

Synthesis of dandelion-like TiO₂ microspheres as anode materials for lithium ion batteries with enhanced rate capacity and cyclic performances

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(Received: 12 January 2012; revised: 3 May 2012; accepted: 10 May 2012)

Abstract: Dandelion-like TiO₂ microspheres consisting of numerous rutile single-crystalline nanorods were synthesized for the first time by a hydrothermal method. Their crystal structure, morphology and electrochemical properties were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and galvanostatic charge and discharge tests. The results show that the synthesized TiO₂ microspheres exhibit good rate and cycle performances as anode materials of lithium ion batteries. It can be found that the dandelion-like structure provides a larger specific surface area and the single-crystalline nanorod provides a stable structure and fast pathways for electron and lithium ion transport, which contribute to the rate and cycle performances of the battery.

Keywords: titanium dioxide; microspheres; nanorods; anodes; lithium batteries

[This work was financially supported by the Joint Project of the National Natural Science Foundation of China and the Natural Science Foundation of Guangdong Province, China (No.U1134002), the Natural Science Foundation of Guangdong Province, China (No.10351063101000001), and the Key Project of Science and Technology in Guangdong Province, China (No.2010A090602003).]

1. Introduction

Although the lithium ion battery is a promising device for energy storage, its safety needs to be improved [1-3]. Owing to its stable structure during lithium insertion/extraction, TiO₂ has attracted tremendous research interests as anode materials for lithium ion batteries [4-6]. Rutile is the most stable thermodynamically among the three common polymorphs of TiO₂ (anatase, rutile, and brookite). Bulky rutile grain TiO₂ exhibits low lithium insertion capacity due to low electron and lithium ion transport rate in the bulky grains [7-8].

Recently, it was found that nanosized rutile TiO₂ could reversibly accommodate 0.5Li (Li_{0.5}TiO₂), similar to anatase [9]. Numerous new nanosized rutile titania materials have been synthesized subsequently, such as nanocrystalline [10], nanoneedles [11], and nanorods [12]. Single-crystalline

nanosized rutile TiO₂ particles have high electron transport rate, and they have received more attention in the application of energy translation and storage [13-14]. Therefore, nanosized rutile TiO₂ can be used as the anode of a lithium ion battery.

In this paper, we reported a new rutile nanostructure TiO₂ that was synthesized by using rutile hollow SnO₂ spheres as templates. The synthesized rutile TiO₂ has the morphology of dandelion-like microspheres consisting of nanorods and exhibits good rate and cycle performances as the anode of a lithium ion battery.

2. Experimental

2.1. Preparation of materials

Hollow SnO₂ spheres were obtained according to the reported procedures [15]. Dandelion-like TiO₂ microspheres

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were prepared as follows: 0.0020 g hollow SnO₂ spheres were dispersed ultrasonically in 10 mL toluene for 10 min, and then 1 mL titanium(IV) butoxide and 1 mL hydrochloric acid (37wt%) were added and mixed for 30 min. The mixture was transferred into a Teflon-lined stainless steel autoclave with a capacity of 20 mL. The autoclave was maintained at 180°C for 4 h and then cooled to room temperature naturally. The resulted product was washed with absolute ethanol and dried in air. All the chemicals used for preparation were purchased from Sinopharm Chemical Reagent Co., Ltd., and used without further purification.

2.2. Structure and morphology characterization

The crystal structure of the prepared sample was characterized by X-ray diffraction (XRD) using a D/Max-III A diffractometer (Rigaku Corp., Japan) with Cu K_α radiation ($\lambda=0.15406$ nm) at 35 kV and 20 mA. The scattering angle range used in the measurement was from 20° to 80°. The morphologies were directly examined by field emission-scanning electron microscopy (FE-SEM; FEI, Quanta 400FEG, Netherlands, at an acceleration voltage of 20 kV), transmission electron microscopy (TEM; JEOL, JEM-2010HR, Japan, operating at 200 kV), and related selected area electron diffraction (SAED) patterns. The N₂-sorption isotherm curve was recorded at 77 K on Micromeritics ASAP 2020 instrument (USA). Specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. Pore sizes and volumes were estimated from the pore size distribution of the desorption branch in the isotherm.

