnS and the GO was reduced to graphene, and the obtained black powder was marked as post-sulfuration SnS/GS composite.