



A new hybrid strategy for fabricating titanium dioxide/tin dioxide/carbon composites with outstanding lithium-ion storage

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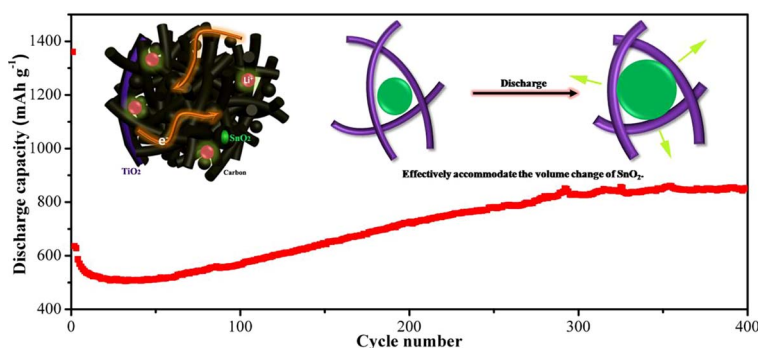


HIGHLIGHTS

- A new hybrid strategy for TiO₂/SnO₂/C composite was proposed.
- The main functions of this hybrid strategy for TiO₂/SnO₂/C anode were discussed.
- This composite showed outstanding electrochemical performance and structure stability.

GRAPHICAL ABSTRACT

The elaborate new hybrid strategy endowed TiO₂/SnO₂/C composite with outstanding electrochemical performance and structure stability.



ARTICLE INFO

Keywords:

Novel hybrid strategy
Composites
Tin dioxide
Anode
Lithium-ion batteries

ABSTRACT

An ideal hybrid mode for titanium dioxide (TiO₂) and tin dioxide (SnO₂) is that the SnO₂ nanoparticles locate in interspaces of 3-deminsional TiO₂ hierarchical structure constructed by one-dimensional units, in which the sizes of interspaces can be adjusted via the inverse movement among the units to smartly accommodate the huge expansion/contraction of SnO₂ anode during long-term cycling process, but its achievement is full of challenges. Herein, a smart strategy has been proposed to facilely fabricate a TiO₂/SnO₂/Carbon (TiO₂/SnO₂/C) composite with a similar nanostructure with above ideal mode for the first time, which is composed of SnO₂/C nanoparticles located in the interspaces among quasi-TiO₂/C nanowires. Expectedly, the as-fabricated TiO₂/SnO₂/C composite exhibits greatly improved lithium storage, delivering high capacities of 851.5 and 415 mAh g⁻¹ after 400 and 700 cycles at 200 and even 1000 mA g⁻¹, respectively. This work may provide a new strategy for development of high performance SnO₂-based composite anodes for lithium-ion batteries.

1. Introduction

Thanks to the high theoretical capacity of 782 mAh g⁻¹ and safe lithium-intercalated potential (0.2–1.2 V), tin oxide (SnO₂) has

attracted great attention as one of promising candidates to replace the currently dominated graphite anode to construct next generation lithium-ion batteries (LIBs) with high energy density and safety. That is because the graphite cannot meet the pressing need of next-generation

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LIBs for high energy density and safety due to its limited theoretical capacity of 372 mAh g^{-1} and low lithium-intercalated potential (0.1–0.2 V). The low lithium-intercalated potential can lead to lithium metal deposition (or formation of lithium dendrite) which will bring the safety issue of battery at high current densities [1–3]. However, the practical application of SnO_2 anode in LIBs is yet not be achieved due to its some inherent problems such as huge volume change and poor conductivity [4–8]. Currently, in the case of handling these issues, it is consistent that elaborate fabrication of SnO_2/C composites with versatile nanostructures is an effective strategy, because the nanostructure SnO_2/C composites have two main advantages: One hand, the nanometer-sized structures can endure much higher strain than their bulk counterparts and hence effectively mitigate the pulverization of active materials, and shorten the diffusion distance of ions and electrons; On the other hand, the carbon as a flexible and conductive matrix can not only buffer the volume expansion of SnO_2 to a certain extent, but also enhance the electrical conductivity of integral material, finally resulting in improved electrochemical performance [9–14].