2.3. Electrochemical measurements

The working electrode was prepared as follows: the prepared sample powders together with 20wt% acetylene black and 10wt% polyvinylidene fluoride (PVDF) binder were mixed in *N*-methylpyrrolidone (NMP). Then, the mixture was coated and compressed onto a copper foil current collector. Electrochemical measurements were carried out by using coin-type test cells (Type CR2032), where the working electrode was the anode and the lithium metal foil was the cathode. LiPF₆ (1 M) in EC/DMC/EMC (1:1:1 in volume ratio) and Celgard 2400 membrane were used as the electrolyte and the separator, respectively. The cell assembly was conducted in an argon-filled glove box (Mikrouna, Super 1220/750/900). The charge/discharge experiments were performed on Land CT 2001A (China) in the voltage range of 2.5-1 V versus Li⁺/Li at different rates.

3. Results and discussion

As confirmed by XRD patterns in Fig. 1, the prepared

sample is identified with a pure tetragonal rutile phase (JCPDS No. 21-1276). No peaks of anatase or brookite phase are detected, indicating the high purity of the prepared products.

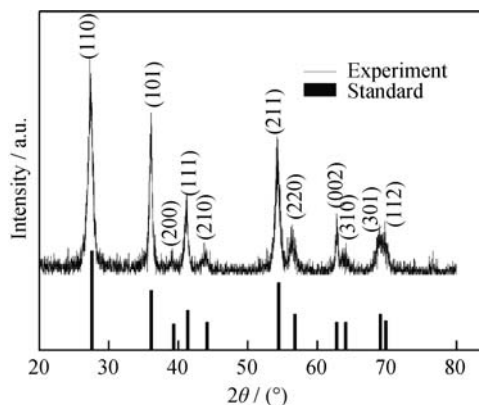


Fig. 1. Typical XRD patterns of the rutile TiO₂ microspheres.

The SEM images show that the prepared sample has the morphology of dandelion-like spheres with an average diameter of 3 μm , as revealed in Fig. 2(a). At a higher magnification, it is found that these dandelion-like microspheres consist of numerous nanorods of 10 nm in diameter, as shown in Fig. 2(b).

Fig. 3 presents the nitrogen adsorption/desorption isotherms of the rutile TiO₂ microspheres, which is typically characteristic of mesoporous materials [16-17]. From the Barrett-Joyner-Halenda (BJH) curve, as shown in the inset, the rutile TiO₂ microspheres contain pores of about 4 nm. The BET surface area of the rutile TiO₂ microspheres is 46 $\text{m}^2\cdot\text{g}^{-1}$.

The TEM image of the rutile TiO₂ microsphere in Fig. 4(a) does not reveal the hollow structure of SnO₂ (Fig. 4(b)) that was used as a template, indicating that the hollow SnO₂ spheres are sacrificed during the formation of TiO₂. The high-resolution TEM image of the nanorod in Fig. 4(c) reveals that the lattice fringes are parallel to the wall and the distance between the adjacent lattice fringes is 0.3191 nm, which is corresponding to the interplanar distance of rutile TiO₂ [110]. The [110] axis perpendicular to the wall indicates that the crystal growth direction of the nanorods is along [001] plane. In addition, the single-crystalline structure of rutile-type TiO₂ nanorods is verified by the spot pattern in the SAED pattern, as shown in Fig. 4(d).

