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ARTICLE TYPE

Hierarchically porous anatase TiO₂ microspheres composed of tiny octahedra with enhanced electrochemical properties in lithium-ion batteries †

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In the present work, a one-step synthetic route is developed for fabricating hierarchical anatase TiO₂ microspheres for the first time. These microspheres are composed of ultrathin rod-like structures in the radial direction, in which ultrathin rods are consisted of tiny octahedral via a growth model of oriented attachment. Based on XRD and electron microscopic analyses, a mechanism for the growth of the microspheres is proposed. This material displays a large capacity of 157.3 mA h g⁻¹ at 1 C after 200 cycles and also exhibits high rate performance and excellent cycling stability. These high performance characteristics may be due to the intrinsic characteristics of the hierarchical porous anatase TiO₂ microspheres, in which the porous structure can permit facile diffusion of the electrolyte. They can also enhance the contact between the electrode surface and the electrolyte, while the ultrathin rods can shorten the transport distance of Li-ions and electrons during electrochemical cycling. At the same, the porous microsphere can also accommodate volume changes in the charge-discharge process.

1. Introduction

Lithium-ion batteries (LIBs) are widely been considered to be one of the most attractive types of energy storage devices due to their high energy storage density, higher power source, and long cycling life.^{1,2} Due to the development of hybrid electric vehicles and electric vehicles, there is increasing demand for LIBs higher energy densities, safety and long-term cycling stability. To date, a large number of metal oxides have been used as anode materials in LIBs.³⁻¹⁰ Material studied include TiO₂,^{4,5} SnO₂,⁶ CoO,⁷ MnO₂,⁸ V₂O₅⁹ and Nb₂O₅.¹⁰ TiO₂, in particular, has attracted much attention due to its low cost, environmental friendliness and chemical stability,^{4,11,12} and it is now one of the most intensively investigated alternative anode materials for LIBs. On the other hand, hierarchically structured materials have been constructed for enhancing lithium storage properties in recent years due to their high porosity, large surface area and thermodynamic stability as well as the stress-strain relief in repetitive lithium-ion insertion/extraction reactions.^{13,14} For instance, Zhang *et al.*¹⁵

have fabricated hierarchical porous rutile TiO₂ microspheres composed of nanorods, which display high reversible capacity. Kim *et al.*¹⁶ devised a strategy to control the hydrolysis rate of the precursor and the aggregation of surfactants for constructing a series of 3D dendritic rutile TiO₂ nanostructures and showed that one structure exhibited high cyclic retention after 50 cycles. We have previously reported hierarchically porous rutile TiO₂ microspheres composed of nanorods which exhibited a large reversible capacity of 160.6 mA h g⁻¹ after 100 cycles at 1 C.¹⁷

Previous reports suggested that the uptake of Li⁺ appears more facile in the anatase TiO₂ lattice than that in rutile TiO₂ lattice. Lou *et al.*¹⁸ synthesized spherical anatase TiO₂ composed of nanosheets with nearly 100% exposed (001) facets and found that this material showed high reversibility over 100 cycles and a good rate capability up to 20 C. Hu *et al.*¹⁹ reported that hierarchical mesoporous anatase TiO₂ spheres delivered a large reversible capacity of 210 mA h g⁻¹ after 40 cycles at a rate of C/5. However, these hierarchical anatase TiO₂ spheres were formed in the presence of surfactants. Since expensive surfactants seemingly have to be used during the synthetic process, the large-scale applications of hierarchical TiO₂ are limited. In addition, the removal of surfactants from the final product may present a challenge, as it may alter the surface chemistry unfavorably for certain applications. Therefore, it is highly desirable to develop facile synthetic routes for fabricating hierarchical anatase TiO₂ without using additives.

More recently, several papers reported the synthesis of

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hierarchical anatase TiO₂ microspheres based on additive-free synthetic strategies.²⁰⁻²² For example, Kuang *et al.*²⁰ prepared hierarchical anatase TiO₂ microspheres composed of nanorods and nanoparticles via a hydrothermal process and subsequent calcinations. Sun *et al.*²² synthesized mesoporous anatase TiO₂ spheres in which H₂SO₄ was used as a phase-inducer for the formation of the anatase particles with a spherical morphology. In fact, these synthetic routes were usually adopted *via* a two-step hydrothermal process combined with a thermal treatment or under relatively high experimental temperatures. In the present work, a one-step synthetic route was developed for fabricating hierarchical anatase TiO₂ microspheres for the first time. The microspheres were formed through the aggregation of ultrathin rods constructed of tiny octahedra through a growth model of oriented attachment.

