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Synthesis of sandwich-like TiO_2@C composite hollow spheres with high rate capability and stability for lithium-ion batteries

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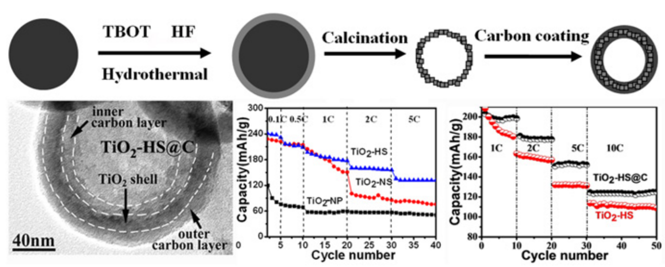
HIGHLIGHTS

- ► Sandwich-like TiO_2@C hollow spheres with {001} facets exposed are obtained.
- ► TiO_2 shells are wrapped in electron-conductive carbon layers.
- ► TiO_2@C hollow spheres show superior rate capability and stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel sandwich-like TiO_2@C composite hollow spheres with {001} facets exposed are obtained through hydrothermal carbon-coating treatment for the first time. Based on investigations by transmission electron microscopy (TEM), scanning electron microscopy (FESEM), XRD, laser Raman spectra, and N_2 adsorption–desorption isotherms, TiO_2 shells are proved to be wrapped in porous carbon layers, which provide conductive support for TiO_2, resulting the improvement in electronic conductivity and diffusion of Li^+. Moreover, these TiO_2 shells expose the reactive {001} facets, which facilitate Li^+ insertion/extraction. Through combining the above advantages, TiO_2@C composite hollow spheres show more superior rate capability and higher stability than TiO_2 nanoparticles (Degussa P25), TiO_2 nanosheets with {001} facets exposed, and TiO_2 hollow spheres before carbon-coating. This method may be extended to synthesize other sandwich-like composite hollow spheres for energy storage.

1. Introduction

The demands for rechargeable batteries are increasing in power sources both of portable electronic equipment and automobile electrical systems. Among various candidate power systems, lithium-ion batteries have attracted much attention because of their high energy storage density, long cycle life, little memory effect, poisonous metals free [1,2]. Crystalline TiO_2 has attracted much attention in recent years because of its excellent physicochemical properties and potential application in lithium-ion

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batteries. With low cost and high stability, TiO_2 has been regarded as a promising substitute for graphite that used in the present commercial lithium-ion batteries [3,4]. However, due to the poor electronic conductivity and low diffusion rate of Li^+, the electrochemical performance of TiO_2 electrode materials is limited [5]. Therefore numerous TiO_2 nanostructures and TiO_2 based nanocomposites have been synthesized to increase the lithium exchange efficiency, specific capacity and cyclability [6–10].

Hollow structures have attracted great attention in Li-ion batteries for their improvement in reversible lithium storage capabilities [11,12]. The hollow structure may provide extra active sites, large surface area and reduced effective diffusion distance for lithium ions, which is beneficial for better specific capacity and rate capability [13]. In the past few years, TiO_2 hollow spheres have been prepared for Li-ion batteries through different methods. Song et al. prepared anatase TiO_2 hollow spheres through a one-step template free method [14]. While Wang et al. reported a sol–gel process using hard templates to fabricate TiO_2 hollow spheres [15]. They both found the TiO_2 hollow spheres showed better electrochemical properties compared to TiO_2 nanoparticles.

Except for synthesizing hollow structures, the exposed facets also have a significant influence on the Li^+ diffusion efficiency. Several theoretical studies have pointed out that due to the special crystal structure of anatase, Li^+ insertion/extraction will be probably facilitated through the {001} facets. Anatase TiO_2 nanosheet with {001} facets exposed have been proved to be an ideal host structure for fast and efficient lithium insertion/extraction [16,17]. In order to obtain stable architectures, several hierarchical TiO_2 nanostructures with {001} facets exposed have also been fabricated and show excellent performance in the Li-ion batteries. Lou and his co-workers have synthesized TiO_2 hollow spheres with {001} facets exposed, which exhibit fast reversible lithium storage [18,19].