From the experimental results and discussion above, a possible mechanism for the morphology evolution of TiO₂ microspheres can be summarized in Fig. 5. Initially, toluene

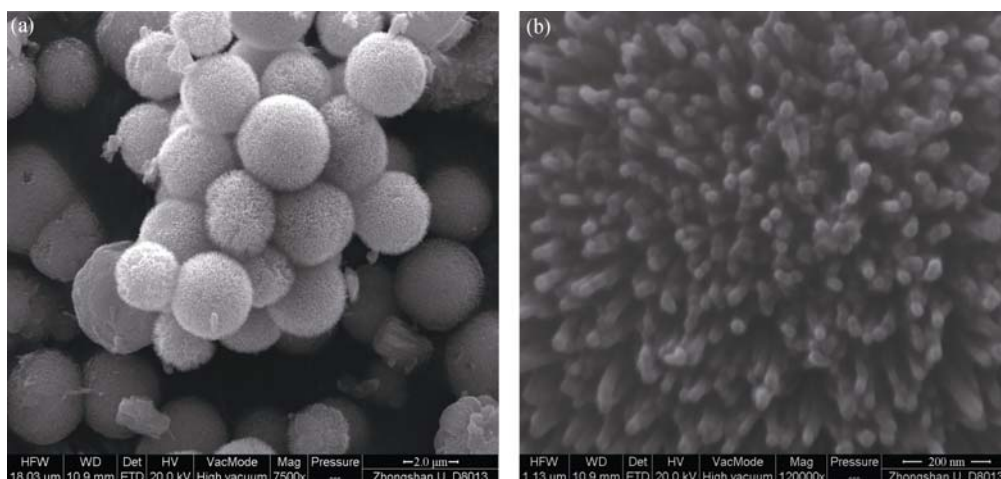


Fig. 2. SEM (a) and HR-SEM (b) images of the rutile TiO_2 microspheres.

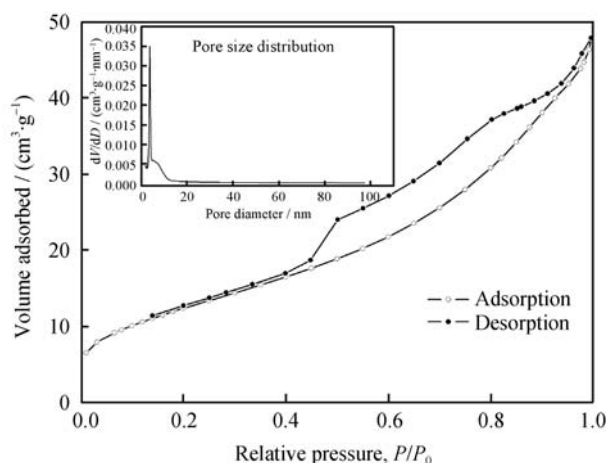


Fig. 3. Nitrogen adsorption/desorption isotherms and BJH pore size distributions (inset) of the rutile TiO_2 microspheres.

is used as the nonpolar solvent for the solution of the precursor, titanium(IV) butoxide, whereas hydrochloric acid is used to avoid precursor hydrolysis by ensuring an acidic

condition and the template hollow SnO_2 spheres are dispersed in hydrochloric acid due to their hydrophilicity. An interface forms between toluene and hydrochloric phases. With an increase of temperature, to minimize system energy, Ti^{4+} precursors diffuse to the high-energy acid/toluene interface and approach to the surface of the hollow SnO_2 spheres, as shown in path I. Simultaneously, on the sphere surface, SnO_2 reacts with hydrochloric-forming water, with the hydrolysis of Ti^{4+} precursors, resulting in the formation of TiO_2 crystal nuclei on the surface of SnO_2 spheres, as shown in path II. With the crystal nuclei available, TiO_2 grows toward the sphere center accompanying the dissolution of SnO_2 , as shown in path III. At last, dandelion-like TiO_2 microspheres are obtained, as shown in path IV. A similar mechanism for the formation of single-crystalline rutile TiO_2 was reported by Yu *et al.* [16]. In this work, novel rutile TiO_2 with special structure, dandelion-like microspheres that consist of numerous nanorods, can be obtained.

