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Multichannel hollow TiO_2 nanofibers fabricated by single-nozzle electrospinning and their application for fast lithium storage

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ABSTRACT

Multichannel hollow TiO_2 nanofibers were synthesized via a facile single-nozzle electrospinning method based on phase-separation mechanism. Compared to normal TiO_2 nanofibers, hollow TiO_2 with higher surface area gave rises to a higher surface contribution and ensured a short diffusion path for ion transport. Thus hollow TiO_2 demonstrated superior cyclic ability and excellent rate capability.

1. Introduction

Substantial efforts have been directed to improve electrode materials for lithium batteries in term of energy density, power density, life-time and safety [1,2]. Titanium dioxide is considered as one of the alternative anode materials to graphite due to various advantages. TiO_2 is an abundant, low cost, and eco-friendly electrode material with a stable structure [3,4]. It exhibits a safe lithium intercalation voltage (~1.7 V), which avoids electrolyte decomposition and lithium dendrite formation [3,5]. However, making the material ripe for practical application is still a great challenge due to the poor cycling performance and rate performance resulting from its low bulk electron and ion conductivities and the aggregation tendency of nanoparticles [6].

A number of efforts have been made to improve its electrochemical performance. One possibility is to improve the transport properties by using TiO_2 nanostructures together with an efficient transport network [7–9]. Hierarchical 1D nanostructures combine various advantages, such as large surface to volume ratio, high electrode–electrolyte contact area, superior mass transport of reactants and products to/from active sites located inside framework or interparticulate meso- and/or micropores, good strain accommodation and connectivity [10,11]. Electrospinning was found to be a facile and versatile method to synthesize 1D nanostructures and showed its potential advantage for lithium-based batteries [12,13]. Core/shell nanofibers are frequently fabricated by coaxial electrospinning, with which two different solutions are spun simultaneously, using a spinneret with two coaxial capillaries [14]. However, the special design of the complicated spinneret and the requirement of suitable multiple fluids by coaxial electrospinning restrict its application and extension.

In this communication, we will demonstrate fabrication of hollow TiO_2 nanofibers with hierarchical porous structure based on phase separation via traditional single-nozzle electrospinning technique as shown in Fig. 1a. The materials so-obtained are not only very easy to fabricate, they also show superior electrochemical performance when tested as anode materials for lithium battery.

2. Experimental

1.5 g PAN (PAN, Mw = 150,000, Aldrich) and 3 g PVP (Mw = 180,000, Aldrich) were dissolved in 20 ml dimethylformamide (DMF) solvent with vigorous stirring. Then 1.5 g tetrabutyl titanate ($Ti(OC_4H_9)_4$) was added to the PVP-PAN blend with vigorous stirring. The electrospinning process can be found elsewhere [15]. The as-collected nanofibers were then put in a muffle furnace and calcined at 500 °C in Air for 5 h to obtain TiO_2 nanofibers.

The morphology was investigated using scanning electron microscope (SEM) (JEOL 6300F) and high-resolution transmission electron microscopy (JEOL 4000EX). X-ray diffraction (XRD) patterns were recorded with a Philips PW3710 using Cu Ka radiation. Nitrogen adsorption and desorption isotherms were measured at 77 K with a Quadrachrome Adsorption Instrument. Swagelok-type cells were assembled in an argon-filled glove box. The working electrodes were

