

One-Pot Hydrothermal Synthesis of Flower-Like SnO₂ Clusters and Their Application for Lithium Ion Battery

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Abstract: Tin dioxide is one of the most promising anode materials for the next generation rechargeable Li-ion batteries owing to its high theoretical capacity (782 mAh g⁻¹). The flower-like SnO₂ clusters were successfully prepared via a facile one-step hydrothermal method using sodium stannate as a Sn source without any additional templates. This unique structure exhibits a high reversible capacity of 607 mAh g⁻¹ at 100 mA g⁻¹ after 30 cycles.

Introduction

Recently, Li-ion batteries are considered as the most important electrochemical devices for energy storage due to their high energy density, light weight and high electromotive force[1,2]. Graphite anode exhibits low potential and excellent cycling stability, but its capacity is very low. Currently, as the most promising candidate for anode materials, metal oxides with high capacities from 700 to 1000 mAh g⁻¹ have been widely investigated to replace the commercial graphite anode for lithium-ion batteries (LIBs)[3,4]. Among them, SnO₂ has attracted attention in particular due to its high theoretical capacity (782 mAh g⁻¹), relatively safe working potential and environmental benignity[5,6]. However, high volume expansion/contraction changes (about threefold) during the Li insertion/extraction process are similar with other high capacity materials such as Si, which leads to pulverization of the electrodes and becomes significant drawback of tin oxide-based electrode materials.

It is impossible to eliminate the volume change and pulverization problem completely, which originates from the complex electrochemical reaction process. One of the effective solutions to circumvent these obstacles is carbon coating, which not only alleviates the volume changes but also increases the electronic conductivity of the electrode[7-10]. Lou et al. used one-pot synthesis of carbon-coated SnO₂ nanocolloids which exhibited enhanced cycling performance (still maintaining 440 mAh g⁻¹ after 100 cycles)[11]. Yang et al. synthesized graphene based mesoporous SnO₂, which exhibited good reversible capacity (916.9 mAh g⁻¹ after 30 cycles at a rate of 0.1C)[12]. However, carbon coating method still suffers its shortcomings. SnO₂ is possible to be reduced at high carbonization temperature[13], and the additional conductive carbon will not only sacrifice the capacity of hybrid composites but also fail to supply residual buffer space to relieve mechanical stress induced during the repeated electrochemical processes[14]. Another effective method is constructing the properly structured features such as particle sizes, morphologies, and pores to improve the lithium ion storage performance of SnO₂ electrode. To date, various structures of SnO₂, such as nanoparticles[15], nanorods[16], nanotubes[17], nanoboxes[18], and mesoporous structures[19], have been prepared. However, these previously reported methods often require hard templates or additives. The necessary removal of such templates or additives is not only laborious but also prone to destroy the product structures through high-temperature treatment. Hence, it is of great importance to develop simple and facile routes that avoid the assistance of hard templates or additives to enable large-scale fabrication of hierarchical SnO₂ nanostructures.

Herein, we reported a simple one-pot hydrothermal synthesis of flower-like SnO₂ clusters structure. The synthesis is performed in ethanol–water and ethylene glycol–water mixed solvent using sodium stannate as the precursor. The as-grown SnO₂ clusters exhibited good cycling stability and high performance.

Experimental

Materials. Sodium stannate, urea, ethanol, ethylene glycol (Sinopharm Chemical Reagent Co., Ltd. Shanghai, China) were of AR grade and used without further purification.

Synthesis of SnO₂ clusters. The SnO₂ clusters were synthesized via a one-pot hydrothermal route. In a typical synthesis, about 5g urea was dissolved in mixed solvent A and B under magnetic stirring for 0.5 h, respectively (A: containing 25 mL ethanol and 25 mL water, B: containing 25 mL ethylene glycol and 25 mL water). And then, 10mM Na₂SnO₃ was added into the solution A and B, respectively. After a few hours of magnetic stirring, the obtained solutions were transferred into Teflon-lined stainless steel autoclave, sealed and maintained at 200°C for 10 h at an electric oven. After the hydrothermal processes, the autoclave was transferred from the electric oven and cooled down to room temperature, and the products were collected by centrifugation. And then the products were washed with distilled water for 5 times. Finally, the as-obtained samples were dried at 70 °C for 10 h to obtain the powders.

The working electrode is prepared by compressing a mixture of active materials (SnO₂), conductive material (acetylene black) and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10. The slurries were coated on Cu foils and dried at 110 °C in a vacuum for 10 h to remove the water and solvent. The 2016-type cell assembly is operated in a glove box filled with pure argon.

Characterization. The composition and crystallographic information of the as-obtained samples were determined by X-ray diffraction (XRD). The morphology of as-synthesized products was studied by SEM. The charge–discharge tests were carried out on a LAND Cell Test System (2001A, Wuhan, China) between cutoff voltages of 3 V and 0.05 V. Cyclic voltammetry (CV) tests in two electrode coin-type cells were performed between 0.01 V and 3 V at a scan rate of 0.2 mV s⁻¹ on a CHI760D electrochemical working station.