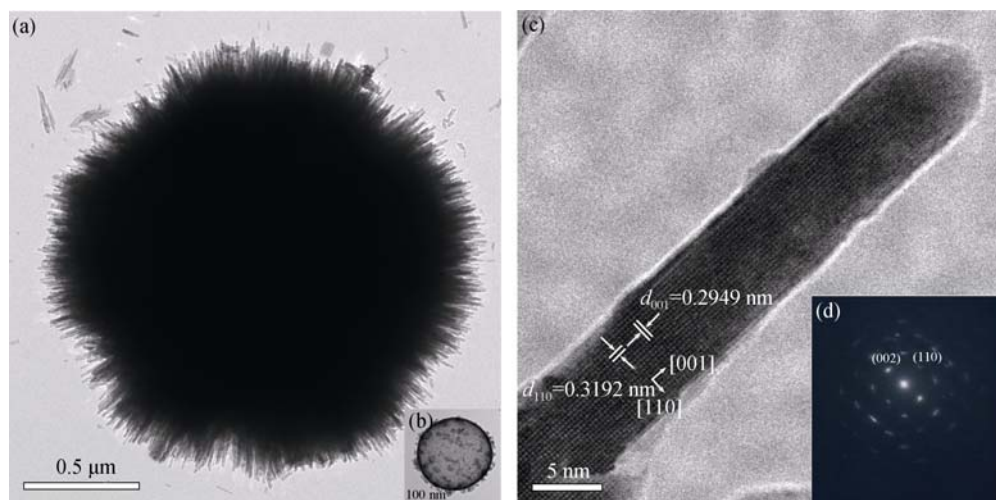


Fig. 4. TEM images of the dandelion-like TiO_2 microsphere (a) and hollow SnO_2 sphere (b); HR-TEM image (c) and related SAED pattern (d) of the nanorod.

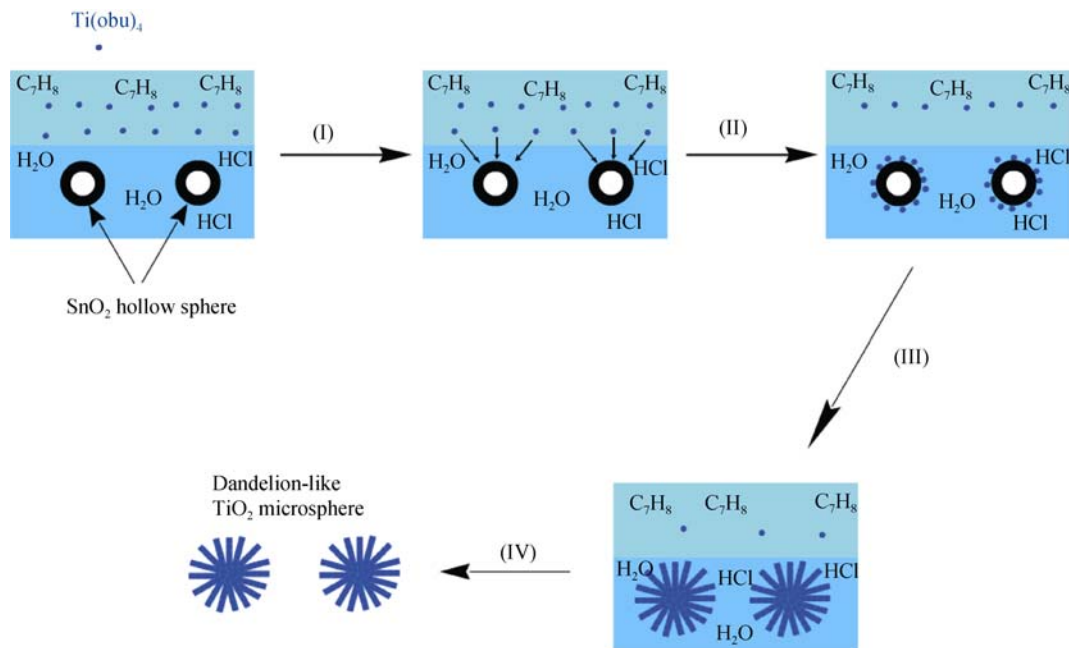


Fig. 5. Schematic illustration of a possible formation process of the dandelion-like TiO₂ microspheres.

