



Facile synthesis of ultrasmall tin oxide nanoparticles embedded in carbon as high-performance anode for lithium-ion batteries



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HIGHLIGHTS

- A composite of ultrasmall SnO₂ embedded in carbon was prepared by a facile strategy.
- The peculiar structure brought the composite sufficient physical buffer ability.
- This composite (SnO₂/C-59) exhibited an excellent electrochemical performance.

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ABSTRACT

Tin oxide (SnO₂) has received great attention as promising anode for lithium ion batteries because it offers a high theoretical capacity (ca. 782 mAh g⁻¹ for Li_{4.4}Sn) and a safe discharge potential versus Li/Li⁺ in comparison to commercialized graphite anodes, whereas it also suffers from the drawbacks of the huge volume change and low electronic conductivity during lithiation/delithiation processes. Herein, we have prepared a SnO₂/C composite of ultrasmall SnO₂ nanoparticles (~6 nm and ~59.4% by weight) embedded in carbon matrix (denoted as SnO₂/C-59) by a facile hydrothermal and subsequent carbonization approach. In this peculiar architecture, uniform distribution of SnO₂, and electronic conductivity of carbon matrix, which can effectively solve the problems of pulverization, loss of electrical contact and particle aggregation during cycling, therefore contributing to excellent lithium storage and cycling stability. A reversible capacity of 839.1 mAh g⁻¹ is obtained at 200 mA g⁻¹ after 217 cycles. More importantly, 712.8 mAh g⁻¹ can be obtained at 800 mA g⁻¹ even after 378 cycles.

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1. Introduction

Tin oxide has attracted extensive interests in the context of energy storage and been considered as a promising alternative for commercial graphite anode due to its high theoretical capacity of 782 mAh g⁻¹, low toxicity, high abundance and safe working potential [1–4]. The theoretical capacity is two times higher than of commonly used graphite (372 mAh g⁻¹). And the safe working potential can effectively avoid the issues of easy presence of lithium plating during high current operation. Unfortunately, there are still obstacles that hinder the practical application of SnO₂ anode materials for LIBs, such as severe pulverization and

capacity fading problems caused by the large volume variation (ca. 300%) during cycling process, subsequently resulting in loss of electrical conduct between adjacent particles [5]. To overcome these issues, several strategies have been employed to buffer the significant volume change such as fabricating novel SnO₂ nanostructure electrode materials and designing composites with SnO₂ and carbon nanomaterials [6,7]. For example, ultrathin SnO₂ nanosheets [8], nanosheets assembled SnO₂ hollow spheres [9], SnO₂ nanotube arrays [10], SnO₂ nanowires [11], SnO₂ nanorods [12], SnO₂ nanofibers and nanotubes with highly porous [13] and so forth have been synthesized to alleviate the absolute volume expansion of SnO₂ electrodes during discharge/charge process. These peculiar architectures effectively shorten the lithium diffusion path, buffer the volume expansion and increase the contact interface between active materials and electrolyte, resulting in improved electrochemical performance, however, a certain amount of capacity fading still exists upon long-term cycling due

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to the breaking down, aggregation and pulverization of these SnO₂ nanostructures [2].

Thus, design and fabrication of carbon supported SnO₂ composites is considered to be another effectively strategy to alleviate the issues aforementioned, which integrates the advantages of carbon and SnO₂ nanostructures [14]. Carbon materials, such as amorphous carbon [15], carbon nanotubes [16] and grapheme [17], have been regarded as the most promising choices for buffer matrixes, owing to their excellent buffering effect and high electronic conductivity. SnO₂ combined with carbon to effectively accommodate the strain of volume change and avoid aggregation and pulverization [18]. Undoubtedly, the composites have been considered as promising anode candidates for lithium ion batteries (LIBs) and attracted great research interest worldwide. For example, carbon nanowires@ultrathin SnO₂ nanosheets@carbon composite [19], CNTs@SnO₂@C coaxial nanocables [2], SWNTS@SnO₂@PPy coaxial nanocables [1], SnO₂ nanosheets grown on graphene sheets [20], encapsulation of nanosized SnO₂ particles in carbon nanotubes [21], SnO₂@carbon core-shell nanochains [22], SnO₂@C yolk-shell spheres [23] and SnO₂/graphene nanocomposites [24], all exhibiting high reversible capacities and improved electrochemical performances. However, these means alone only have limited improvement in lithium storage performance of SnO₂/carbon hybrid nanostructures. And the problems such as low tap density, complex preparation process and high cost of raw materials still exist. For the purpose of making the SnO₂/carbon hybrid nanostructures practical use in LIBs, great efforts still need to be done. Absolutely, there is a huge potential to synthesize and design SnO₂/carbon anode materials with better lithium storage performance for LIBs.

Herein, we prepared a SnO₂/C-59 composite by a simple hydrothermal and subsequent carbonization approach, avoiding special apparatus, tedious fabrication processes, toxic organic solvents, expensive raw materials and severe conditions. Firstly, we synthesized the SnO₂/carbonaceous polysaccharide precursor by using Na₂SnO₃·4H₂O and D-glucose as the raw materials through simple hydrothermal process. Then, the SnO₂/C-59 composite was obtained by the SnO₂/carbonaceous polysaccharide precursor carbonization under Ar atmosphere. Observed by TEM, the SnO₂ with average size of ca. 6 nm uniformly distributed in carbon matrix. The synergistic effect of ultras-small SnO₂ NPs, uniform distribution and electrically conductive carbon matrix, which providing SnO₂/C-59 composite with excellent electrochemical performance as an anode material for LIBs.