2. Experimental

2.1 Preparation and characterizations

Typically, 8 g of urea was dispersed in 25 mL of 2 M HCl aqueous solution. After stirring for several a few minutes, 1 mL of titanium isopropoxide (TTIP) was added dropwise under vigorous stirring. Until the solution transformed to transparent, the resulting solution was transferred into a Teflon stainless steel with a capacity of 40 mL. The autoclave was kept at 120 °C for different time and then naturally cooled to room temperature. The white precipitate was harvested via centrifugation, washed thoroughly with deionized water for several times, and then dried at 70 °C overnight. X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert spectrometer by using CoK α radiation ($\lambda = 1.78897 \text{ \AA}$), and the data were changed to CuK α data. Scanning electron microscopy (SEM, S4800 instrument) and transmission electron microscopy (TEM, FEI F20 S-TWIN instrument) were applied for the product morphology. N₂ adsorption-desorption was measured on a Micromeritics ASAP 2020 instrument (Micromeritics, Norcross, GA, USA). Scanning electron microscopy (SEM, S4800 instrument) and Transmission electron microscopy (TEM, FEI F20 S-TWIN instrument) were applied for the structural characterization of the samples.

2.2 Electrochemical measurements

For the electrochemical measurement, 70 wt% the resulting TiO₂ were admixed and ground with 20 wt% acetylene black carbon and 10 wt% polyvinylidene fluoride (PVDF). The mixture was spread and pressed on copper foil circular flakes as working electrodes and dried at 110 °C in vacuum overnight. Lithium foils were used as the counter electrodes. The electrolyte used was 1 M LiPF₆ in a 1:1:1 (volume ratio) mixture of ethylene carbonate (EC), ethylene methyl carbonate (EMC) and dimethyl carbonate (DMC). The separator was Celgard2400 (America) micro-porous polypropylene membrane. Cell assembly was carried out in a glove box filled with highly pure argon gas (O₂ and H₂O levels < 1 ppm). Form factor of the half cell is CR2025. Cyclic voltammetry (CV) was performed using an electrochemical workstation (CHI 600C). Charge-discharge tests were performed in the voltage range of 1.0-3.0 V (vs. Li⁺/Li) at different current

rates (1 C = 168 mA g⁻¹) on Land automatic batteries tester (Land, CT 2001A, Wuhan, China).

3. Results and discussion

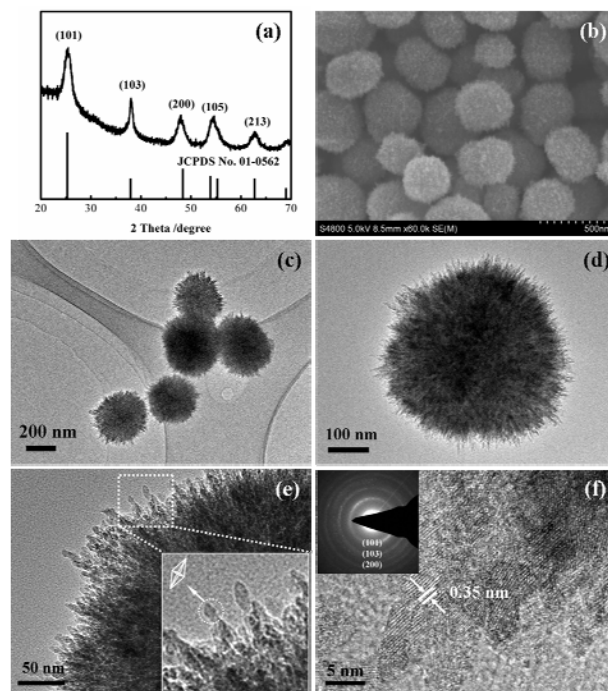


Fig. 1 Hierarchical anatase TiO₂ microspheres obtained at 120 °C for 12 h: (a) XRD pattern, (b) SEM image, (c-e) TEM and (f) HRTEM images. The inset in (f) is the SAED pattern.