Fig. 6(a) displays the charge/discharge curves of the electrodes made by the dandelion-like TiO₂ microspheres at

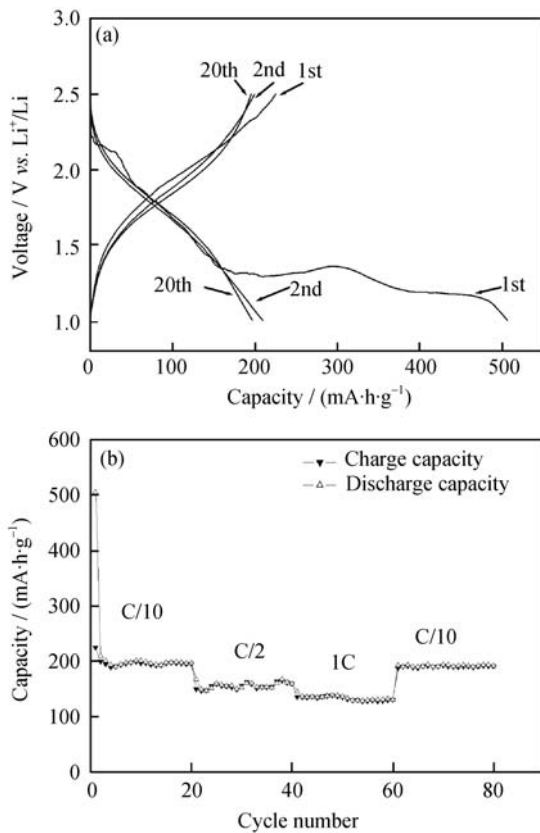


Fig. 6. (a) Charge/discharge curves of the rutile TiO₂ microspheres at C/10 and (b) cyclic performance of the rutile TiO₂ microspheres cycled at C/10, C/2, 1C, and C/10 between 1 and 2.5 V.

the rate of C/10. The initial discharge and charge capacity of the electrode are 505 and 225 mA·h·g⁻¹, respectively, indicating a reversible efficiency as low as 45% for lithium insertion and extraction in the initial charge/discharge curves. The large irreversible capacity loss originates from the formation of stable lithium titanium oxide at deeper lithium insertion [18]. The reversible capacity is 225 mA·h·g⁻¹ at the first cycle and remains 195 mA·h·g⁻¹ at the 20th cycle, which are higher than those of nanostructure rutile TiO₂ samples that have been reported [11-12]. For example, at the rate of C/10, the reversible capacity is 128 mA·h·g⁻¹ for rutile TiO₂ nanoneedles [11] and 183 mA·h·g⁻¹ for rutile TiO₂ nanorods [12]. This indicates that the dandelion-like TiO₂ microspheres have good reversible lithium insertion capacity.

Fig. 6(b) presents the rate and cycle performances of the dandelion-like TiO₂ microspheres. The average specific capacities are 196, 155, and 132 mA·h·g⁻¹ for the discharge rates of C/10, C/2, and 1C, respectively. These rate performances of the TiO₂ microspheres are comparative to the reported rutile TiO₂ [9, 18]. Additionally, after 20 cycles at each rate, the capacity of the dandelion-like TiO₂ microspheres can be restored to their initial capacity at C/10, indicative of the good cycle performance of the dandelion-like TiO₂ microspheres. The good rate and cycle performance of the dandelion-like TiO₂ microspheres should be related to their special structure of dandelion-like microspheres that consist of numerous single-crystalline nanorods. The dandelion-like structure provides a larger specific surface area and the single-crystalline nanorod provides a stable structure and

fast pathways for electron and lithium ion transport, which contribute to the rate and cycle performance.

4. Conclusions

Dandelion-like rutile TiO₂ microspheres that consist of numerous nanorods can easily be synthesized by using rutile hollow SnO₂ spheres as templates. As the anode material of lithium ion batteries, the dandelion-like TiO₂ microspheres exhibit both high rate capacity and cyclic stability. These excellent electrochemical performances could be attributed to the single-crystalline building blocks as well as the unusual dandelion-like morphology. The former provides fast pathways for electron and lithium ion transport, and the latter provides a larger special surface.

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