



Arrayed titanium dioxide shells architecture as anode of lithium ion microbattery



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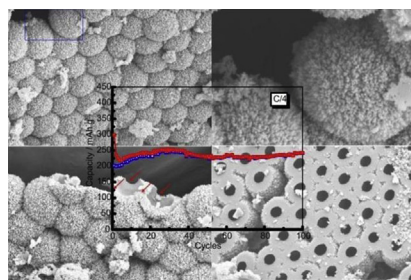
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HIGHLIGHTS

- TiO₂-NCs electrode was constructed as anode of lithium ion microbattery.
- Hierarchical structure of TiO₂ with {001} facets yields good rate capability and cycle stability.
- Highly mesoporous and microporous nature contributes to rate performance.

GRAPHICAL ABSTRACT



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ABSTRACT

TiO₂ nanocones (TiO₂-NCs) are constructed into arrayed spherical shells through a liquid-phase deposition reaction with polymer template, to improve the performance of TiO₂ as anode of lithium ion microbattery. The morphology and structure characterizations indicate that TiO₂ grows into nanocones with exposed {001} facets and is self-assembled into mesoporous structure. Meanwhile, macroporous channels are formed among the arrayed shells. Electrochemical measurements demonstrate that the TiO₂-NCs reveal excellent performance in terms of improved lithium storage property and rate capability. The improved performance can be ascribed to the channel structure for the convenience of ionic transportation and the high-energy facets for the improvement of ionic reactivity.

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1. Introduction

Lithium ion batteries are today used for a wide range of applications in micro-device fields (MDF) and hybrid electric vehicles (HEV) [1–8]. In the MDF, miniaturization is important to make a high energy and power on a small footprint area, which requires

nanostructured materials for batteries. Lithium ion microbattery is a miniaturized power source with thin-film structured electrodes to miniaturize essentially the geometry of standard batteries, and many nanostructured materials [9–17], especially carbon-based materials, have been developed to be used as the negative materials for this microbattery. Unfortunately, the cycle stability of traditional carbon materials is poor and the formation of the solid electrolyte interphase (SEI) on carbon materials due to its low lithium inserted potential is a serious threat to the safety of the battery [18–20].

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Titanium-containing oxides, such as TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$, have better structure stability and higher lithium insertion potential (~ 1.5 V vs. Li^+/Li) than carbon materials and thus provide lithium ion batteries with excellent cycle performance [21,22]. Compared with other titanium oxides, anatase TiO_2 exhibits superior properties, including the simplicity for synthesizing with nanostructure and high lithium storage capacity [23]. Anatase TiO_2 with a tetragonal crystal structure has been widely investigated and a large number of nanostructured anatase TiO_2 materials have been constructed for photocatalysis, gas sensor and electrochemical energy conversion and storage devices [7,11,13,24–27]. Earlier studies demonstrated that highly-active {001} facets of anatase TiO_2 exhibit superior photocatalytic activity when normalized by the surface area [28–30], and recent studies showed that these facets also provided unusual opportunities for electrochemical energy storage [31,32]. To exploit the activity of anatase TiO_2 with exposed {001} facets [23], a series of studies have been performed for the synthesis of sheet-like TiO_2 (TiO_2 nanosheet) [33–36]. However, the formation of the nanosheet should be in a special reactor (autoclave) and the final product is usually as powders, which limit its applications.

In our previous report, we prepared cone-like TiO_2 (TiO_2 -NCs) with exposed {001} facets through a convenient process and then assembled them into hollow spheres with polymer template [37]. We used the TiO_2 -NCs as the support of tin oxide nanoparticles to develop a novel negative composite for lithium ion battery. In this composite, the high Li^+ -transport dynamics of titanate hollow spheres (TiO_2) and high capacity of tin oxide (SnO_2) were intimately integrated into a hierarchical architecture of nanocones, while the unique spatial arrangement of SnO_2 component in the nano-cavities effectively accommodates the volume change during lithiation/de-lithiation, hence rendering the composite stable cycling life. The developed TiO_2 -NCs exhibits enhanced lithium storage capacity compared to the TiO_2 nanospindles [25] and improved rate capability compared to the porous TiO_2 [38].

