



One-pot synthesis of bicrystalline titanium dioxide spheres with a core–shell structure as anode materials for lithium and sodium ion batteries

Zichao Yan, Li Liu*, Jinli Tan, Qian Zhou, Zhifeng Huang, Dongdong Xia, Hongbo Shu, Xiukang Yang, Xianyou Wang*

Key Laboratory of Environmentally Friendly Chemistry and Applications of Ministry of Education, School of Chemistry, Xiangtan University, Hunan, Xiangtan 411105, China

HIGHLIGHTS

- Anatase@TiO₂(B) spheres were firstly synthesized.
- Anatase@TiO₂(B) spheres show excellent electrochemical performance for Li insertion/extraction.
- Anatase@TiO₂(B) spheres also show excellent electrochemical performance for Na insertion/extraction.
- The excellent performance is due to the unique bicrystalline hierarchical structure.

ARTICLE INFO

Article history:

Received 14 May 2014
Received in revised form
28 June 2014
Accepted 29 June 2014
Available online 7 July 2014

Keywords:

Lithium ion batteries
Sodium ion batteries
Titanium dioxide
Bicrystalline hierarchical spheres
One-pot method

ABSTRACT

Bicrystalline titanium dioxide spheres (anatase@TiO₂(B) spheres) with enhanced electrochemical activity in lithium and sodium ion batteries have been successfully synthesized via a facile one-pot solvothermal method. The anatase@TiO₂(B) spheres have a core–shell structure with TiO₂(B) nanosheets sheathing the anatase TiO₂ sphere core which consists of nanoparticles, as characterized by X-ray diffraction, scanning electron microscopy (SEM), and high-resolution transmission microscopy (HRTEM). The anatase@TiO₂(B) spheres show excellent lithium storage performance, which have high initial discharge capacity (114.8 mAh g⁻¹) with almost no capacity fading after 100 cycles and still maintain at 91.7 mAh g⁻¹ after 375 cycles at a super-high current density of 5040 mA g⁻¹ (30 C). What's more, they also show excellent rate capability in sodium ion batteries at various current densities ranging from 85 to 850 mA g⁻¹. The unique hierarchical structure of anatase@TiO₂(B) spheres with excellent cycle performance and rate capability make a compelling case for their development as anode materials for both lithium and sodium ion batteries.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Currently, environmental disruption and economic recession of burning non-renewable and unsustainable fossil fuels have gained a great deal of awareness of renewable energy storages [1,2]. Lithium ion batteries (LIBs) with superior electrochemical properties (e.g., large energy density, high rate capability, and long cycling life) have been considered of great valuable for commercial applications and theoretical studies [3]. However, its success is still limited due to their high cost on dollars per kilowatt hour basis [1].

Recently, sodium ion batteries (NIBs) with higher availability and potential for lower cost of raw materials have drawn scientists' attention [4]. As we all know, there are too many restrictions for these battery technologies, such as electrolytes, separators, and electrode materials. Among all of those restrictions, anode material is a crucial factor for both LIBs and NIBs in electrochemical property and safety [5,6]. Lithium and sodium insertion into carbon anode materials were extensively studied by a lot of scientists [7–9]. For LIBs, graphite is a widely used anode material in commercial lithium ion batteries, but it still has limitations and weaknesses, such as electrical disconnection, structural deformation and initial loss of capacity. Ti-based anode material with its inherent chemical stability, minimal toxicity, low cost, and high discharge potential has been considered as one of the most suitable candidates for LIBs

* Corresponding authors. Tel.: +86 731 58292206; fax: +86 731 58292477.
E-mail addresses: liulili1203@126.com (L. Liu), wxianyou@yahoo.com (X. Wang).

anode materials [10,11]. Moreover, for NIBs, it is generally accepted that, unless high pressures are used, sodium insertion into graphitic carbons is minimal [12–14]. So, it is of great urgent for us to find a perfect anode material for both LIBs and NIBs, especially for future NIBs.

As a newly used anode material, TiO_2 with various crystalline polymorphs has been extensively studied in LIBs, and recent reports show the properties as Na hosts [15–17]. Although TiO_2 has many advantages as LIBs and NIBs anode material, the low ion diffusivity and poor conductivity badly affect the electrochemical property and restrict the widespread application of TiO_2 . What's more, crystalline phase, morphology, and size of particles also have important influence on its electrochemical properties.

Among various polymorphs of TiO_2 (rutile, anatase, brookite etc.), anatase TiO_2 with excellent electrochemical stability has attracted considerable interest due to its 3D networks. This structure leads to empty zigzag channels in the anatase framework, which not only gives possible interstitial sites for Li or Na accommodation, but also increases the electrochemical stability of anatase TiO_2 . Compared with anatase TiO_2 , $\text{TiO}_2(\text{B})$ with a relatively open tunnel structure and large interlayer spacing can provide a better electrochemical activity, which is also considered as a suitable active material for lithium storage and sodium ion intercalation [18–22]. However, the single phase of anatase TiO_2 or $\text{TiO}_2(\text{B})$ with good cycle performance or rate capability in LIBs have been found relative poor electrochemical performance in NIBs [18,19,21,23]. Considering that the bicrystalline of anatase TiO_2 and $\text{TiO}_2(\text{B})$ might contain both structural and electrochemical advantages of anatase TiO_2 and $\text{TiO}_2(\text{B})$. So, it would be of great interest to construct bicrystalline materials of anatase TiO_2 and $\text{TiO}_2(\text{B})$ with excellent electrochemical performance in LIBs and NIBs.