Fig. 1 shows the characterization of the sample synthesized at 120 °C for 12 h. The XRD patterns shown in Fig. 1a reveals that all the diffraction peaks can be indexed to anatase TiO₂ (JCPDS 01-0562), indicating that the pure anatase TiO₂ was obtained in this reaction system. The significant broadening of the peaks indicates that the size of the TiO₂ crystallites was small. SEM, shown in Fig. 1b, revealed that the synthesized sample consisted of spheres with uniform morphology. These spheres have a hierarchical structure and their diameter was ~ 300-400 nm. TEM, depicted in Fig. 1c, indicates that the hierarchical microspheres were relatively monodisperse. High-resolution TEM (Fig. 1d) of a single microsphere confirms that the hierarchical microspheres were formed by the aggregation of ultrathin rod-like structures. A HRTEM image focused on the surface of a single hierarchical microsphere is depicted in Fig. 1e and shows that the ultrathin rod-like structures were composed of tiny particles with a zigzag shape. As shown in the inset of Fig. 1e, these tiny particles are octahedra with diameters of only a few nanometers. It clearly shows that the ultrathin rod-like structures were formed *via* the connection of tiny octahedra. Such a growth model of “oriented attachment (OA)” on specific faces has been widely used to explain the formation of anatase nanorods²³ and nanowires.^{24,25} Fig. 1f shows a HRTEM image of some tiny octahedral crystals on the surface of a microsphere. It was found that these octahedra were highly crystalline and their lattice fringe was approximately

0.35 nm, corresponding to the d_{101} spacing in the XRD pattern. A selected-area electron diffraction (SAED) pattern (inset in Fig. 1f) of a hierarchical anatase TiO₂ microsphere revealed a set of diffraction rings, which can be indexed to the (101), (103) and (200) planes of anatase TiO₂ (JCPDS 01-0562).

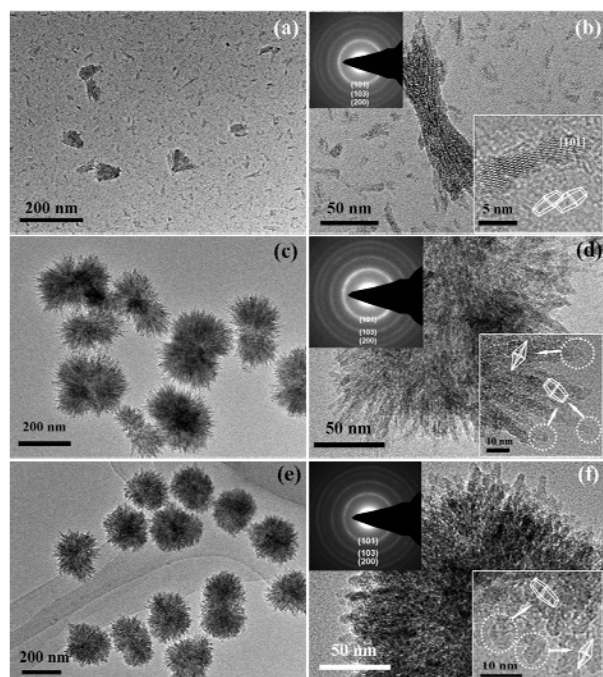
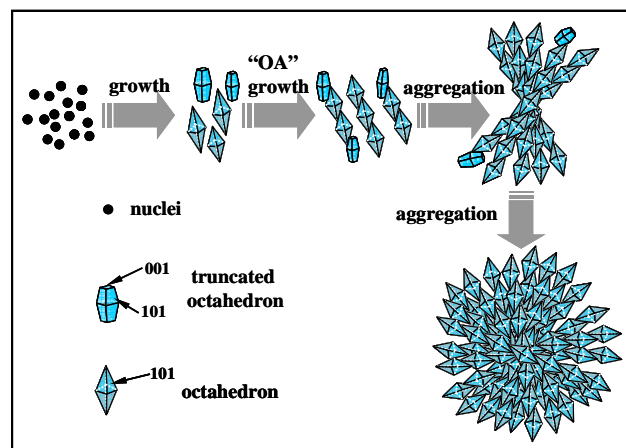


Fig. 2 TEM images of anatase TiO₂ in different reaction times: (a-b) 1, (c-d) 1.5 and (e-f) 6 h. The insets in (b, d and f) are the corresponding SAED patterns.