With the aim to construct novel nanostructured anode for high performance lithium ion microbattery, we developed a novel shell architecture TiO_2 as the negative material in this work. The material design is based on the fact that nano-structured TiO_2 with {001} facets can be deposited on the surface of polystyrene spheres (PS) functionalized by adsorption of polyelectrolytes [37], which is a water-soluble polymer containing ionizable groups and can provide polyanion and polycation to induce the nucleation of TiO_2 . With the developed technology of PS assembly [39,40], we constructed the TiO_2 -NCs into ordered monolayer spherical shells on a titanium foil, namely TiO_2 -NCs/Ti electrode. This electrode has large specific surface areas, active facets and channel structures, which is essential for Li insertion/extraction and for Li^+ -transport, hence delivering high-rate capability and high storage capacity.

2. Experimental

2.1. Materials synthesis

Based on the method of PS functionalization and the technology of templates assembly [37,40], a monolayer of sulfonated PS (s-PS) coated with polyelectrolytes was assembled on a glass substrate by confined convective assembly. Initially, this monolayer of s-PS was transferred onto a titanium foil ($5 \times 5 \times 0.127$ mm³, 99.99%, Alfa Aesar) by a floating-transfer method. After being dried in air at room temperature, the substrate coated with a monolayer of s-PS was heated in an oven to 110 °C for 5 min, then immersed vertically in a freshly prepared liquid-phase deposition (LPD) solution (50 ml

containing $(\text{NH}_4)_2[\text{TiF}_6]$ (0.05 mol l⁻¹) and H_3BO_3 (0.15 mol l⁻¹). The pH value of the LPD solution was adjusted to 2.9 by adding HCl (2 mol l⁻¹) and the LPD solution was incubated at 50 °C for 8 h. After the reaction, the sample was washed with water and dried at room temperature, immersed in toluene (100 ml) to remove the PS templates, and calcined at 450 °C for 3 h in an oven under argon atmosphere.

To be able to estimate the mass of the deposited TiO_2 film, the number of the TiO_2 -NCs spherical shells was determined, which was 9.5×10^{10} for a 5×5 mm² flat Ti substrate. Considering for 3D structures, a TiO_2 -NCs spherical shell with 300 nm wall thickness and a density of 3.895 g cm⁻³, the mass of deposited TiO_2 can be calculated. For a 5×5 mm² TiO_2 film, the mass of deposited TiO_2 is equal to 0.096 mg.

2.2. Materials characterization

The morphology of the sample was examined by field-emission scanning electron microscopy (FE-SEM; ZEISS Ultra 55, Germany) and transmission electron microscopy (TEM; JEM-2100HR, Japan). Crystallographic information for the sample was investigated with X-ray powder diffraction (XRD; Bruker D8 Advance, Germany). The surface area of the sample was measured using a Micromeritics ASAP 2020-physisorption analyzer (USA).

2.3. Electrochemical measurements

The electrochemical measurements were carried out using a coin-type cell (CR2025) with a metallic lithium foil as the counter and reference electrodes. The working electrode was the TiO_2 -NC/Ti and the electrolyte was LiPF_6 (1.0 mol l⁻¹) in a 1:1 (w/w) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Cyclic voltammetry was conducted on a Solartron Analytical 1470E CellTest System (England) at different scanning rates and the charge/discharge tests were performed using a LAND CT2001A (China) battery testing system at different current rates with a voltage window of 1.0–3.0 V (vs. Li^+/Li).

3. Results and discussion

With our developed technology, a large area of titanium foil covered by functionalized s-PS (sulfonated polystyrene spheres) templates can be achieved easily. FE-SEM image (Fig. 1a) shows that the s-PS layer is flat and smooth, indicating that the template is a single layer, which ensures the formation of a monolayer of TiO_2 spherical shells. High-magnification FE-SEM (Fig. 1b) clearly reveals that the s-PS templates were assembled on a substrate of the titanium foil in arrayed monolayer successfully via a floating-transfer method. It is noteworthy that the polyelectrolytes adsorbed by s-PS play a key role during the process of self-organized TiO_2 on the surface of templates. As shown in Fig. 1, TiO_2 can hardly be organized on the surface of the bare s-PS (Fig. 1c). On the surface of the s-PS covered with the polyelectrolytes, however, well-defined and uniform TiO_2 layers can be successfully achieved (Fig. 1d). This result suggests that the deposition of TiO_2 using the LPD method is highly sensitive to a polyelectrolyte modification of the polymer surfaces, and the polyelectrolytes can induce the nucleation of TiO_2 on the surface of s-PS in the initial deposition. Moreover, TiO_2 were formed in nanocones and self-organized into 3D networks structure on the substrate, as shown in the inset of Fig. 1d.

Fig. 2 reveals the detailed features of the as-prepared samples. It can be seen from the side view (Fig. 2a) and the bottom view (Fig. 2b) that macroporous channels (red arrows in web version shown) were formed among spheres and between spheres and

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