



TiO₂ Nanotube Arrays Grafted with MnO₂ Nanosheets as High-Performance Anode for Lithium Ion Battery



Qiancheng Zhu, Hao Hu, Guojian Li, Chenbo Zhu, Ying Yu *

Institute of Nanoscience and Nanotechnology, College of Physical Science and Technology, Central China Normal University, Wuhan 430079, PR China

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ABSTRACT

Unique TiO₂ nanotube arrays (TNAs) grafted with MnO₂ nanosheets is synthesized for the first time as an anode for Li battery. The character of the special structure is MnO₂ nanosheets grown on the outer, inner surface and tip of the TNAs. The composite combines the advantages both from MnO₂ with high capacity (1230 mA h g⁻¹) and TNAs with excellent cycle stability and superior electrical conductivity. Besides, the MnO₂ nanosheet layer with different thickness on the surface of TNAs is fabricated through controlling hydrothermal reaction time and it is found that the thickness has a significant impact on capacity, cycle performance and conductivity. Additionally, a very abnormal phenomenon that we call "late rise of capacity" is discovered in the capacity test after several hundreds of cycle times, for which a possible mechanism is proposed according to material characterization.

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1. Introduction

Lithium ion batteries (LIBs) have been considered as attractive power sources for a variety of applications ranging from electronic devices to electric vehicles and fixed energy storage facilities because of their long lifespan and high energy density [1–5]. Various transition metal oxides have been widely studied as electrode materials for rechargeable lithium-ion batteries due to their high theoretical capacity, safety, environmental benignity, and low cost [6–13]. Among these metal oxides (LIBs), manganese dioxide (MnO₂) has been recognized as one of the most intensively investigated metal oxides owing to its high theoretical capacity of 1230 mA h g⁻¹, relatively low electrochemical motivation force, and natural abundance [14–19]. However, due to volume expansion, aggregation and intrinsically low electronic conductivity, MnO₂ suffers from rapid capacity fade during cycling process. Some methods have been used to solve the problem and nanostructured MnO₂ materials, including nanowires, nanotubes, and nanoflakes etc, have been developed to enhance its performance [8,16,20–23]. Besides, MnO₂ nanoparticles loaded onto a conductive layer using deposition technique has been reported to show high electrochemical

performance as well [24–26]. Yet thoroughly solving the problems is still a long way to go.

Titanium dioxide (TiO₂) has attracted a lot of attention among transition metal oxides as active anode material in LIBs in virtue of its attractive properties including low cost, environmental friendliness, increased safety for the higher Li-insertion potential (1.6–1.8 V vs Li⁺/Li) compared to commercialized carbon (graphite) materials, and low volume expansion during charge/discharge processes [27–30]. Unfortunately, in comparison to conventional anode materials, TiO₂ has a relatively low theoretical capacity of around 335 mA h g⁻¹ and intrinsically slow transport kinetics for both electrons and Li ions, which prevent this material from optimal electrochemical performance [31–33]. To improve the performance of traditional TiO₂, one-dimensional (1D) TiO₂ materials such as nanotubes, nanowires, and nanorods have been developed for LIBs [34,35]. Especially, self-supported 1D nanostructures such as TiO₂ nanotube arrays (TNAs) as ordered arrays directly grown on current collecting substrates are particularly charming owing to their electron transport properties. The large interior and exterior surfaces of nanotube walls are accessible to Li⁺ in the electrolyte, leading to a small Li⁺ insertion/extraction current density per surface area. The thin wall thickness provides short solid-state Li⁺ diffusion pathways and high tolerance to the structural changes during repeated Li⁺ charge/discharge processes [36,37].

Recently, a number of metallic oxides (MO) with a high specific capacity (700–1000 mA h g⁻¹) were therefore used to synthesize

* Corresponding author. Tel.: +86 27 67867037; fax: +86 27 67861185.
E-mail address: yuying01@mail.ccnu.edu.cn (Y. Yu).

hybrid TiO_2 -MO nanocomposites. In this way, the advantages of the high capability for MO and the electrochemical stability of TiO_2 will be combined together [38–42]. However, to the best of our knowledge, very limited articles have been reported about the hybridization of TiO_2 and MnO_2 compound. For example, Liao et al. synthesized TiO_2 -C/ MnO_2 core-double-shell nanowire arrays through a hydrothermal and immersion method, which showed a capacity of 332 mA h g^{-1} at a current rate of 2 C ($1\text{C} = 335 \text{ mA g}^{-1}$) and 186 mA h g^{-1} even at 20 C. Besides, this core-double-shell nanostructure possessed an excellent stability with almost no capacity attenuation in 100 cycle times at 1 C. However, the battery capacity is rather limited by the amount of MnO_2 because of the immersion method [43]. Li et al. synthesized MnO_2 @graphene/ TiO_2 nanostructure, which showed a capacity of 243 mA h g^{-1} even after 150 cycles at a rate of 250 mA g^{-1} [44].