What is more, in order to further insure the good structure stability of SnO_2/C composites during a long-term cycling process, TiO_2 is introduced into SnO_2/C as a structure support to form ternary nanostructure $\text{TiO}_2/\text{SnO}_2/\text{C}$ composites due to its much lower volume change ($< 4\%$) (SnO_2 ($\sim 300\%$) and carbon ($\sim 10\%$)). It is suggested that the $\text{TiO}_2/\text{SnO}_2/\text{C}$ composites should exhibit improvement in capacity, rate and life performance by means of complement each other's advantages among components. In general, however, the introduced TiO_2 commonly coats on the surface of SnO_2/C and, the current works about the $\text{TiO}_2/\text{SnO}_2/\text{C}$ are mainly focus on thickness adjustment of TiO_2 coating or adjusting the gap sizes between TiO_2 and SnO_2 [15–22]. Although TiO_2 possesses outstanding structure stability, the thickness of TiO_2 coating shouldn't be as thick as possible, because the performance of battery will be affected by the thicker TiO_2 coating due to the low practical theoretical capacity and poor conductivity of TiO_2 component. But, the thinner TiO_2 coating would be eventually broken by constantly accumulated stress which induced by repeated volume expansion/contraction of SnO_2 component during cycling process. It is believed that an ideal combination mode for TiO_2 and SnO_2 is that the SnO_2 nanoparticles locate in interspaces of 3-diminsional (3D) hierarchical structure of TiO_2 assembled by nanowire units, in which the sizes of interspaces can be adjusted via the inverse movement among the units to smartly accommodate the huge expansion/contraction of SnO_2 anode during long-term cycling process, as shown in Fig. 1. Predictatively, fabrication of nanostructures of $\text{TiO}_2/\text{SnO}_2/\text{C}$ composites with an ideal combination mode mentioned above is full of challenges not to mention facile fabrication and simultaneous introduction of conductive carbon.

Herein, a smart strategy has been proposed to facilely fabricate a $\text{TiO}_2/\text{SnO}_2/\text{C}$ composite (denoted as $\text{TiO}_2 \text{ NWs@SnO}_2/\text{C}$) possessing a similar structure with above mentioned ideal nanostructure for the first time. The preparation of $\text{TiO}_2 \text{ NWs@SnO}_2/\text{C}$ has been achieved by a facile one-step hydrothermal treatment and followed carbonization approach using the easily prepared hydrogen titanate ($\text{H}_2\text{Ti}_3\text{O}_7$, denoted as HTO), potassium stannate (IV) and glucose as the titanium, tin and carbon source, respectively, as shown in Fig. 2. In this unique nanostructure of $\text{TiO}_2 \text{ NWs@SnO}_2/\text{C}$, the carbon-coated SnO_2 nanoparticles smartly locate in the interspaces of 3-diminsional network structure constructed by carbon coated- TiO_2 nanowires, as shown in the 3D schematic (Fig. 2). It is worthy of noting that the glucose plays an essential role in successful preparation of $\text{TiO}_2 \text{ NWs@SnO}_2/\text{C}$. Ellipsoid-shaped resultant is obtained instead of $\text{TiO}_2 \text{ NWs@SnO}_2/\text{C}$ if absence of glucose during hydrothermal process (Fig. 2). Expectedly, this characteristic structure endows the $\text{TiO}_2 \text{ NWs@SnO}_2/\text{C}$ with outstanding lithium storage performance, capacities of 851.5 and 415 mAh g^{-1} are maintained after 400 and 700 cycles at 200 and even 1000 mA g^{-1} , respectively.

