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Cotton-templated fabrication of hierarchical SnO_2 mesoporous microtubes as the anode material of lithium ion battery

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ABSTRACT

SnO_2 mesoporous microtube materials were fabricated by a sonochemical method from biological template of cotton, which was used as the anode material of lithium ion battery. The cotton fibers were first given ultrasound treatment in $SnCl_2$ solution. Then the microtube structure was obtained after calcinations at different temperatures of 500, 650 and 800 °C. The scanning electron microscopy (SEM) images showed the morphology of the SnO_2 mesoporous microtube which was composed of SnO_2 nanoparticles. The effect of calcinations temperature on the electrochemical performance of SnO_2 microtubes was studied. The results showed that the cycle performance of the sample under 500 °C was relatively better than those of the samples under 650 and 800 °C, exhibiting an initial specific capacity of 709 mA h g^{-1} which was calculated based on the overall electrode loading and retaining 393.9 mA h g^{-1} up to 20 cycles.

1. Introduction

Graphite is widely used as anode materials in commercial lithium ion batteries (LIBs), but it has a low theoretical specific capacity of 372 mA h g^{-1} [1], which cannot meet the increasing demand for batteries with higher energy densities. It is essential to develop electrodes with high energy density, stable cycling [2], and environmental-friendly properties. Tin oxides, which have higher theoretical capacities (790 mA h g^{-1}) compared to graphite, have been proposed as alternative anode materials in lithium ion battery [3]. However, the practical application of tin oxide as an anode is hindered by its poor cyclability, resulting from large volume changes over 300% during discharge/charge, leading to electrode pulverization and electrical disconnection [4]. To overcome the problems above, designing hollow and porous nanostructures is a feasible solution which attracts considerable attention [5,6]. The high surface area and small size can enhance the surface activity of SnO_2. Moreover, the space in such structures can store more lithium ions and buffer the large volume change during the charge and discharge progress, leading to improvement in cycling capacity [7]. Furthermore, tubular nanostructured SnO_2 has attracted much interest due to its improved performance in lithium ion batteries [6]. As the two ends of the nanotubes are totally open, the lithium ion can transport more conveniently. Considering the factors above, various methods have been reported to acquire the SnO_2 nanotubes, such as infiltration technique [5], utilizing electrospinning and atomic layer deposition [8], and template assisted solvothermal synthesis [9].

Here, SnO_2 mesoporous microtubes were prepared via a sonochemical template method as anode materials for LIBs. Since it is cheap, widely available, chemically and mechanically robust, cotton has been chosen to be raw material or template to prepare various materials, such as gas sensors [10,11], water sterilization [12]. In this paper, we took these advantages of cotton to prepare SnO_2 and obtained hierarchical SnO_2 mesoporous microtubes.

2. Experimental section

Materials synthesis: All the chemical reagents were analytical grade and used without further purification. Absorbent cotton was purchased from Jiangxi sanitary materials factory, China.

Hierarchical SnO_2 mesoporous microtubes were prepared as follows: $SnCl_2 \cdot 2H_2O$ (0.46 g) was dissolved in 20 mL of ethanol solution and keep magnetic stirring for 3 h. Then, 10 mL of deionized water was added into the above solution under stirring with 15 min, and the solution was used as a precursor. Immediately following the above, dried cotton fibers (0.3 g) were immersed completely into the precursor with ultrasound under 45 kHz for 3 h. Then, the treated cotton was taken out of the solution and washed several times with absolute ethanol to remove the residual impurity ions. Then it was dried in air at 50 °C for 12 h. In order to remove the original cotton fibers, the obtained SnO_2–cotton hybrid was subjected to calcination treatment at 500, 650, and 800 °C for 5 h with a heating rate of

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2 K min^{-1} in air. The obtained samples were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Electrochemical tests: The electrodes were prepared by mixing 80 wt% SnO_2 microtubes, 10 wt% polyvinylidene fluoride (PVDF), 10 wt% acetylene carbon black in *N*-methyl-2-pyrrolidone (NMP) to produce a slurry which was then coated onto a copper foil and dried overnight at 120 °C in a vacuum oven. A 2025 coin-type cell was assembled in an argon-filled glove box with Li metal foil as counter electrode, polyethylene film as the separator, and 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (1:1) as the electrolyte. Charge–discharge measurements were performed on LAND CT-2001A over a voltage range of 0.005–3 V (vs. Li/Li^+) at a current density of 50 mA g^{-1}. The specific capacities were calculated based on the overall electrode loading. Cyclic voltammograms (CV) experiment was performed in the potential window of 0.02–2.9 V at a scanning rate 0.5 mV s^{-1}.

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction (XRD) patterns of the SnO_2 samples obtained at different calcination temperatures from 500 to 800 °C. All the diffraction peaks in XRD pattern can be well indexed to a tetragonal rutile structure of SnO_2 (cassiterite, JCPDS no. 41-1445), which shows good phase purity. With the increase of temperature, the XRD peaks became gradually sharper, indicating the increase in crystal size because of the more drastic sintering process.

