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Short communication

Three-dimensional tin dioxide/carbon composite constructed by hollow nanospheres with quasi-sandwich structures as improved anode materials for lithium-ion batteries

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HIGHLIGHTS

- The three-dimensional SnO_2/C composite was prepared by a facile route.
- This architecture endowed the composite superior physical and chemical properties.
- This composite exhibited improved cycling performance and high rate capability.

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ABSTRACT

Tin dioxide (SnO_2)-based materials have been considered to be promisingly alternative advanced anode materials for lithium-ion batteries and thus attracted wide attention. So far, the research focus of SnO_2-based anode materials is to search and develop effective strategies for overcoming the obstacles, such as rapid capacity fading and poor rate capability, which seriously impede the practical application of SnO_2-based electrodes. Herein, we have successfully combined nanoscale SnO_2 with 3-dimensional carbon (C) conductivity framework to form a 3-dimensional unparalleled SnO_2/C composite constructed by closely interconnected hollow nanospheres with quasi-sandwich structures. When evaluated as anode materials for lithium-ion batteries, the as-prepared SnO_2/C composite exhibits improved cycling performance and high rate capability, delivering a high capacity of 576.6 mAh g^{-1} at 200 mA g^{-1} even after 500 cycles, and a capacity of 411.7 mAh g^{-1} even at 5 A g^{-1} during rate test. The unparalleled 3-dimensional architecture should be responsible for the good electrochemical performance.

1. Introduction

Emerged as one of the most promising alternative anode materials, SnO_2 has attracted extensive attention due to its high theoretical capacity of 782 mAh g^{-1} and better overcharge protection than graphite [1]. However, the practical application of SnO_2 in LIBs still suffers from a number of obstacles, which mainly includes: (i) huge and dramatic volume change during lithiation/delithiation due to their characteristic electrochemical reactions, that causes the aggregation and pulverization of active materials, and fractures and loss of electrical contact in electrodes, ultimately resulting in fast capacity fading, (ii) formation and accumulation of unstable solid electrolyte interface (SEI), which slows down the ion transfer and electronic conductivity, and (iii) intrinsic low electrical conductivity of transition metal oxides, that limits their operation at high discharge/charge rates [2]. So far, great efforts have been made to circumvent these issues mentioned above. It was found that compositing SnO_2 with carbon is an effective strategy for improving the electrochemical properties of SnO_2, in terms of cycling stability and rate capability, since the superiorly conductive, elastic and flexible carbon could not only buffer the huge volume change, suppress the pulverization and aggregation of SnO_2, and strengthen the stability of electrode structure, but also improve the electronic conductivity of whole electrode, and facilitate electron and ion transport throughout the electrode. Thus, lots of SnO_2/carbon composites, such as SnO_2@C yolk-shell nanospheres,

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SnO_2@C nanochains, SnO_2–C hybrid, SnO_2 nanoparticles encapsulated in micro/mesoporous carbon foam, and monodisperse SnO_2 anchored reduced graphene oxide nanocomposites, had been reported and exhibited improved performance [3–7].

In this present work, an interesting and effective way to improve the electrochemical performance of SnO_2 is reported on the basis of fabricating 3-dimensionally structural composite constructed by hollow SnO_2/carbon nanospheres (denoted as 3D-C@SnO_2@HC). It is worth noting that, in single SnO_2/carbon nanosphere, the HC is coated by middle SnO_2 nanoparticles and outmost carbon derived from glucose (C) to from quasi-sandwich structure during hydrothermal treatment process under the co-presence of tin (II) chloride dehydrate and glucose (as shown in Scheme 1). Thus, this peculiar architecture possesses four merits: (i) the 3-dimensional architecture constructed by closely interconnected hollow carbon nanospheres offers a mechanically robust, continuous, and high conductivity framework; (ii) the spherically distributed SnO_2 could increase the contact interface between active materials and electrolyte, and shorten the diffusion distance for lithium-ion and electron during cycling process; (iii) the closely interconnected hollow carbon spheres and outermost carbon coating layer could effectively buffer the volume change of SnO_2, prevent SnO_2 from aggregation and pulverization, prevent the SEI film from continual formation, keep the electrode integrity and improve electronic conductivity of overall electrode during long-term cycle process; (iv) the rich hollow space offers larger free space for buffering the dramatic volume change of SnO_2 and releasing the stress formed during discharge/charge process. Undoubtedly, the as-prepared 3D-C@SnO_2@HC exhibited improved performance as promising anode materials for LIBs, such as long cycle stability and high rate capability, delivering a high capacity of 576.6 mAh g^{-1} at 200 mA g^{-1} even after 500 cycles, and a capacity of 411.7 mAh g^{-1} even at 5 A g^{-1} during rate test.