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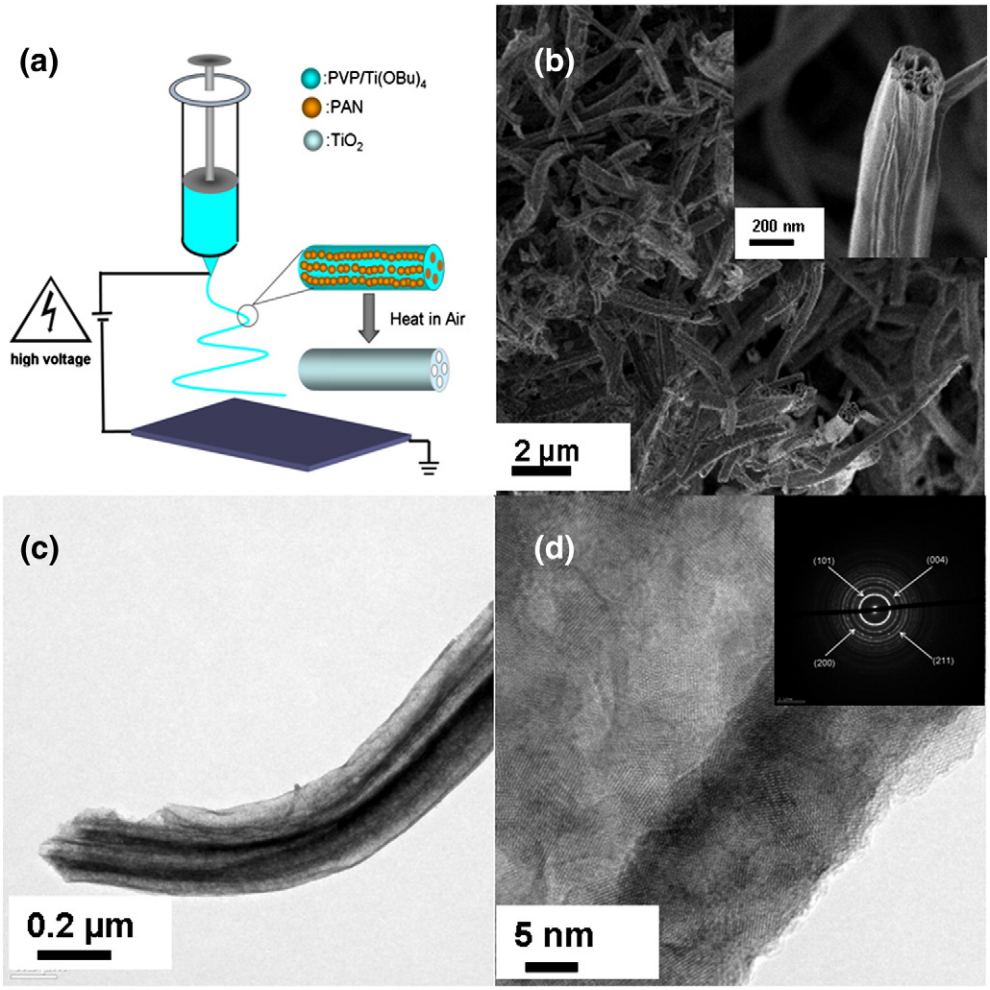

Fig. 1. (a) Schematic illustration of the fabrication procedure of hollow TiO_2 fibers through the electrospinning process. (b) FE-SEM images of hollow TiO_2 fibers and (c, d) TEM images of hollow TiO_2 fibers. Inset of panel d: SAED pattern.

prepared by mixing the nanofibers, carbon black and poly(vinyl difluoride) at a weight ratio of 70:20:10 and pasted on pure Cu foil. The loading weight was 1.5–1.8 mg/cm^2. The electrode was dried under vacuum at 120 °C overnight. Pure lithium foil was used as the counter electrode. The electrolyte consisted of a solution of $LiPF_6$ in a 1:1 vol/vol mixture of ethylene carbonate and diethyl carbonate. Galvanostatical discharge–charge experiments were tested in a voltage range of 1.0–3.0 V.

3. Results and discussion

A possible formation mechanism of these hollow multichannel nanofibers is based on evaporation-induced phase separation during electrospinning [16–18]. The DMF solution of PAN/PVP/TBOT undergoes phase separation on DMF evaporation, resulting in multiple highly stretched PAN/DMF droplets (orange sphere) in the surrounding PVP/TBOT/DMF (blue) matrix (Fig. 1a). The necessary transport of the comparatively small TBOT to the outer boundary of the fiber may be easily possible. Thus, after calcination in air, the polymers will be decomposed and the carbon-free TiO_2 nanofibers with hollow multichannel structure formed. The structure of the hollow nanofibers renders easy electrolyte access possible into the bulk electrode material and hence provides fast lithium ion transport channels, which are necessary for high rate performance. To get further evidence of the improved performance of our hollow nanofibers, we also prepared TiO_2 nanofibers without a hollow structure by pyrolyzing electrospun nanofibers from PVP/TBOT/DMF (i.e. without PAN) and used their performance as a reference.

The obtained multichannel hollow TiO_2 nanofibers have an average diameter of ~200 nm (Fig. 1b). The inset of Fig. 1b displays the cross section of the final fibers showing the multichannel tubular structure with various channel diameters of tens of nanometers. Fig. 1c confirms the hollow multichannel structure of the TiO_2 nanofibers. The average thickness of the channel walls is about 20 nm. High-resolution transmission electron microscopy (HRTEM) combined with selected-area electron diffraction (SAED), shown in Fig. 1d, displays the fine microstructure of anatase TiO_2. The diffraction rings in the SAED patterns (inset of Fig. 1d) are attributed to different planes of anatase, for example (101), (004), (200) and (211) planes.

All diffraction peaks in the XRD patterns indicate pure anatase without the presence of other polymorphs (JCPDS No. 78-2486) (Fig. 2a). The average crystallite sizes of the powder samples calculated from Scherrer equation for normal fibers and hollow fibers are around 12 and 10 nm, respectively, well consistent with the HRTEM observations (Fig. 1d). The phase structure of the hollow TiO_2 fibers was further confirmed by Raman spectroscopy (Fig. 2b), and all the peaks were an excellent match with bulk anatase TiO_2 [19]. The mesoporous nature of the hollow TiO_2 fibers was further confirmed by Brunauer–Emmett–Teller (BET) measurements conducted at 77 K. As shown in Fig. 2c, the N_2 adsorption–desorption