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Full Length Article

Controllable synthesis of SnO_2@carbon hollow sphere based on bi-functional metallo-organic molecule for high-performance anode in Li-ion batteries

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ABSTRACT

Constructing hollow structure and nano-sized SnO_2 particles are two normal strategies to improve lithium storage performance of SnO_2-based electrode. But it is still challengeable to fabricate ultrasmall SnO_2 embedded in carbon hollow sphere in a controllable way. Herein, we have synthesized a kind of SnO_2@carbon hollow sphere via a confined Friedel-Crafts crosslinking of a novel metal-organic compound (triphenyltin chloride, named Sn-Ph) on the surface of SiO_2 template. The as-prepared SnO_2@carbon hollow sphere has 10 nm-sized SnO_2 particles embedded in amorphous carbon wall. Furthermore, 100, 200 and 400 nm-sized SnO_2@carbon hollow spheres can be obtained by regulating the size of SiO_2 template. When they are applied in lithium-ion batteries, the carbon structure can act as barriers to protect SnO_2 particles from pulverization, and hollow core stores electrolyte and very small SnO_2 particles of 10 nm shorten the diffusion distance of lithium ions. Thus, SnO_2@carbon hollow sphere presents superior electrochemical performance. The first discharge and charge capacities reach 1378.5 and 507.3 mAh g^{-1} respectively, and 100 cycles later, its capacity remains 501.2 mAh g^{-1}, indicating a capacity retention of 98.8% (C^{100th}/C^{2nd}).

1. Introduction

Due to the high energy density and long life span of lithium-ion battery, it has been regarded as one of the most important energy storage devices [1–4]. With growing demand for lithium-ion batteries in real life, many studies are carried out to search for novel electrode materials with higher energy and power densities [5–9]. SnO_2 has been selected as an important research object because of its high theoretical capacity of 782 mAh g^{-1} [10–12]. However, SnO_2 has some essential shortcomings that still are big challenges; for example, large volume expansion (300%) leads to pulverization of electrode, along with rapid capacity decaying [13–15]. Meanwhile, its poor electric conductivity always results in increase of resistance and inferior rate performance. Carbon barrier is frequently introduced in SnO_2 anode with the aim of conquering the structural drawbacks of naked SnO_2 and achieving enhanced electrochemical performance [16–21]. On the other hand, hollow structures are attracting increasing attention in recent years because they can provide volume expansion space, shorten Li^+ transfer length and enlarge contact surface area between electrode/electrolyte interfaces [22–27]. Therefore, it is believed that SnO_2/carbon (SnO_2/C) hollow spheres integrating above-mentioned structural features supply a choice to gain novel high-capacity and high-power anodes.

In recent years, many papers had reported the preparation of SnO_2/C hollow spheres. For example, a SnO_2@C composite anode was synthesized by Chen et al., which was obtained by diffusing $SnCl_2$ into mesoporous carbon spheres and subsequent heating treatment under air at 400 °C. The annealed SnO_2@C hollow sphere had 9 nm-sized SnO_2 particles, which led to a capacity of 450 mAh g^{-1} after 50 cycles at 1/5C [28]. Wang and his coworkers developed a double-void-space SnO_2/C hollow structure through a hydrothermal route, which exhibited an improved capacity of 408.4 mAh g^{-1} after 50 cycles at 100 mA g^{-1} [29]. Chen et al. prepared a monodispersed SnO_2/C hollow sphere via a facile hard template route. Owning to its SnO_2/carbon interlayer structure, this hollow sphere presented a stable capacity of 500 mAh g^{-1} after 50 cycles at 100 mA g^{-1}, displaying a capacity retention of 69.5% (C^{50th}/C^{2nd}) [30]. The above methods have been widely employed to construct SnO_2/C hollow spheres; however, most of these methods are based on old and frequently-used hydrothermal synthesis, and the size of SnO_2 nanoparticles are always very large. Thus, there is still an urgent requirement to develop novel and effective method to fabricate SnO_2/C hollow spheres.

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In this present paper, a novel metal organic compound, triphenyltin chloride (named Sn-Ph) with three benzene rings and one Sn atom, is used as a building block to construct SnO_2@C hollow sphere. As shown in Fig. 1, Sn-Ph is first coated on the SiO_2 surface by a covalent bond-induced surface-confined crosslinking. After carbonization and subsequent removal of template, SnO_2@C hollow spheres are obtained. The as-prepared SnO_2@C composite has 10 nm-sized SnO_2 particles embedded in carbon shell. More importantly, the size of hollow core can be well tailored by adjusting the size of SiO_2. When it is applied as electrode for lithium-ion batteries, SnO_2@C hollow sphere presents several advantages: (i) 10 nm SnO_2 particles reduce the volume expansion stress during cycling process; (ii) well embedded SnO_2 particles in carbon prevent pulverization and aggregation; (iii) hollow structure serves as electrolyte reservoir and shorten the transfer distance of Li^+; (iv) nanopores of carbon shell act as paths for ion transport and make inner SnO_2 particles easily accessible. Due to these merits, the as-prepared SnO_2@C hollow sphere exhibits superior electrochemical performance. For example, a high capacity of 501.2 mAh g^{-1} after 100 cycles at 200 mA g^{-1} is achieved, giving a good capacity retention of 98.8% (C^{100th}/C^{2nd}).

