



Rutile TiO₂ nanorod arrays directly grown on Ti foil substrates towards lithium-ion micro-batteries

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ABSTRACT

Nanosized rutile TiO₂ is one of the most promising candidates for anode material in lithium-ion micro-batteries owing to their smaller dimension in ab-plane resulting in an enhanced performance for area capacity. However, few reports have yet emerged up to date of rutile TiO₂ nanorod arrays growing along c-axis for Li-ion battery electrode application. In this study, single-crystalline rutile TiO₂ nanorod arrays growing directly on Ti foil substrates have been fabricated using a template-free method. These nanorods can significantly improve the electrochemical performance of rutile TiO₂ in Li-ion batteries. The capacity increase is about 10 times in comparison with rutile TiO₂ compact layer.

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1. Introduction

As microelectronic devices are constantly demanding higher energy and power density on a smaller footprint area, conventional lithium batteries fall short of meeting the needs of emerging micro electromechanical systems. The need of better performance within least possible space encourages comprehensive investigation on micro batteries based on nano-scaled structure. Vertical nanorod arrays growing directly on a current collector have become a most attractive option for Li-ion battery electrode [1–5]. Sharing the common advantages of nanostructured electrodes such as a larger contact area with electrolyte and higher insertion/extraction rates, vertical nanorod arrays distinguish themselves from other nanoscale materials by their unique one-dimensionality [6–8]. This structure is favorable for accessible diffusion of electrolyte and ensures a natural connection between active materials and current collector [2,6,9,10]. Previously, fabricating such nanorod arrays relied on template-synthesis methods. V₂O₅ [11], SnO₂ [12], LiMn₂O₄ [13], LiFePO₄ [14], Fe₃O₄ [15] nanorod arrays have been fabricated using porous membranes as templates. In spite of these progresses, template synthesis substantially suffers from aggregation resulting in the difficulty of producing large-area nanorod arrays. Thus efforts have

been devoted to making template-free nanorod arrays for Li-ion micro battery electrode [5,15–17].

Titanium dioxide (TiO₂) has been widely studied as an anode material for Li-ion batteries [17–25], because it is abundant, low cost, and environmentally benign, along with good cycle capability [26–29]. Since the electrochemical properties of TiO₂ electrodes can be improved significantly by optimizing the size, morphology or porosity of the structure, nanostructured TiO₂ for Li-ion battery anode has been extensively studied [29–36]. Recently, researches have been carried out for the application of nanostructured TiO₂ in Li-ion micro-batteries [2,23,29]. One of the most attractive examples was reported by Edström and co-workers [2], who fabricated aluminum nanorods current collector covered by uniform TiO₂ thin layer to form a 3D nanostructure TiO₂ electrode with enhanced electrochemical performance. However, this template-dependent method is still a complicated and time-consuming procedure.

Generally speaking, Li-insertion into rutile is usually reported to be less favorable at room temperature [37]. Previous research showed that the obstacle is mainly due to the kinetic restrictions [38–40]. During the process of Li-insertion into micrometer-sized rutile, the Li⁺ diffusion coefficient is much lower in the ab-planes (10^{−15} cm² s^{−1}) than along c-axis (10^{−6} cm² s^{−1}), restricting Li⁺ from readily reaching the thermodynamically favorable octahedral sites [38,39]. Therefore, it is favorable to prepare nanostructure (for example nanorods) to improve the electrochemical performance of rutile TiO₂ electrode [40–42]. Recently, single-crystalline rutile TiO₂ nanorod arrays have been synthesized and greatly improved the performance of dye-sensitized

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solar cells [43,44]. However, there is still limited report on rutile TiO_2 nanorod arrays prepared for Li-ion micro-battery electrode application.

In this paper, we used a template-free strategy to prepare highly refined rutile TiO_2 nanorod arrays growing along c-axis directly on a Ti foils substrate. Here, the arrays of rutile nanorod were produced by a facile solvent-thermal method. We demonstrate that the nanorod arrays can highly enhance the electrochemical performances of rutile TiO_2 in Li-ion micro-batteries.

