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Short communication

Growth of single-crystal α-MnO_2 nanotubes prepared by a hydrothermal route and their electrochemical properties

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ABSTRACT

Single-crystal α-MnO_2 nanotubes are synthesized by a facile hydrothermal method without the assistance of a template, a surfactant and heat-treatment. The single-crystal α-MnO_2 nanotube electrode possesses a high specific capacitance with a good power capability. The excellent pseudo-capacitive properties are attributed to a nanotubular microstructure and a large tunnel cavity in the α-MnO_2 crystal structure. Single-crystal α-MnO_2 nanotubes with good electrochemical performance can be a promising candidate as supercapacitor materials.

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1. Introduction

Supercapacitors (SCs) which feature a high specific power and a long cycle capability have received intensive attention in recent years [1]. Among all of the potential materials, manganese oxides have been investigated widely as they could serve as low-cost and environmental friendly materials to replace the widely used hydrous RuO_2 without compromising specific power and specific energy.

One-dimensional (1D) nanostructured materials have attracted great interest because of their unique physicochemical properties that arise from their high surface area, novel size effects, and significantly enhanced kinetics [2,3]. Currently, template synthesis is one of the most commonly used methods to fabricate 1D nanostructured materials [4,5]. This template-assisted synthesis method is not only tedious but also requires multiple synthesis steps, expensive templates, and corrosive chemical treatment. By comparison, the hydrothermal synthesis method has proved to be an efficient way to prepare 1D nanostructured materials [6]. In addition, micro-architectures can be tailored by adjusting the synthesis temperature, the processing time and pressure, and by selecting different solvents and concentrations.

One-dimensional nanostructured manganese oxides, in the form of nanowires, nanorods, nanobelts and nanoneedles, have been successfully prepared via hydrothermal methods [7–13]. By contrast, only a few studies on the hydrothermal preparation of 1D nanostructured manganese oxides in nanotubes have been reported [14,15]. Single-crystal β-MnO_2 nanotubes were reported [14] to be prepared successfully by a hydrothermal method through oxidizing $MnSO_4$ with $NaClO_3$ in the presence of an organic surfactant (poly(vinyl pyrrolidone)). More recently, single-crystal α-MnO_2 nanotubes were obtained by a facile hydrothermal treatment of $KMnO_4$ in hydrochloric acid solution [15]. The hydrothermal route featured a low synthesis temperature and no surfactants were required. Therefore, this method is employed in the present work to prepare MnO_2 nanotubes. The work focuses on the optimization of the microstructures and crystal structures of manganese dioxides in order to improve their supercapacitive properties.

2. Experimental

The processing route followed the procedure reported recently with minor modifications [15]. In the present synthesis, 0.608 g $KMnO_4$ and 1.27 ml HCl (37 wt.%) were added to 70 ml distilled water with stirring to form the precursor solution. After stirring, the solution was transferred to a Teflon-lined, stainless-steel autoclave with a capacity of 100 ml. The autoclave was kept in an oven at 140 °C for 12 h, and then cooled down to room temperature. The resulting brown precipitates were collected, rinsed and filtered to a pH 7. The as-prepared powders were then dried at 80 °C in air.

The crystal structures and microstructures of the products were characterized by means of X-ray diffraction (XRD, Shimadzu 6000, λ = 1.5405 Å), scanning electron microscopy (SEM, Hitachi, S-4300)

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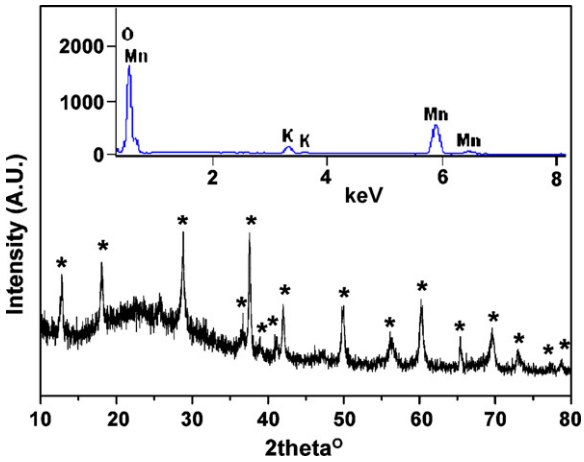

Fig. 1. XRD pattern and EDX spectrum (inset) of prepared MnO_2 nanotubes. (The *stars* denote the peaks of α-MnO_2, JCPDS: 44-0141.)

and transmission electron microscopy (TEM, JEOL3010) with energy dispersive X-ray (EDX) spectroscopy (Oxford) and selected area electron diffraction (SAED) accessories.

To measure the electrochemical performance of the as-synthesized MnO_2 nanotubes, the MnO_2 nanotubes (80 wt.%) was mixed with a binder (10 wt.%) (polytetrafluoroethylene) and acetylene black (10 wt.%). The mixture of the MnO_2 nanotubes was then rolled to form a uniform film that was vacuumed-dried at 120 °C for 12 h. A circular piece of the film (1 cm^2) was cut and pressed on nickel to form the working electrode. Weight of the electrode was measured by a balance (AND GR-202) with an accuracy of 0.01 mg. The exposed apparent surface area is 1 cm^2 and the typical loading of MnO_2 is about 0.5 mg.