2. Experimental section

2.1. Preparation of samples

A typical preparation process was as follows: SnO₂/carbonaceous polysaccharide precursor was first synthesized by a simple hydrothermal approach: 0.35 g of Na₂SnO₃·4H₂O (0.2 and 0.4 g were also investigated) and 1.2 g of D-glucose were dissolved in 14 mL of deionized water and stirred for 1 h. The solution was then transferred into a 25 mL Teflon-lined stainless steel autoclave, sealed, and kept at 180 °C for 8 h in an oven before cooling down to room temperature. Then, the product was harvested by centrifugation and washed with deionized water and ethanol. The as-prepared precursor was subsequently carbonization at a temperature of 500 °C for 3 h, under argon protective atmosphere at a ramping rate of 0.5 °C min⁻¹. Finally, the SnO₂/C-59 composite was obtained. The sample prepared by using different mass of Na₂SnO₃·4H₂O was labeled at three different contents of SnO₂ in SnO₂/C composite (i.e., 46.6, 59.4 and 71 wt.% corresponding to 0.2, 0.35, and 0.4 g of Na₂SnO₃·4H₂O, respectively), which were labeled as SnO₂/C-46, SnO₂/C-59 and SnO₂/C-71, respectively.

2.2. Structure and electrochemical characterization

The morphology and microstructure of the products were obtained using field emission scanning electron microscopy (FE-SEM, JEOL JSM-7401F) and transmission electron microscopy (TEM, JEOL JEM-2010) with a selected area electron diffraction pattern (SAED). The crystal structure and composition were characterized by X-ray diffraction measurement (XRD, Rigaku, D/max-Rbusing Cu K α radiation) and laser Raman spectroscopy (Renishaw in Via). Thermogravimetric analysis (TGA) of the as-prepared SnO₂/C composites were carried out with a thermogravimetric analysis instrument (TGA, SDT Q600 V8.2 Build 100).

Electrochemical measurements were performed using 2016-type coin cells assembled in an argon-filled glove box (German, M. Braun Co., [O₂] < 1 ppm, [H₂O] < 1 ppm). The working electrodes were composed of the active material (SnO₂/C), conductive material (acetylene black, AB), and binder (poly-vinylidene fluoride, PVDF) in a weight ratio of SnO₂/C/AB/PVDF = 70:20:10 and pasted on Cu foil. Pure lithium foil was used as the counter electrode. A glass fiber (GF/A) from Whatman was used as the separator. The electrolyte consisted of a solution of 1 M LiPF₆ in ethylene carbonate and dimethyl carbonate (EC + DMC) (1:1 in volume). The galvanostatic discharge/charge cycles were carried out on a CT2001a cell test instrument (LAND Electronic Co.) over a voltage range of 0.01–3.0 V at room temperature. Cyclic voltammetry (CV) was implemented on a CHI660D electrochemical workstation at a scan rate of 0.1 mV s⁻¹ between 0.0 and 3.0 V. For SnO₂/C composites working electrode, all the specific capacities reported and current densities used were based on their total mass.

3. Results and discussion

The morphology of the as-prepared SnO₂/C-59 composite was characterized by using SEM and TEM. We can see from Fig. 1(a) that the composite exhibits a not uniform particle sizes and larger particle sizes reaching over 500 nm. Interestingly, when we observed it using TEM, as shown in Fig. 1(b), SnO₂ nanoparticles (NPs) (black dots) with uniform particles size were homogeneously embedded in the carbon matrix (gray). In addition, the selected-area electron diffraction (SAED) pattern (inset of Fig. 1(b)) indicates that the SnO₂ NPs reveal polycrystalline in nature because there are three diffraction rings corresponding to the (110), (101) and (211) planes of polycrystalline SnO₂, respectively. It is clearly seen from the high-resolution TEM (HRTEM) (shown in Fig. 1(c)) that the SnO₂ NPs (indicated by black arrows) have an average size of ca. 6 nm. The visible set of lattice fringes with d-spacing of 0.26 shown in Fig. 1(c) are the characteristic of (101) lattice planes of the rutile SnO₂. It should be noted that most of SnO₂ NPs were wrapped in the carbon matrix rather than exposed on the outer surface and the amorphous carbon (indicated by gray arrows) located in between the SnO₂ NPs, not only prevents the aggregation of SnO₂ NPs, but also avoids the exfoliation of SnO₂ NPs during cycling, as a result, maintaining the integrity of the whole electrode. Fig. 1(d) is the EDS spectrum taken from the as-made sample. The strong peaks for C, Sn and O elements are expected from the carbon matrix, SnO₂ NPs, respectively. Then, the Si and Cu peaks come from micro-grid used as the sample stage in TEM measurements.

For confirming the excellent electrochemical properties of SnO₂/C-59 come from its peculiar architecture, we also prepared other two kinds of composites (SnO₂/C-46 and SnO₂/C-71) displayed in Fig. 2. The typical size of SnO₂/C-46 (the mass of Na₂SnO₃·4H₂O is 0.2 g) particles is around 50 nm and the particles intimately connected to each other, which could be clearly seen from the SEM (Fig. 2(a)) and TEM images (Fig. 2(b)). The SnO₂ NPs nanoclusters

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