To shed light on the formation mechanism of the hierarchical anatase TiO₂ microspheres composed of tiny octahedra, a series of samples were synthesized at different reaction times. Fig. 2 shows TEM images of three samples synthesized at 120 °C for 1, 1.5 and 6 h. It can be seen from Fig. 2a that a large number of tiny particles and ultrathin rods were formed after a short reaction time, indicating that the nuclei formed relatively quickly. At the same time, the first stage of aggregation was also observed. As confirmed in Fig. 2b, the aggregation occurred *via* bonding between numerous ultrathin rods. The inset of Fig. 2b shows a HRTEM image of a single ultrathin rod and clearly shows that the rod was formed by connection of tiny octahedra *via* an OA growth model. These tiny octahedra (truncated octahedral) were highly crystalline and their size was found to be apparently 3-5 nm. The contact between two octahedral crystals resulted in a perfect lattice match during the OA process. A SAED pattern (inset in Fig. 2b) revealed a set of diffraction rings than can also be indexed to the (101), (103) and (200) planes of anatase TiO₂ (JCPDS 01-0562). With increasing time a large number of hierarchical spheres with a diameter of ~200 nm were found, as depicted in Fig. 2c. Fig. 2d shows a hierarchical sphere and confirms that the spheres were formed by aggregation of ultrathin rods composed of tiny octahedra or truncated octahedra (Fig. 2d inset). After the time was further increased to 6 h, the spheres grew 200-300 nm, as presented in Fig. 2e. A HRTEM image of a hierarchical sphere in Fig. 2f confirms again that they were

constructed of ultrathin rod-like structures, themselves composed of tiny octahedra or truncated octahedral (Fig. 2f inset). It can also be observed that these ultrathin rods aggregated together to form a porous structural microsphere. On the other hand, all the diffraction peaks of three samples can be perfectly indexed to anatase TiO₂, and their intensity increased obviously with increasing reaction time, indicating that the pure anatase TiO₂ can be formed even at a very short time in the present reaction system, as depicted in Fig. S1.



Scheme 1 Schematic of a tentative mechanism for the formation of hierarchical TiO₂ microspheres.

Based on our XRD, SEM and TEM data, a proposed mechanism for the formation of the microspheres is illustrated in Scheme 1. In the present work, the synthesis was executed at 120 °C under alkaline conditions. The nucleation may have begun and a large number of anatase TiO₂ particles formed in the initial stage of the reaction. According to reports,^{26,27} anatase TiO₂ has been shown to nucleate into truncated octahedral seeds composed of eight equivalent {101} facets and two equivalent {001} facets as the exposed surfaces. The surface free energy of the {001} facets is ~1.4 times larger than that of the {101} facets based on the Donnay-Harker rule.²⁸ Therefore the “oriented attachment” on the high-energy {001} facets as a mechanism of crystal growth has been widely used to explain the formation of rod-shaped anatase TiO₂ elongating along the [001] direction in a zigzag pattern.^{25,27,29} However, Adachi *et al.*³⁰ found that preferable oriented attachment on the {101} facets rather than {001} facets can also occurred due to the presence of surfactants adsorbed on {001} facets, reducing their surface energy. In the present work, a large quantity of NH₄⁺, from the decomposition of urea, might have the same effect³¹ resulting in the oriented attachment on the {101} facets of octahedral crystals in the initial stage. With increasing reaction time, the rods composed of octahedral crystals tended to aggregate. The principal attractive force between the two objects is a van der Waals attraction and Brownian motion could bring two rods into contact. This would imply that the attractive force between two objects would be rather weak, allowing better alignment of rods during the homoepitaxial aggregation process. It would also be worthy of notice that oriented aggregation along the radial direction to form spherical object and, thus, the most reduction in surface energy. At least,

five steps have been identified as occurring throughout the hydrothermal reaction, as illustrated in Scheme 1: (i) the formation of anatase nuclei; (ii) the formation of truncated octahedral seeds through coalescing of anatase nuclei; (iii) fast growth involving high energy (001) facets of truncated octahedral seeds forming octahedral crystals were formed; (iv) bonding between adjacent anatase TiO₂ octahedral crystals occurred along the [001] direction and the formation of rod-shaped anatase TiO₂ with a zigzag pattern; and (v) the aggregation of the rods in the radial direction to form hierarchically porous microspheres.