2. Materials and methods

In a typical synthesis, as a similar recipe described in the literature [44], 10 mL of toluene was mixed with 1 mL of 1 M titanium tetrachloride in toluene (97% Aldrich) and 0.1 mL of tetrabutyl titanate in a Teflon-lined stainless steel autoclave (50 mL). The mixture was stirred at ambient conditions for 1 min followed by the addition of 1 mL of hydrochloric acid (37 wt.%). After stirring for another 5 min, one piece of Ti foil substrate ($0.65 \text{ cm} \times 0.65 \text{ cm}$) was placed at an angle against the wall of the Teflon-liner. The Ti foil was initially cleaned by sonication in acetone, subsequently immersed in a H_2O_2 (30 wt.%, 5 mL) solution for 10 min, and finally rinsed with ethanol and deionized water. Solvent-thermal synthesis was conducted at 180°C for 2 h in an electric oven. After synthesis, the autoclave was naturally cooled to room temperature for 70 min. Then the TiO_2/Ti substrate was washed thoroughly with ethanol and allowed to dry under room temperature. To evaluate the mass of active materials, TiO_2 nanorod arrays were carefully peeled off from the substrates using a doctor blade and weighed on precision balance (METTLER TOLEDO XS105). In control experiment, rutile TiO_2 compact layer was formed by spin-coating Ti substrate ($0.65 \text{ cm} \times 0.65 \text{ cm}$) with TiO_2 colloidal and then annealing at 800°C in air for 2 h. Approximately 0.5 mg rutile TiO_2 nanoparticles were deposited on 1 cm^2 Ti foil for comparison. The colloidal was prepared according to the reference [45].

The crystal structure of the as-prepared film was examined by X-ray diffraction (XRD). The XRD patterns were recorded in a Bruker-AXS Micro-diffractometer (D8 ADVANCE) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) from 20° to 70° at a scanning speed of $0.33^\circ \text{ min}^{-1}$. X-ray tube voltage and current were set at 40 kV and 40 mA, respectively. Morphological and lattice structural information were attained from field emission scanning electron microscopy (FESEM, HITACHI S-4800), high-resolution transmission electron microscopy (TEM, JEOL 2010F) and selected-area electron diffraction (SAED). The typical FESEM measurement was carried out using a method reported by Liu et al. [43]. For TEM study, a small piece of TiO_2 nanorods layer detached from the Ti substrate was dispersed in 2 mL of absolute ethanol, followed by sonication for 20 min. The samples were picked up by immersing a carbon-coated 200 mesh copper grid into the solution for a few seconds and dried under ambient conditions for imaging.

The electrochemical study was tested in a two-electrode Swagelok cell. The cell was prepared inside the glove box under argon atmosphere ($<2 \text{ ppm H}_2\text{O}$ and O_2) using a clean lithium metal disk (8 mm diameter) as counter electrode, a glass-fiber separator soaked with the electrolytic solution of 1 M LiPF_6 (EC:DEC = 1:1), and the Ti/ TiO_2 nanorods as the working electrode. The Ti substrate was also performed as a current collector [2]. The galvanostatic cycling tests were carried out with a LAND battery testing system in the range between 1.0 and 3.0 V versus Li^+/Li .

3. Results and discussion

XRD shows that the films directly deposited on Ti substrate are rutile TiO_2 , Fig. 1 displays that all the diffraction peaks of the nanorod arrays agree well with the tetragonal rutile phase (SG, $\text{P4}_2/\text{mmn}$; JCPDS No. 21-1276, $a = b = 0.459330 \text{ nm}$ and $c = 0.29592 \text{ nm}$). Compared to the standard pattern, the enhanced diffraction (002) peak