The above two strategies mainly try to control the topological structures or exposed crystal facets to optimize the capability of TiO_2 anode materials. Another alternative approach to overcome the disadvantages in TiO_2 based materials for Li-ion batteries is using nanocomposite materials. In particular, nanopainting with carbon has recently been found effective for improving cyclability and electronic conductivity [20]. Kelder et al. synthesized carbon-coated TiO_2 nanoparticles using phenyl phosphonic acid followed by special thermal treatments, which showed an improvement in electronic conductivity. What's more, the carbon layer can work as a buffer to mitigate the mechanical stress caused by Li^+ insertion and extraction [21,22].

Combining the nanostructure design of electrode materials and the nanocomposite concept, we herein report a new hierarchical anode nanostructure: sandwich-like TiO_2@carbon composite hollow spheres with anatase TiO_2 {001} facets exposed (denoted as TiO_2-HS@C). The TiO_2-HS@C was synthesized through a two-step coating process as showed in Scheme 1. Uniform carbon spheres were obtained by hydrothermal treatment of glucose with the addition of CTAB (TEM image is presented in Fig. S1). Then precursor of TiO_2 was coated on carbon spheres in the presence of HF to control the exposed facets of anatase TiO_2. Afterward, TiO_2 hollow spheres with {001} facets exposed (denoted as TiO_2-HS) were obtained through the removal of the carbon cores. The carbon layers were then coated on the shells of TiO_2 hollow spheres by the pyrolysis of glucose under hydrothermal conditions. Finally, the products were dried and heat-treated under N_2 atmosphere to carbonize the carbon precursors, to produce the sandwich-like TiO_2-HS@C.

Compared to commercial TiO_2 nanoparticles (Degussa P25), the TiO_2 nanosheets with {001} facets exposed (denoted as TiO_2-NS, synthesized according to the work of Xie et al. [23]) and TiO_2 hollow spheres without carbon-coating (TiO_2-HS), these TiO_2@C composite hollow spheres show larger specific capacity, much better rate capability and higher cyclability. In this article, we will discuss the relation between the structural characteristics and electrochemical performance.

2. Experiment section

2.1. Materials preparation

All the reagents were of analytical grade and were used without further purification.

2.1.1. Synthesis of carbon spheres

Carbon spheres were synthesized by a previously reported method [24]. In a typical synthesis, 2.87 g glucose and 0.2 g cetyltrimethyl ammonium bromide (CTAB) were dissolved in 30 mL distilled water to for an aqueous solution. Then the solution was placed in a 50-mL teflon-lined stainless steel autoclave, and maintained at 180 °C for 9 h in an air-flow electric oven. After the hydrothermal treatment, it was allowed to cool naturally to room temperature. The solid brown product was collected by centrifuging at 7000 rpm for 10 min, and washed with ethanol and water for three times, respectively. Finally, the obtain product was dried in air at 80 °C for 6 h.

2.1.2. Synthesis of TiO_2 hollow spheres with {001} facets exposed (TiO_2-HS)

TiO_2 hollow spheres with {001} facets exposed (TiO_2-HS) were prepared through the following method. For a typical procedure, 0.2 g carbon spheres were dispersed in 30 mL ethanol with the assistance of ultrasound. Then 0.34 mL $Ti(OC_4H_9)_4$ (TBOT) was added to the black suspension, and dispersed under ultrasound. Subsequently, a solution including 10 mL ethanol, 0.75 mL hydrofluoric acid solution (with a concentration ca. 47 wt.%) and 0.25 mL distilled water was dropped to the suspension under stirring. After the addition of HF, the mixture was kept stirring for 6 h at room temperature, after which it was transferred to a 50-mL teflon-lined stainless steel autoclave. Then it was maintained at 180 °C for 24 h in an air-flow electric oven. After cooling to room temperature, The product was collected by centrifuging at 7000 rpm for 10 min, and washed with ethanol and water for three times, respectively. Afterward, it was dried in air at 80 °C for 6 h. The final products were obtained after calcination at 500 °C in flowing air for 4 h with a heating rate of 2 °C min^{-1}, resulting the formation of TiO_2-HS.

2.1.3. Synthesis of sandwich-like TiO_2@carbon composite hollow spheres (TiO_2-HS@C)

In order to improve the cyclability and rate capability of TiO_2-HS, we have prepared TiO_2@carbon composite hollow spheres. In a typical synthesis, 0.1 g of as-synthesized TiO_2-HS sample was

Scheme 1. Schematic illustration of the synthesis process of TiO_2 hollow spheres and TiO_2@C sandwich-like hollow spheres.