All electrochemical tests were conducted in a one-compartment, three-electrode electrochemical bath which contained 1.0 M sodium sulfate aqueous solution as the electrolyte, a platinum foil (2 cm × 2 cm, Aldrich) as the counter electrode and an Ag|AgCl electrode (CHI111) as reference electrode. The electrochemical properties were examined by a Solartron SI1287 electrochemical Interface and a Solartron SI1260 Impedance Analyzer. The electrochemical impedance spectroscopy (EIS) was investigated at the

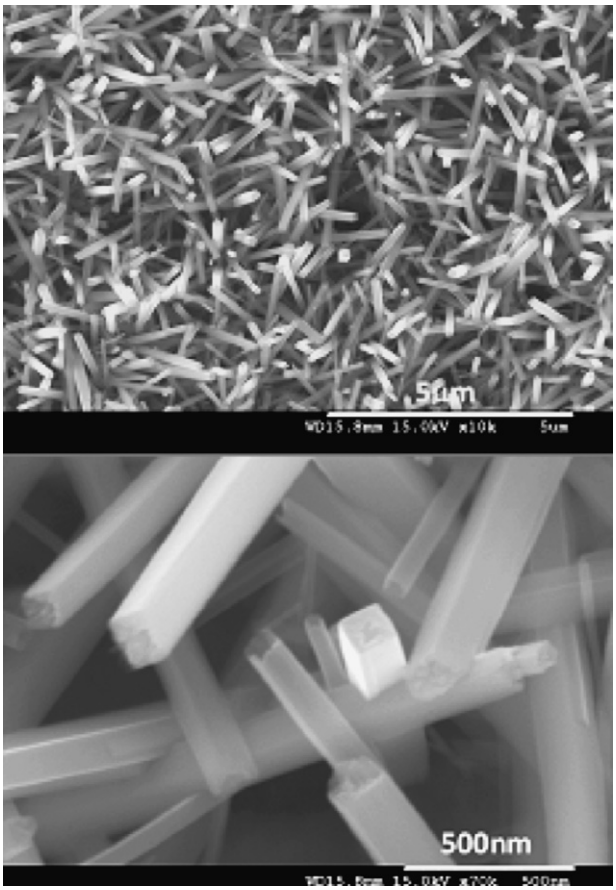

Fig. 2. SEM images of prepared MnO_2 nanotubes in different magnifications.

open-circuit potential over the frequency range of 10^5 to 0.1 Hz with an a.c. amplitude of 10 mV.

The charge, *Q*, was obtained by integration of area under the cyclic voltammetry (CV) plot, and the specific capacitance, *C*, was then deduced based the charge, the mass of the active materials, *m*,

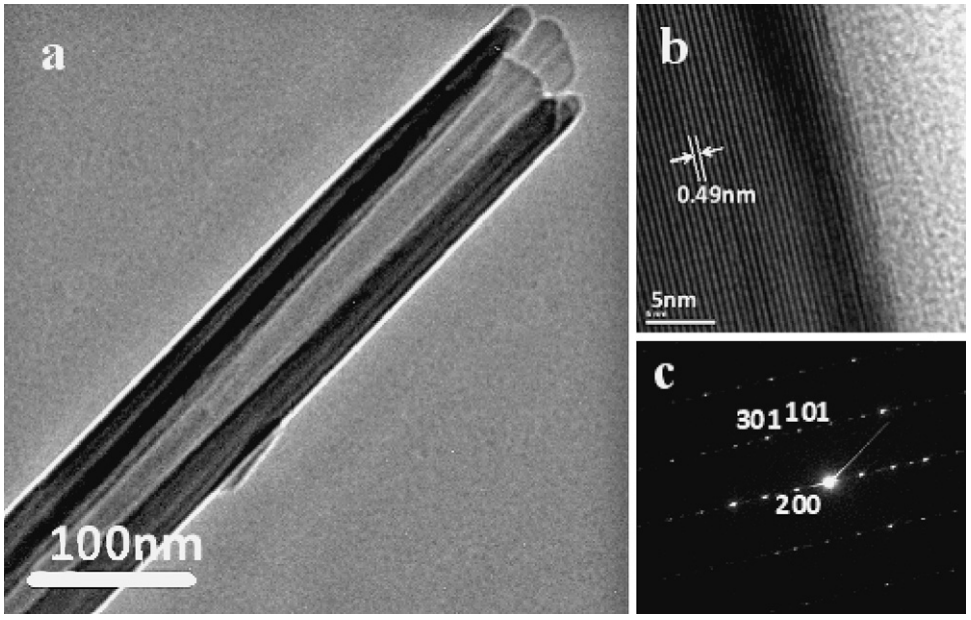

Fig. 3. (a) TEM, (b) HRTEM images and (c) SAED pattern of prepared MnO_2 nanotubes.

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