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Ultra-thin anatase TiO_2 nanosheets with admirable structural stability for advanced reversible lithium storage and cycling performance

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ABSTRACT

Anatase TiO_2 ultra-thin nanosheets (TiO_2-NS) are synthesized by a facile hydrothermal method. Several merits are realized when employing the prepared TiO_2-NS as lithium ion battery anode material, compared to TiO_2 nanoparticles. Firstly, the as-prepared TiO_2-NS has high charge capacities and a specific surface area up to 98.8 m^2g^{-1}, which is beneficial for the insertion of lithium ion. Secondly, the large specific surface area is helpful in enlarging the electrode/electrolyte interfacial area. Finally, the EIS result verifies short electron transfer paths. More importantly, the stability of the nanosheet structure is indirectly confirmed by the excellent cycling performance of charge capacity and the curve of charge capacities *versus* cycle number at different current densities. After galvanostatic charge/discharge of the batteries for 1000 cycles, the HRTEM images of post-mortem batteries directly reveal a good reversibility of the lithium ion insertion/extraction process aided by TiO_2-NS. Thus, all these advantages and the special structure facilitate an excellent cycling performance: the charge capacity with the maximum value of 250 mAh g^{-1} keeps half after 2000 cycles at a current density of 840 mA g^{-1} (5 C).

1. Introduction

Due to the minacious depletion of fossil fuels and the acceleration of global warming, intense attention has been paid to energy industry, among which, lithium-ion batteries (LIBs) with an exceptional combination of high energy and power density are splendid since they were proposed for the first time [1–4]. The anode material used in commercial LIBs is graphite, but it is unsafe because the Li-insertion voltage is below 0.2 V *vs.* Li^+/Li, which would contribute to the reduction of electrolyte on the surface of the electrode and then formation of the solid electrolyte interface (SEI) film [5,6]. To solve the unsafety issues of carbon materials, vast researches have focused upon carbon-free Li-ion battery anode materials [7–14], among which, TiO_2 is an excellent candidate due to its higher operating voltage, which can guarantee enhanced safety, as well as extended cycle life time [5,15]. Moreover, TiO_2 is abundant and non-toxic [16,17]. Among the various polymorphic forms of titanium dioxide, anatase phase is considered to be the most promising competitor on account of its better Li-ion insertion capacity than the others [18–20].

There are plenty of studies on TiO_2 anodes. Scientific workers spend a lot of time and energy to pursue better results, and the most commonly used methods are the following three types: controlling morphology [21–25], doping [26,27] and composite structure [28–30]. However, TiO_2 is suffering from inherent drawbacks as a potential anode material in LIBs, namely low ionic diffusivity and electronic conductivity, yet which can be improved by changing the morphology of TiO_2. The dimensions of TiO_2 crystallites strongly influence the capacity performance and cycle stability of LIBs, which are dependent on the ability of lithium ion insertion and extraction [31,32]. Unlike the other bulk morphologies, nanosized anatase TiO_2 displays extraordinary properties, including short diffusion path and large specific surface area, which assist the transfer of lithium ion and electron, as well as the storage of Lithium ion [33–36]. Among various nanostructures,

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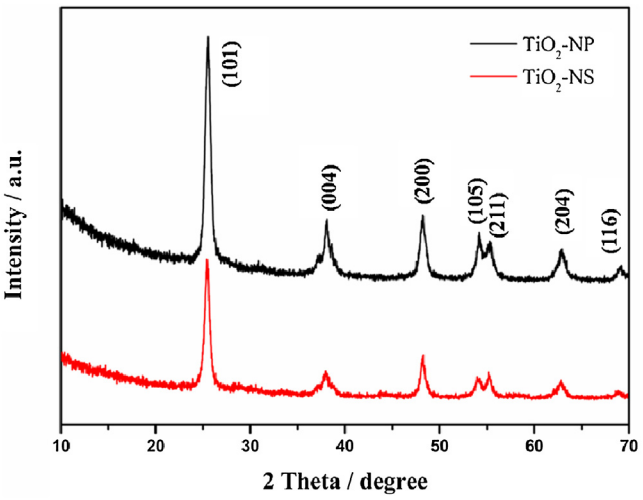

Fig. 1. X-ray diffraction patterns of TiO_2-NS and TiO_2-NP annealed at 400 °C in air for two hours.

such as nanorods, nanoparticles et al., nanosheets exhibit better electrochemical performance not only on account of all the virtues of nanostructures, but also superior structural flexibility. Far away from the shortcoming of agglomeration in ordinary nanostructures [37], ultrathin TiO_2 nanosheets help to shorten Li-ion diffusion paths and electron transmission paths, enlarge the electrode/electrolyte contact area, and facilitate strain relaxation during the insertion/extraction processes [17,35,38].