As investigate the porous nature of the hierarchical microspheres, N₂ adsorption-desorption isotherms were measured, as depicted in Fig. S2. An H1 hysteresis loop at P/P₀ > 0.8 indicated the presence of mesopores, which reflects the large number of pores observed in the HRTEM images in Fig. 1 and Fig. 2. The BET surface area of the hierarchical microspheres was approximately 244 m² g⁻¹.

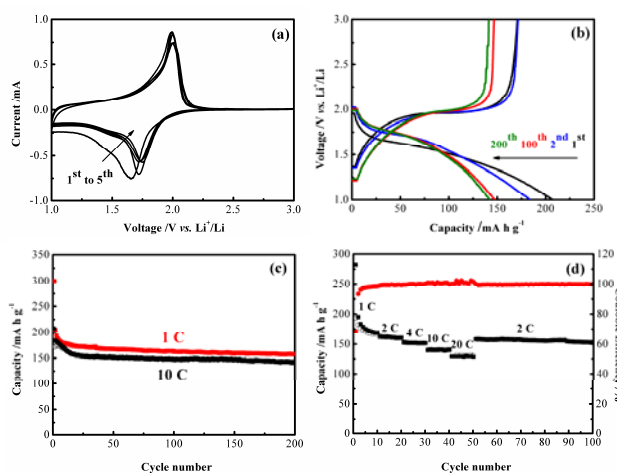
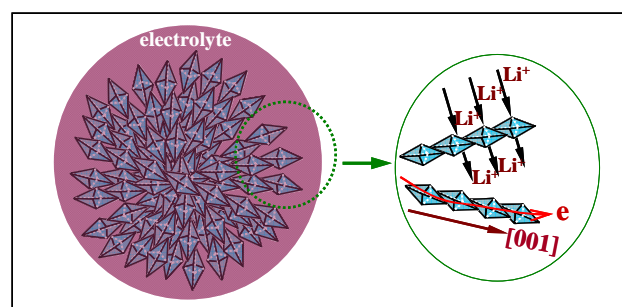


Fig. 3 The electrochemical properties of anatase TiO₂ obtained at 120 °C for 12 h: (a) CV curves with a scan rate of 0.5 mV s⁻¹, (b) charge-discharge profiles at a current density of 10 C, (c) cycling performance at different current densities, and (d) rate capability from 1 to 20 C (1 C = 168 mA g⁻¹).

Recently, there has been a great deal of interest in using hierarchical microspheres as electrode materials in rechargeable LIBs.^{18,19} Our anatase TiO₂ microspheres offer large specific surface areas and shorter transport distances, suggesting good Li-ion intercalation properties. Fig. 3a shows representative CV curves of the microspheres at a scan rate of 0.5 mV s⁻¹ in a range of 1.0–3.0 V. The CVs show two well-defined peaks at ~1.7 and 2.0 V. The former is attributed to Li-ion insertion into the anatase TiO₂ structure, and the latter can be identified as the formation of Li_{0.5}TiO₂. An apparently irreversible process was observed in the initial cathodic scan, suggesting that extraction of the Li-ion in the Li_{0.5}TiO₂ is not completely reversible. These results are in agreement with the previous studies.^{18,19} Fig. 3b shows the charge-discharge voltage profiles at a current rate of 10 C. Two voltage plateaus can be observed at ~1.7 and 2.0 V during the discharging and charging processes, respectively. The initial discharge process displayed a large capacity of 207.4 mA h g⁻¹ and a subsequent charge capacity of 171.6 mA h g⁻¹, leading to a

