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Design and preparation of interconnected quasi-ball-in-ball tin dioxide/carbon composite containing void-space with high lithium storage properties

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ABSTRACT

Rapid capacity fading is one of the major obstacles that seriously impede the applications of tin dioxide (SnO_2)-based electrodes. Compositing SnO_2 with carbon to form SnO_2/carbon composites with rational nanostructures has been proven to be an effective strategy to overcome the problem of rapid capacity fading to a certain extent. Herein, an interestingly interconnected quasi-ball-in-ball nanostructure SnO_2/carbon composite, denoted as Cs@void@SnO_2@C, has been successfully fabricated by a simple and novel strategy. When used as anode materials for lithium-ion batteries, the Cs@void@SnO_2@C exhibits high lithium storage and long cycling performance, delivering a reversible capacity of 793.7 mAh g^{-1} after 450 cycles at 200 mA g^{-1}, and a reversible capacity of 486.3 mAh g^{-1} after 1000 cycles even at 1000 mA g^{-1}. The uniquely interconnected quasi-ball-in-ball structure should be responsible for the good electrochemical performance, which is further confirmed by comparing with two control samples of Cs@SnO_2@C and Cs@SnO_2.

1. Introduction

Due to the limited lithium storage capacity and low lithium intercalation potential of graphite anode materials for lithium-ion batteries (LIBs), substantial efforts have been devoted to explore and research alternative anode materials to replace them to satisfy the pressing demand of electric/hybrid vehicles for higher capacity and safer power [1–8]. As one of various promising candidates, SnO_2 has been gained extensive attention owe to the high theoretical capacity of 782 mAh g^{-1}, and relatively safe working potential [9]. When tested as anode materials for LIBs, however, the SnO_2 showed a poor rate capability and bad cycling performance, which could be ascribed to huge volume variation and intrinsic poor electronic conductivity of SnO_2 semiconductor during repeated discharge/charge process [10]. Moreover, the serious aggregation of tin particles and continual formation of a thick solid electrolyte interphase (SEI) will occurred during repeated lithium insertion process, bringing about adverse factors to impact the cycling performance, such as pulverization of the electrodes, formation of the electrochemically inactive Li_2O, and depletion of the electrolyte [4,11–13]. Therefore, a great of inevitable efforts must be made to improve the electrochemical performances of SnO_2, for example, try to rationally design and prepare SnO_2-based materials with unique nanostructures taking into account all of the above considerations.

More recently, a variety of nanostructured SnO_2/carbon composites with peculiar morphologies, such as SnO_2@C yolk–shell, SnO_2@C nanochains, CNT@SnO_2@C, SWNTS@SnO_2@PPy, SnO_2 nanorods/GS and SnO_2 NSs/graphene, have been reported, and all they exhibited better lithium storage and cycling performance as anode materials for LIBs, which can be attributed to the fully synergistic effects of nanostructured SnO_2 and highly flexible and good conductive carbon: on one hand, the characteristics of nanostructured SnO_2, such as larger surface area and high surface-to-volume ratio, can effectively buffer the absolutely huge volume change of SnO_2, increase the contact interface between active materials and electrolyte, and shorten the diffusion path for lithium-ion and electron during cycling process; on the other hand,

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the carbon component of SnO_2/carbon composites can not only accommodate the volume change of SnO_2 partly, prevent SnO_2 from aggregation and pulverization, prevent the SEI film from continual formation, and ensure the electrode integrity during prolonged cycling process, but also enhance electronic conductivity of overall electrode and further facilitate electron and ion transport throughout the electrode [3,14–18]. Thus, design and fabrication of SnO_2/carbon composite materials is expected to be a promising strategy for improving the electrochemical properties of SnO_2, in terms of capacity, cycling stability and rate capability.

Inspired by previous studies, we prepared an interesting quasi-ball-in-ball SnO_2/carbon composite, denoted as Cs@void@SnO_2@C, by a simple and novel route. The preparation process showed in Fig. 1: Step I, the obtained polysaccharide spheres (PS) (Fig. S1) with a size of 200–500 nm was coated by SiO_2 via tetraethyl orthosilicate hydrolysis deposition; Step II, the Ps@void@SnO_2@polysaccharide was gained via Ps@SiO_2 (Fig. S2, the size of SiO_2 coating layer is among 30–50 nm) hydrothermal treatment under presence of $SnCl_2$, NH_4F and glucose; Step III, the final Cs@void@SnO_2@C was obtained by Ps@void@SnO_2@C calcination under Ar. It is worth noting that the SnO_2 and polysaccharide coating and SiO_2 removal occurred in step II simultaneously, effectively simplified the preparation process. The possible formation mechanism was discussed in following results and discussion section. In this as-prepared composite, interconnected carbon nanospheres (Cs) were well encapsulated into hollow SnO_2@Carbon coating (core@shell, and denoted as SnO_2@C) nanostructure, as well as a large-void-space was formed between carbon spheres and inner well of SnO_2@C in particular. In other words, the SnO_2 was sandwiched between inner Cs and outermost carbon coating (C) and large-void-space located between Cs and SnO_2 was elaborately formed. We prepared the Cs@void@SnO_2@C to be used as promising anode material for LIBs due to three merits of this peculiar architecture: 1) the nanoscale and quasi-spherically distributed SnO_2 can increase the contact interface between active materials and electrolyte, and shorten the diffusion path for lithium-ion and electron during cycling process; 2) the interconnected carbon spheres and outermost carbon coating layer can buffer the volume change of SnO_2 partly, prevent SnO_2 from aggregation and pulverization, prevent the SEI film from continual formation, particularly maintain the electrode integrity and enhance electronic conductivity of overall electrode during prolonged cycling process; 3) the void space can provide larger-free-space for buffering the huge volume change of SnO_2 and releasing the stress formed during discharge/charge process in particular. No surprise, the Cs@void@SnO_2@C showed a better electrochemical performance compared to the two control samples of Cs@SnO_2@C and Cs@SnO_2, and even other similar composites (listed in Table S1). A high reversible capacity of 793.7 mAh g^{-1} was obtained for Cs@void@SnO_2@C even after 450 cycles at 200 mA g^{-1}, but only 430.4 and 415.1 mAh g^{-1} for Cs@SnO_2@C and Cs@SnO_2 after 100 cycles, respectively.