2. Experimental

2.1. Preparation of monodispersed SiO_2 nanospheres

The SiO_2 nanospheres were prepared via a Stöber method. First, 64 mL ammonium hydroxide ($NH_3{\cdot}H_2O$, 25wt.%) and 100 mL ethanol were mixed with 100 mL deionized water. Under a mechanical agitation of 300 rpm/min, another solution containing 20 mL tetraethylorthosilicate (TEOS) and 200 mL ethanol was added quickly. 12 h later, 400 nm-sized SiO_2 was collected after centrifugating and washing with deionized water and ethanol for three times. In ordered to carry out surface modification in the next step, as-obtained SiO_2 sphere was washed with 1, 2-dichloroethane for three times and re-dispersed in 1, 2-dichloroethane. Accordingly, 100 and 200 nm-sized SiO_2 were prepared by changing the dosage of ammonium hydroxide to 8 and 16 mL respectively.

2.2. Surface modification of SiO_2 nanospheres

The prepared SiO_2 (6 g) was dispersed in 100 mL 1, 2-dichloroethane under an ice-water bath. Then a solution of 5 mL 4-chloromethyl benzoyl chloride (CMBC) in 40 mL 1, 2-dichloroethane was dropped slowly into the flask. One hour after ending the dropping process, ice-water bath was withdrawn and the reaction was kept for another 24 h. The obtained suspension was centrifugated and washed with 1, 2-dichloroethane for three times. Subsequently, surface modified SiO_2 was harvested (denoted as SiO_2-CH_2Cl).

2.3. Preparation of SiO_2@xSn-Ph

SiO_2-CH_2Cl (3 g) was dispersed in 100 mL 1, 2-dichloroethane at 80 °C. Subsequently, 2 g $FeCl_3$ and 3 g Sn-Ph was added. Then a mixed solution of 4.5 ml dimethoxymethane and 40 mL 1, 2-dichloroethane was added into the flask drop by drop. After reacted for 12 h, the product was filtered off and washed with deionized water and ethanol for three times.

2.4. Preparation of SnO_2@C hollow sphere

At first, SiO_2@xSn-Ph was carbonized at 600 °C for 1 h with a heating rate of 10 °C/min. To remove template, the carbonized SiO_2@xSn-Ph was immersed into 2 mol/L NaOH at 80 °C for 8 h. The SnO_2@C hollow spheres can be collected by washing the products with deionized water and drying at 80 °C for 12 h.

2.5. Materials characterization

The structure and morphology of the as-prepared hollow sphere was characterized by X-ray diffraction (XRD, D/MAX-UItima IV, Rigaku Corporation, Japan), field-emission scanning electron microscopy (SEM, SU8010, Hitachi, Japan), transmission electron microscopy (TEM, JEM 2100F, Japan), Nitrogen adsorption-desorption porosity measurement machine (ASAP 2460, Micromeritics, USA). The thermogravimetric data was acquired by thermo-gravimetric analysis (TGA, Q50, TA Instruments Ltd, USA) in air from 100 to 700 °C and Fourier Transform reflection–infrared curves were measured via a Nicolet 6700 FTIR spectroscopy (Nicolet, USA).

2.6. Electrochemical measurement

The electrochemical performance was measured via assembling CR 2032 coin cells in an argon-filled glove box, using lithium metal as counter electrode and polypropylene microporous film (Celgard 2400) as separator. The working electrode was consisted of SnO_2@C hollow sphere, super P and Polyvinylidene Fluoride (PVDF) in a weight ratio of 85:5:10. The loading mass of each electrode was 0.7–0.75 mg.

Galvanostatic charge/discharge performance was tested on LAND CT 2001A batteries testing system (CT2001A, Wuhan LAND Corporation, China) at the voltage range between 0.01 and 3.0 V at room temperature. Cyclic voltammetry (CV) was acquired from an electrochemical workstation (CHI660E, Shanghai Chenhua, China) with a scan rate of 0.1 mV s^{-1} between 0.01 and 3 V.

3. Results and discussion

The preparation procedure of SnO_2@C hollow sphere is displayed in Fig. 1. SiO_2 nanospheres prepared by Stöber method are utilized as template [31]. SEM and TEM images of SiO_2 nanospheres are given in Fig. 2a, from which it can be observed that as-obtained SiO_2 nanospheres are monodisperse with an average diameter of 400 nm. Normally, these SiO_2 spheres are covered with —OH group on the surface during the condensation of ethylsilicate. In other words, SiO_2 spheres are hydrophilic. Nevertheless, Sn-Ph with three phenyls shell is highly hydrophobic. So Sn-Ph cannot be coated on surface of SiO_2 spheres because of impatient interface.

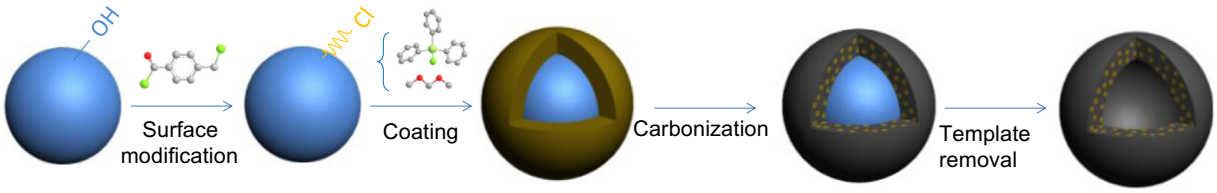

Fig. 1. Schematic illustration for the synthesis of SnO_2/C hollow sphere.