2. Experimental section

2.1. Preparation of samples

Preparation of HC@SiO_2: typically, the hollow carbon nanospheres (HC) were first prepared reference to previous work [8]. Then, 200 mg of HC 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 (TBOS) was added into the suspension and continued to stirring for 6 h. After that, the precipitate HC@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. The purpose of preparing HC@SiO_2 was to improve the dispersion of HC in the water.

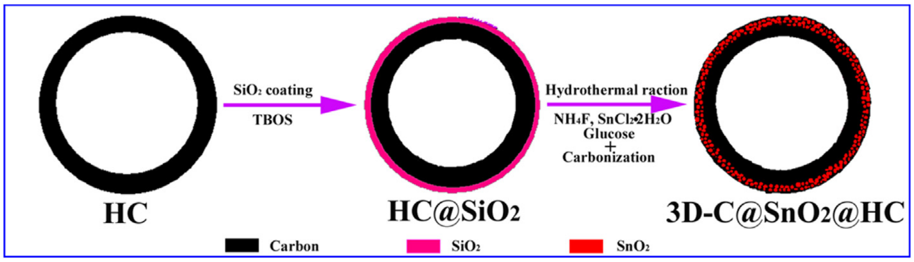
Preparation of 3D-C@SnO_2@HC: typically, 100 mg of as-prepared HC@SiO_2 was dispersed into 60 mL of deionized water by ultrasound for 1 h. Then, 1.2 g of glucose was added into the suspension and stirred for 10 min. Subsequently, 0.2 g of tin (II) chloride dehydrate ($SnCl_2 \cdot 2H_2O$) was added into 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 (HC@SnO_2@polysaccharide) was collected by centrifugation, washed with deionized water and ethanol thoroughly, and dried in an oven at 60 °C overnight. The 3D-C@SnO_2@HC composite was gained finally 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 argon atmosphere. The preparation process is showed in Scheme 1. It is worth noting that the SiO_2 coating could be etched by NH_4F solution under hydrothermal condition, avoiding the additional etching process, which had been verified in our previous work [9,10].

2.2. Materials characterizations

The morphology and microstructure characterizations of samples were investigated by using field emission scanning electron microscopy (FE-SEM, JEOL JSM-7401F) and transmission electron microscopy (TEM, JEOL JEM-2010) with an energy dispersive X-ray spectrometer (EDX) and a selected area electron diffraction pattern (SAED). The crystal structure and composition of samples were measured by X-ray diffraction measurement (XRD, Rigaku, D/max-Rbusing Cu K radiation) and laser Raman spectroscopy (Renishaw in Via). The composition and state of sample was further studied by X-ray photoelectron spectroscopy (XPS) experiments measured on an AXIS ULTRA DLD instrument, using aluminum K X-ray radiation. Thermogravimetric analysis (TGA) was conducted with a thermogravimetric analysis instrument (TGA, SDT Q600 V8.2 Build 100).

2.3. Electrochemical characterization

Electrochemical measurements were evaluated using 2016-type coin cells constructed in an argon-filled glove box (German, M. Braun Co., $[O_2] < 1$ ppm, $[H_2O] < 1$ ppm). The working electrodes were composed of the active material (3D-C@SnO_2@HC), conductive material (acetylene black, AB), and binder (sodium carboxymethyl cellulose, CMC) in a weight ratio of active material/AB/CMC = 70:20:10 and pasted on Cu foil, subsequent the electrodes were dried in a vacuum oven at 110 °C for 12 h. The mass of active material loaded on electrode was ca. 1.12 mg. The pure lithium foil and glass fiber (GF/A) from Whatman was used as the counter electrode and separator, respectively. The electrolyte used here is consisted of a solution of $LiPF_6$ (1 M) in ethylene carbonate and dimethyl carbonate (EC + DMC) (1:1 by volume). The galvanostatic



Scheme 1. Illustration of the preparation process of the 3D-C@SnO_2@HC.