2. Experimental section

2.1. Preparation of samples

The preparation of interconnected polysaccharide nanospheres (denoted as Ps): typically, 0.5 M of glucose aqueous solution was transferred into a Teflon-lined stainless steel autoclave, and then placed in an oven at 180 °C for 8 h. After cooled down to room temperature naturally, the dark brown precipitate, namely Ps was collected by centrifugation, washed with deionized water and ethanol thoroughly, and dried in an oven at 60 °C overnight.

Preparation of Ps@SiO_2: 200 mg of Ps was dispersed into 140 mL of mixture solution of deionized water and anhydrous ethanol (V/V = 1/1) with 400 mg of cetyl trimethyl ammonium bromide and 1.5 mL of ammonia ($NH_3 \cdot H_2O$) by ultrasound for 1 h. After stirred for 0.5 h at room temperature, 0.3 mL of tetraethyl orthosilicate was added into the suspension and continued to stirring for 6 h. Then, precipitate Ps@SiO_2 was collected by centrifugation, washed with water and ethanol thoroughly, and then dried in a vacuum oven at 60 °C for 24 h.

Preparation of Cs@void@SnO_2@C: typically, 100 mg of as-prepared Ps@SiO_2 was dispersed into 60 mL of deionized water by ultrasound for 1 h. Then, 1.2 g of glucose was added into the suspension and stirred for 10 min. Subsequently, 0.2 g of tin (II) chloride dehydrate ($SnCl_2 \cdot 2H_2O$) was added into the suspension under stirring. After stirring for 30 min, 0.044 g of ammonium fluoride (NH_4F) was added into the mixed suspension and then stirred another 30 min. After that, this mixed suspension was transferred into a Teflon-lined stainless steel autoclave, and then placed in an oven at 180 °C for 48 h. After cooled down to room temperature naturally, the dark brown precipitate (Ps@void@SnO_2@polysaccharide) was collected by centrifugation, washed with deionized water and ethanol thoroughly, and dried in an oven at 60 °C overnight. The Cs@void@SnO_2@C composite was gained via the obtained dark brown precipitate carbonization at a temperature of 500 °C for 3 h with a ramping rate of 0.5 °C min^{-1} under

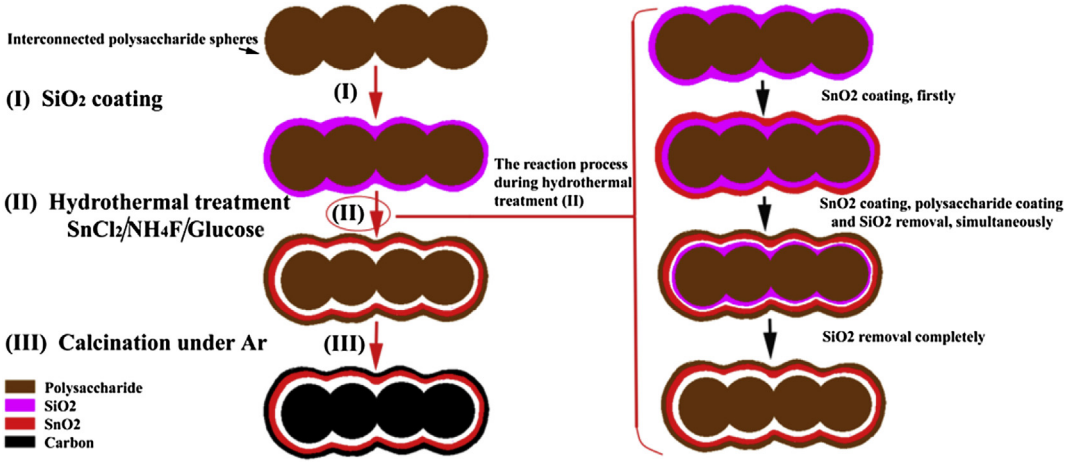

Fig. 1. The schematic illustration of preparing Cs@void@SnO_2@C.