In this paper, the architecture of TiO_2 nanotube arrays grafted with MnO_2 nanosheets is proposed and fabricated for the first time. MnO_2 nanosheets are deposited on both the outer, inner surface and tip of the aligned TNAs. This unique nanostructure will make MnO_2 nanosheets firmly bound on TNAs so that MnO_2 can be stable during charge/discharge process. Besides, the huge space that TNAs provide can restrain the expansion of MnO_2 nanosheets grown on the outer and inner surface of the TNAs. During the investigation, it is found that there is a competitive relationship between the performance of capacity and cycle stability allowing the change of the thickness of MnO_2 layer on TNAs. For example, the MnO_2 nanosheet with thin layer possesses excellent cycle stability, but the capacity is quite low since the amount of MnO_2 is limited. On the contrary, the MnO_2 nanosheet with too thick layer may have a higher capacity at the primary cycles, but the capacity has a rapid fade with the charge/discharge cycles. Finally, we found that the suitable deposition of MnO_2 nanosheets on the surface of TNAs is beneficial to the ascension of the battery capacity along with an excellent lifespan. For example, one of the samples (TM-10) showed a capacity of 610 mA h g^{-1} at a current rate of 350 mA g^{-1} and a capacity of 385 mA h g^{-1} at a rate of 700 mA g^{-1} even after 700 cycle times. Furthermore, a very abnormal phenomenon that we call “late rise of capacity” is discovered in the capacity test after several hundreds of cycle times, which can be interpreted as

the structure change of materials rather than the property change.

2. Experimental section

2.1. Synthesis of TNAs

TiO_2 nanotube arrays were synthesized by electrochemical anodization of Ti foil at room temperature [36,45,46]. Prior to anodization, Ti foil with thickness of 0.3 mm was ultrasonically cleaned with acetone, ethanol and water for 10 minutes respectively. Then it was subjected to potentiostatic anodization for 4 h in a two-electrode electrochemical cell with a carbon rod as counter electrode. A constant voltage of 50 V was employed for the anodization and the electrolyte used was 0.4 wt% NH_4F , 2 wt% citric acid, 20 ml deionized (DI) water and 180 ml ethanediol. After reaction, the Ti foil was taken out and ultrasonically cleaned in DI water for a few seconds and subsequently, the anodized Ti foil was annealed at 450°C for 3 h with a ramp rate of 5°C min^{-1} to obtain crystalline TNAs on the Ti foil.

2.2. Synthesis of TNAs@ MnO_2 nanosheets with different thickness

TNAs grafted with MnO_2 nanosheets with different layer thickness were fabricated by a one-pot hydrothermal method using different reaction time. In a typical procedure, TNAs was transferred to a Teflon-lined autoclave with 70 ml acidic potassium permanganate solution (a mixture of 0.03 M KMnO_4 and 0.01 M HCl). Subsequently, the autoclave was kept at 120°C for 5, 10 and 20 h for the formation of TNAs grafted with MnO_2 nanosheets with different layer thickness, named TM-5, TM-10 and TM-20, respectively. Finally, the composites were annealed at 450°C for 3 h with a ramp rate of 5°C min^{-1} .

2.3. Material characterization

The prepared samples were characterized with X-ray diffraction meter (XRD, Bruker D8-advance). Scanning electron microscopy (SEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, JEOL, JEM2010FEF) were also introduced to observe the morphology and microstructure of TNAs grafted with MnO_2 nanosheets.

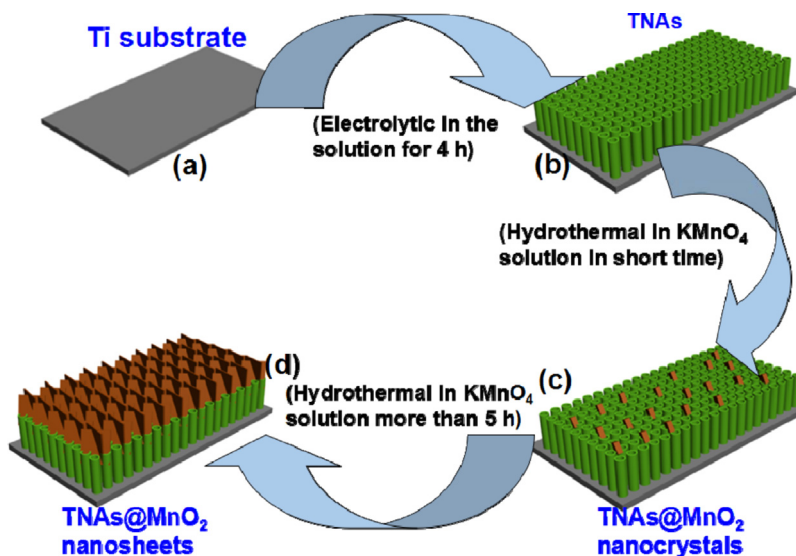


Fig. 1. Schematic illustration of the formation of TNAs@ MnO_2 nanosheet composite: (a) 0.3 mm Ti substrate, (b) formation of TNAs by electrochemical anodization method, (c) formation of TNAs@ MnO_2 nanocrystalline particles in short reaction time and (d) formation of TNAs@ MnO_2 nanosheet composite more than 5 h.

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