high Coulombic efficiency of 82.7%. This was ascribed to the hierarchical structure which exhibits excellent “bulk” and nanomaterials properties.¹⁴ Fig. 3c presents the cycling performance of a cell consisting of the microspheres at different current densities. At a current density of 1 C, an initial discharge capacity of 299.9 mA h g⁻¹ was achieved. Even after 200 cycles a capacity of 157.3 mA h g⁻¹ was retained, which was very close to the theoretical capacity of 168 mA h g⁻¹. When the current was increased to 10 C, a slight decrease in capacity was observed. An initial discharge capacity of 207.4 mA h g⁻¹ was observed and the reversible capacity was decreased to 142.3 mA h g⁻¹ after 200 cycles. These results are better than those of anatase spheres that are composed of nanosheets with exposed (001) facets.¹⁸ The rate capability of the hierarchical anatase TiO₂ microspheres was also investigated and the results are depicted in Fig. 3d. Capacities of 166.3, 159.7, 151.4, 140.3 and 130.2 mA h g⁻¹ were reached at current densities of 1, 2, 4, 10 and 20 C, respectively. When the current density was backed to 2 C, the capacity of 152.6 mA h g⁻¹ was obtained after 50 cycles. In addition, the Coulombic efficiency rapidly increased to nearly 100% after initial cycling.



Scheme 2 Transport pathway of Li⁺ ions and electrons in hierarchical TiO₂ microspheres.

According to a previous report,³² the capacity and rate performance of electrode materials depends primarily on the diffusion of Li-ions and electrons between the electrolyte solution and the particle interface. Porous nanomaterials with small particle sizes and large surface areas are known to promote Li-ion and electron diffusion through an electrode film as they can provide shorter diffusion path lengths. Our porous materials, with surface areas as large as 244 m² g⁻¹ (Scheme 2), can allow diffusion of electrolyte inside the microspheres. They can also enhance the contact between the electrode and the electrolyte, resulting in improved rate capabilities. In addition, the ultrathin rods can shorten the distance of Li-ion and electron diffusion, which has been reported for similar systems.^{33,34} The tiny octahedra attached *via* the (101) facets along [001] direction and might provide a path for the conducting of electrons.

4. Conclusions

In summary, a one-step synthetic route was developed for fabricating hierarchical anatase TiO₂ microspheres *via* the aggregation of ultrathin rods in the radial direction. The ultrathin rods were composed of tiny octahedral which formed *via* growth model of oriented attachment. Based on XRD and electron microscopic analyses, a mechanism for the growth of the

microspheres was proposed. It was found that the reaction time heavily influenced the formation of the hierarchical microspheres during the self-assembly process. A cell with the TiO₂ microspheres as the anode displayed a large capacity of 157.3 mA h g⁻¹ at 1 C after 200 cycles. This material also exhibited high rate performance and excellent cycling stability. These high performance characteristics may be due to the intrinsic characteristics of the hierarchical porous anatase TiO₂ microspheres, in which the porous structure can permit facile diffusion of the electrolyte. They can also enhance the contact between the electrode surface and the electrolyte, while the ultrathin rods can shorten the transport distance of Li-ions and electrons during electrochemical cycling. At the same, the porous microsphere can also accommodate volume changes in the charge-discharge process.

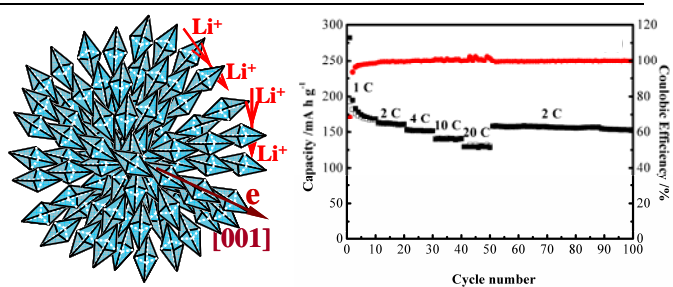
Acknowledgements

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Hierarchical porous anatase TiO₂ microspheres composed of ultrathin rod-like structures in the radial direction were fabricated for the first time, in which ultrathin rods were consisted of tiny octahedral via a growth model of oriented attachment, and also exhibited high rate performance and excellent cycling stability for Li-ion intercalation reaction.