Herein, we adopt a facile one-pot hydrothermal method to synthesize ultrathin anatase TiO_2 nanosheets (TiO_2-NS) with high yielding. The as-synthesized TiO_2 nanosheets are mesoporous, and the thickness of the TiO_2-NS is only several nanometers, which contributes to large specific surface area. Furthermore, the ultrathin nanosheets facilitate intercalation of lithium ion, resulting in high reversible lithium storage. The stability of the structure results in an excellent cycle performance, the cell capacity decay is only half after 2000 cycles at 5C (840 mA g^{-1}). In contrast, the common TiO_2 nanoparticles (TiO_2-NP) of diameter ~20 nm were also synthesized in our experiment.

2. Experimental section

2.1. Synthesis of TiO_2-NS and TiO_2-NP

The TiO_2-NS was synthesized by a facile one-pot hydrothermal method. First, 1.05 g titanium iso-propoxide (TTIP) was added into 0.74 g concentrated hydrochloric acid; then 0.12 g P123 was dissolved in 3 g ethanol. After continuous stirring for 15 min, these two solutions were mixed. Half an hour later, the obtained solution was dispersed into ethylene glycol (EG) with a volume ratio of 1:8. Then the mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 150 °C for 20 hrs. After reaction, the resulting sample was rinsed with ethanol for three times and then collected by centrifugation. Subsequently, the product was dried in an oven at 80 °C overnight followed by annealed at 400 °C in air to remove the residual EG and increase its crystallinity. The TiO_2-NP was synthesized according to a common method widely used [39].

2.2. Materials characterization

The crystalline structures were investigated by X-ray diffraction (XRD, Bruker, Germany) using a D8 Focus diffractometer. The morphologies were monitored by scanning electron microscope (SEM, sirion 200, FEI). Transmission Electron Microscope (TEM) studies were carried out using a JEOL 2010. High-resolution Transmission Electron Microscope (HRTEM) images were obtained from a JEM-2010FEF (UHR). Texture characterizations were performed by Brunauer-Emmett-Teller (BET) nitrogen adsorption-desorption isotherms (JW-BK, Beijing, China).

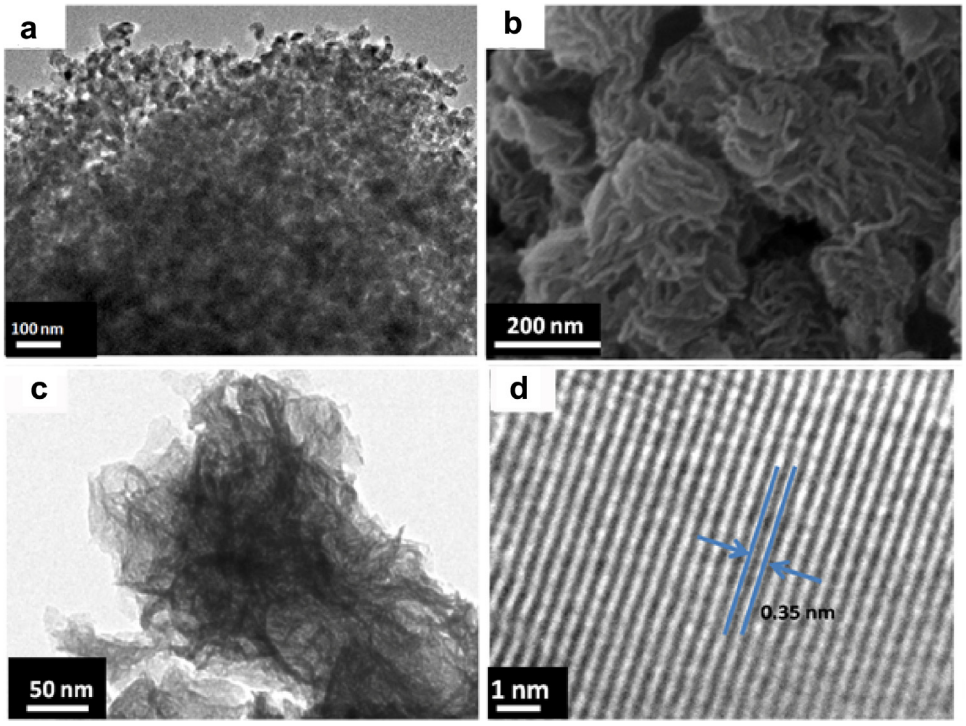

Fig. 2. SEM image of (a) TiO_2-NP and (b) TiO_2-NS; (c,d) HRTEM images of TiO_2-NS.