2. Experimental section

2.1. Preparation of $\text{TiO}_2 \text{ NWs@SnO}_2/\text{C}$ composite

All chemicals (analytical grade) were purchased from Shanghai Aladdin Biochemical Technology Co., LTD and used without further purification. In a typical process, 1 ml of tetrabutyl titanate was added into 20 ml of 7.5 M NaOH aqueous solution dropwise and subsequently stirring for 30 min. The gained white suspension was transferred into a stainless steel autoclave with a Teflon-lining and placed in an oven heated to 180 °C in advance for 24 h. After the autoclave cooled down to room temperature naturally, the inside white precipitate (sodium titanate) was collected by repeated centrifugation, thoroughly washed with deionized water and ethanol. Then, the freshly collected precipitate was re-dispersed in 100 ml of 0.1 M HCl and moderately stirring overnight to fully exchange Na^+ by H^+ to prepare hierarchical structure of HTO assembled by nanowires. After the ion exchange, the HTO was collected using the same way as sodium titanate, and then dried in a vacuum oven at 60 °C overnight. 0.15 g of HTO were dispersed into 60 ml of deionized water by ultrasound for 20 min, then addition of 0.1 g of $\text{K}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ and 1.2 g of glucose with continuous stirring. Stirring for 30 min before the suspension solution was transferred into a stainless steel autoclave with a Teflon-lining and then placed in an oven at 180 °C for 24 h carefully. After cooled down to room temperature, the collection approach of resultant precipitate with a dark brown color was same as the HTO. Finally, the $\text{TiO}_2 \text{ NWs@SnO}_2/\text{C}$ composite was obtained by carbonization of the collected brown precipitate at a temperature of 500 °C for 3 h under argon atmosphere. For comparison, the anatase TiO_2 nanowires were prepared by calcination of HTO at a temperature of 500 °C for 3 h under air atmosphere.

2.2. Materials characterization

The microstructure characteristics of $\text{TiO}_2 \text{ NWs@SnO}_2/\text{C}$ composite were deeply studied by scanning electron microscopy (SEM, JEOL JSM-7401F) and transmission electron microscopy (TEM, JEOL JEM-2010). The crystal and component characteristics of $\text{TiO}_2 \text{ NWs@SnO}_2/\text{C}$ composite were systematically investigated by X-ray diffraction measurement (XRD, Rigaku, using $\text{Cu K}\alpha$ radiation), Raman spectroscopy (Renishaw in Via) and X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD instrument with using aluminum $\text{K}\alpha$ X-ray radiation) instruments. The surface area and carbon content of $\text{TiO}_2 \text{ NWs@SnO}_2/\text{C}$ composite were demonstrated by nitrogen (N_2) adsorption/desorption instrument (Micromeritics ASAP 2010 instrument) and thermogravimetric analysis (TGA, SDT Q600 V8.2 Build 100), respectively. The atomic ratio of Sn/Ti was measured by iCAP6300-type inductively-coupled plasma spectrometer (ICP) technique.

2.3. Electrochemical measurements

The 2016-type coin cells assembled in an argon-filled glove box (German, M. Braun Co., $[\text{O}_2] < 1 \text{ ppm}$, $[\text{H}_2\text{O}] < 1 \text{ ppm}$) were used to systematically evaluate the lithium storage performance of $\text{TiO}_2 \text{ NWs@SnO}_2/\text{C}$ composite. Typically, the working electrodes were made up of active material ($\text{TiO}_2 \text{ NWs@SnO}_2/\text{C}$, the mass contents of SnO_2 , TiO_2 and carbon coating in active materials are estimated to be 43 wt%, 40.7 wt% and 16.3 wt%), 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, and then punched into disc-shaped electrodes. The mass of active material loaded on electrodes was ca. 1.2 mg. The separator and counter electrode choose Cellgard 2400 membrane and pure lithium foil, respectively. The electrolyte used here is an organic solution of LiPF_6 (1 M) in ethylene carbonate and dimethyl carbonate (1:1 by volume ratio). The galvanostatic discharge/charge cycle measurement was achieved on a CT2001a cell test instrument (LAND Electronic Co.) with a voltage

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