As for morphology and size, various nanosized TiO_2 with special morphologies, such as nanoribbons [13], nanotubes [21], nanosheets [22] and hollow nanospheres [24], have been fabricated to improve the specific capacity and rate performance. Even though nano-materials offer numerous advantages, such as huge surface area and high rate capability, they also have to suffer from low tap density, poor stability and serious side reactions [21]. Therefore, fabricating hierarchical micron-sized TiO_2 and $\text{TiO}_2\text{-C}$ composites have been considered as effective way to overcome these disadvantages and improve the electrochemical performance of TiO_2 [25,26]. Recently, micro-nanosized hierarchical structures composed with nano-sized assemblies and mesoporous nanoparticles with high packing density have been widely concerned by researchers owing to the multilevel and porous structure that can provide both extraordinarily high activated surface and robust stability [27–30]. So, electrode materials with hierarchical structure composed by nanosized particles can take the advantages of nanometer size effects, high tap density and high stability arisen from the micro- or sub-micro-sized assemblies, which could improve electrochemical property of electrode material remarkably. From the above aspects, it is of great significance to fabricate TiO_2 bicrystalline hierarchical spheres composed by nano-sized assemblies with high tap density and electrochemical activity from the view of both practical application and scientific research.

The conventional fabrication procedures of spherical structure generally involved templates, which related to tedious synthesis and high cost [31,32]. In this work, we synthesized the anatase@ $\text{TiO}_2(\text{B})$ hierarchical spheres with $\text{TiO}_2(\text{B})$ nanosheets sheathing anatase spheres core via a facile and green one-pot solvothermal method. The hierarchical structure contains the electrochemical advantages of bicrystalline structure and nanometer size effects. Moreover, it also increases the tap density and stability of the material due to the nano-sized assemblies and spherical

morphology. Here, we show the excellent electrochemical property of the anatase@ $\text{TiO}_2(\text{B})$ spheres for both LIBs and NIBs.

2. Experimental

2.1. Synthesis of anatase@ $\text{TiO}_2(\text{B})$ spheres

As shown in Fig. 1, anatase@ $\text{TiO}_2(\text{B})$ spheres were achieved via a one-pot facile solvothermal route. A mixture of 15 ml alcohol and 5 ml water was added dropwise into another mixture of 20 ml acetone solution of PVP and 5 ml tetrabutoxytitanium until no more white precipitate of titanium hydroxide was produced. After the solution was gently stirred for 2 h at room temperature, 5 ml NaOH solution (1.25 M) were added dropwise into the white suspension. After the suspension was stirred vigorously for 3 h at room temperature, the reaction suspension was then transferred to a 100 ml Teflon-lined stainless steel autoclave and kept in an electric oven at 180 °C for 6 h. The white precipitate was rinsed with distilled water, 0.1 M HCl, and distilled water until pH 7 was reached. After drying at 80 °C for at least 1 day, the as-prepared sample was calcined in a tubular furnace at 450 °C for 4 h in air to remove residual organics, and anatase@ $\text{TiO}_2(\text{B})$ spheres were obtained. In order to investigate the effect of different amount of NaOH solution, 2.5 ml and 7.5 ml NaOH solution were used to observe the change of TiO_2 . For comparison, anatase TiO_2 spheres were also prepared in the same way except for the addition of NaOH solution.

2.2. Structure and morphology characterization

The structures of the as-synthesized samples were characterized by X-ray diffraction. X-ray powder diffraction data were obtained using a Rigaku D/MAX-2500 powder diffractometer with a graphite monochromatic and Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) operated at a scan rate of 5°min^{-1} in the 2θ range of $10^\circ\text{--}80^\circ$. Scanning electron microscope (SEM) images of the samples were collected using a JEOL JSM-6610 scanning electron microscope, which were used to observe the morphology of the samples. Besides, high-resolution transmission electron microscopy (HRTEM) and fast-Fourier transform (FFT) measurements were carried out using a JEOL JEM-2100F transmission electron microscope at an acceleration voltage of 200 kV.

2.3. Electrochemical characterization

The working electrodes for lithium and sodium cells were fabricated by mixing the as-synthesized samples, carbon black, and Polyvinylidene fluoride (PVDF) binder with a weight ratio of 70:20:10 in N-methyl pyrrolidinone, which were then pasted on copper foil followed by drying under vacuum at 110 °C for 10 h. For lithium cells, the testing cells were assembled with the working electrode thus fabricated, metallic lithium anode, Celgard 2300 film separator and 1 M LiPF_6 in 1:1 ethylene carbonate (EC)/dimethyl carbonate (DMC) electrolyte, whereas sodium cells were assembled with metallic sodium as the negative electrode, glass fiber separator (Whatman GF/D), and 1 M NaClO_4 in propylene carbonate (PC) electrolyte. The assembly of the testing cells was carried out in an argon-filled glove box, where water and oxygen concentration were kept less than 5 ppm. The charge–discharge cycle tests of LIBs (168 mA g^{-1} was assumed to be 1 C rate) and NIBs were run at different current densities between 1.0–3.0 V and 0.01–2.5 V, respectively. All the cells were allowed to age for overnight before testing.

Cyclic voltammetry (CV) tests and EIS experiments were performed on a Zahner Zennium electrochemical workstation. CV tests

Download English Version:

<https://daneshyari.com/en/article/7736170>

Download Persian Version:

<https://daneshyari.com/article/7736170>

[Daneshyari.com](https://daneshyari.com)