Results and discussion

XRD

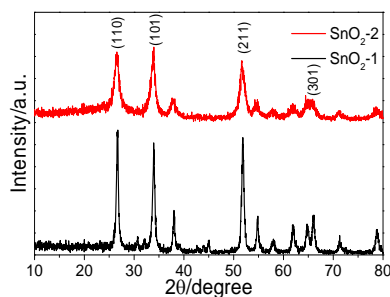


Fig. 1 XRD patterns of SnO₂ prepared in various solvents, ethanol and water, (volume ratio=1:1)(SnO₂-1), and ethylene glycol and water (SnO₂-2).

Fig. 1 shows the XRD patterns of the as-prepared SnO₂ derived from the hydrothermal process with various solvents. It can be seen that all the diffraction peaks can be well indexed to the tetragonal SnO₂ with the rutile structure (JCPDS Card No. 41-1445), which confirms that pure SnO₂ could be obtained by this facile route. There is no distinct difference in peak position and intensity between the SnO₂-1 and SnO₂-2.

SEM measurements

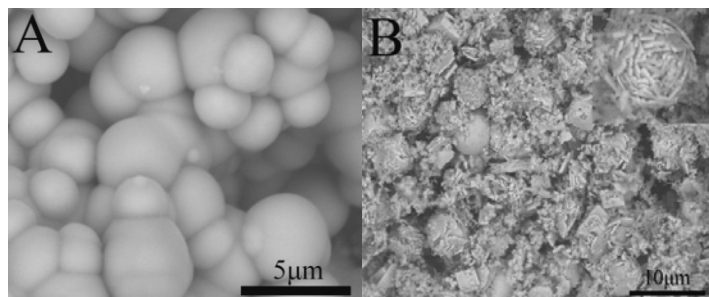


Fig. 2 SEM images of SnO₂-1(A), SnO₂-2(B).

The morphology of as-synthesized SnO₂ was studied by SEM. As shown in Fig. 2A, it is apparent that the SnO₂-1 consists of interconnected spherical particles with a size in the range of 1–4 μm. Fig. 2B shows the SEM image of a typical sample composed of many flower-like microstructures approximately 5 μm in diameter, which are built from several fan-like sheets.

Electrochemical properties

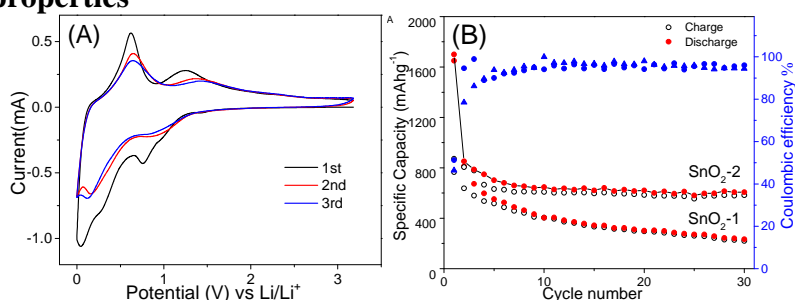


Fig. 3 (A) First three cycles of the CV curves of the SnO₂-2. (B) Cycling stability of SnO₂-1, and SnO₂-2 at a current of 100 mA g⁻¹.

The electrochemical property of the as-prepared SnO₂-2 was further evaluated using the cyclic voltammetry. Fig. 3A shows the first three cyclic voltammograms of the SnO₂-2 electrode conducted at a scan rate of 0.2 mV s⁻¹ from the 3 to 0.01 V vs Li/Li⁺. In the first cycle, the CV curve clearly indicates a cathodic peak at 0.76 V during the first discharge, which can be attributed to the reduction of SnO₂ to Sn and the formation of solid-electrolyte interface (SEI) [20]. And the clear cathodic peak located at around 0.04 V can be attributed to the alloying reaction between Sn and Li to form Li_xSn alloy [21]. During the charging process, two oxidation peaks at around 0.62 and 1.25 V can be attributed to the dealloying of Li_xSn, and the partial conversion of Sn to SnO₂, respectively. The peak positions and intensities of all the redox couples echo well from 2nd to 3rd cycle, indicating the good reversibility of the electrochemical reactions.

The galvanostatic charge-discharge tests demonstrate good capacity retention of the SnO₂ electrode within the voltage range of 0.05–3 V at a current density of 100 mA g⁻¹. Fig. 3B displays the discharge-charge capacity vs. the cycle number for the SnO₂ electrode. As can be seen, the initial discharge capacities of the SnO₂-1 and SnO₂-2 electrodes are 1650 and 1700 mAh g⁻¹, respectively. The charge capacities of the SnO₂-1 and SnO₂-2 electrodes are 766 and 872 mAh g⁻¹, respectively. The Coulombic efficiency of the SnO₂-1 and SnO₂-2 is 46% and 51%, respectively. After 30 charge/discharge cycles, the SnO₂-2 electrode maintained a discharge capacity of 607 mA h g⁻¹, which is 2.6 times higher than the value for the SnO₂-1 electrode (234 mAh g⁻¹). This implies that the SnO₂-2 electrode exhibits stable structure and excellent reversibility.

Conclusions

In summary, flower-like SnO₂ clusters were successfully prepared via a facile one-step hydrothermal method using sodium stannate as a Sn source without any additional templates. The stable structure and excellent reversibility can be attributed to unique morphology and structure. And we expected that this work would narrow the gap between the basic research and the practical application of the SnO₂-based materials in LIBs.

Acknowledgements

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