Fig. 1(b–d) shows morphologies of SnO_2 microtubes produced by ultrasonication, which were calcined at 500 °C. As reported previously, the natural cotton fibers are revealed to have a thin flattened tubular cell with a pronounced spiral twist with a length of several centimeters [10]. It can be seen that the obtained SnO_2 microtubes mimick the shape of the cotton fibers with a little shrinkage in size, forming a replica of the templates. The diameters of SnO_2 microtubes calcined at 500 °C are estimated to be 5–15 μm. Fig. 1(c) shows that the ends of SnO_2 microtubes are totally open after removing the cotton templates during heating in air. The SnO_2 replicas are composed of irregular flakelets assemblies, as shown by the high magnification image in Fig. 1(d).

To observe the structure further, the SnO_2 microtubulars samples are also characterized by TEM and HRTEM, as shown in Fig. 2. It can be clearly seen from Fig. 2(a, c and e) that the SnO_2 particles keep the solid sphere structure with fine nanocrystallites. Lattice plane spacings calculated from the HRTEM images (Fig. 2 (b, d and e)) are 0.34 nm and 0.26 nm that correspond to (11 0) and (101) crystal planes of cassiterite. It can be seen apparently that with the increasing calcination temperature, the size of SnO_2 nanocrystallites gradually increases (the HRTEM b, d and e also indicate the increasing phenomenon), which is in accordance with the previous work [13,14]. Moreover, there are many mesopores between the SnO_2 nanocrystallites which could be favorable for the access of lithium ion and buffer the large volume change during the charge and discharge progress.

The electrochemical measurements for SnO_2 nanocrystallites at different annealing temperature are shown in Fig. 3. In the first

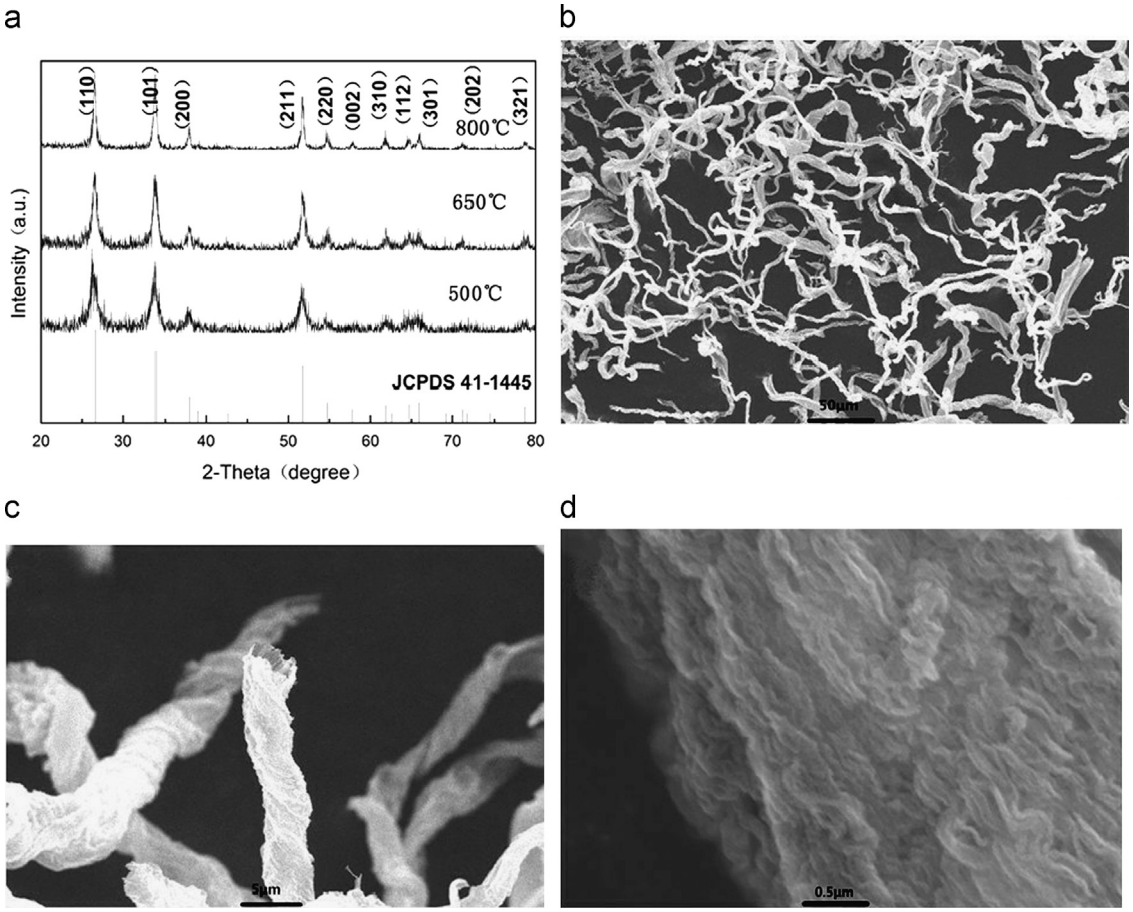

Fig. 1. (a) X-ray diffraction patterns of the SnO_2 microtubes obtained by calcinations at various temperatures from 500 to 800 °C; (b–d) SEM images of the SnO_2 microtubes calcined at 500 °C.