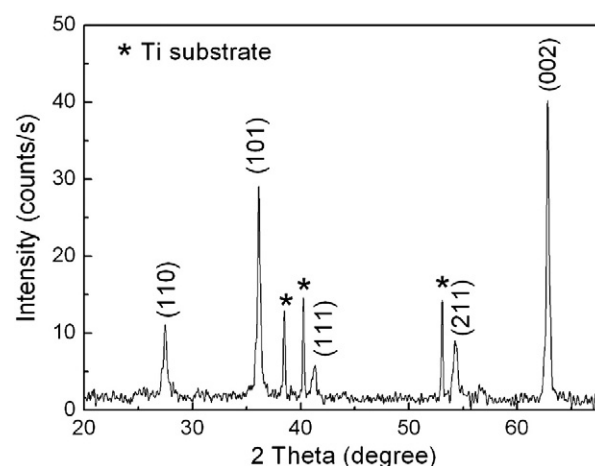


Fig. 1. X-ray diffraction pattern of prepared rutile TiO_2/Ti sample.

and comparatively low diffraction intensity for (101) and (211) indicate TiO_2 nanorods are well crystallized and the growth of the nanorods has a preferred orientation. The TiO_2 nanorods mostly grow along c-axis with the growth axis perpendicular to the substrate surface. Each nanorod is single crystal, as evidenced by the SAED pattern (Fig. 2(d)).

Fig. 2(a)–(c) is FESEM top view images of a typical TiO_2 nanorod arrays sample at different magnifications. The images at different locations and magnifications reveal that the entire surface of the Ti substrate is covered uniformly with aligned TiO_2 nanorods. The top surface of the nanorods appears to be flat tetragonal crystallographic planes while the side surface is smooth. Nanorod arrays are nearly perpendicular to the Ti substrate. These results are consistent with the morphology of rutile nanorod arrays reported recently [41,42] and indicate that the TiO_2 nanorod arrays have been grown on Ti substrate. As determined from FESEM and TEM images (Fig. 2(c) and (d)), the average diameter and length of nanorods, was 40–50 nm and 1.5–2.0 μm , respectively. This unique nanostructure ensures that every nanorod is in contact with Ti substrate and also interfaced with electrolyte. These features are very important for high power-density microelectrodes [2,6]. The chemical stoichiometry of the nanorods was further examined with EDX (Fig. 3). HRTEM image shows that the nanorods are completely crystalline along their entire lengths. The distance between the adjacent lattice fringes can be assigned to the interplanar distance of rutile TiO_2 (110), which is $d_{110} = 3.25 \text{ \AA}$. The (110) axis is perpendicular to the nanorod side walls, and the nanorods grow along the (001) direction, consistent with the XRD data. In average, 0.5 mg TiO_2 nanorod arrays are grown on 1 cm^2 Ti foil.

The voltage–capacity curve of rutile nanorods in Fig. 4(a) is similar to the previous report [41]. A sloping region in the range of 2.0–1.2 V during discharge and charge is visible. The sloped behavior is consistent with that of nanosized rutile reported previously [40–43], which may be due to the Li surface storage of the rutile nanorods [40].

The galvanostatic charge/discharge curve of TiO_2 nanorods/Ti foil is presented in Fig. 4. The curve cycles between 1.0–3.0 V at a current density of $15 \mu\text{A cm}^{-2}$ which is equal to approximately 30 mA g^{-1} (0.2 C, the theoretical capacity of TiO_2 is 167.7 mAh g^{-1}). During the first discharge (Li insertion), a total capacity of $268.2 \mu\text{Ah cm}^{-2}$ is achieved at the end of the first discharge with a reversible capacity of $160.1 \mu\text{Ah cm}^{-2}$, leading to an irreversible capacity of $108.1 \mu\text{Ah cm}^{-2}$. Compared with rutile TiO_2 compact layer, the rutile TiO_2 nanorod arrays exhibit a significant improvement of the area capacity. An area capacity increase by more than 10 times was achieved (Fig. 5) due to the unique architecture of nanorods. Firstly, it is generally believed size effect is more significant for nanorods, as the nanorods with smaller dimension in ab-planes shorten the Li diffusion distance and improve Li-insertion activities [38–41]. Secondly, the nanorod arrays possibly provide much

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