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Inexpensive synthesis of anatase TiO_2 nanowires by a novel method and its electrochemical characterization

Feixiang Wu, Xinhai Li *, Zhixing Wang, Huajun Guo, Ling Wu, Xunhui Xiong, Xiaojuan Wang

School of Metallurgical Science and Engineering, Central South University, Changsha 410083, PR China

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ABSTRACT

We demonstrate a simple, rapid, inexpensive and novel approach for the synthesis of a kind of anatase TiO_2 nanowires. The method is based on a hydrothermal method under normal atmosphere without using the complex Teflon-lined autoclave, high concentrations NaOH solution and long reaction time. The as-prepared materials are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical measurements. The obtained anatase TiO_2 nanowires show excellent performance. The initial Li insertion/extraction capacity is 260 and 224 mA h g^{-1} at 20 mA g^{-1}, respectively. In the 20th cycle, the reversible capacity still remains about 216 mA h g^{-1}, exhibiting excellent cycling stability. The discharging capacity is about 159 mA h g^{-1} in the 20th cycle at 200 mA g^{-1}, demonstrating a good high-rate performance. Anatase TiO_2 nanowires might be a promising anode material for lithium-ion batteries.

1. Introduction

Rechargeable lithium-ion cells are key components of the portable, entertainment, computing, and telecommunication equipment because of their high-energy storage density, high voltage, long cycle life, high-power sources, and ambient temperature operation. In this area, cathode materials have been widely studied, such as $LiMn_2O_4$, $LiCoO_2$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, $LiFePO_4$, etc. [1–4]. However, the anode materials also play an important role in the lithium-ion batteries. The carbon negative electrode used in rechargeable lithium-ion cells suffers from a number of problems. Titanium oxide (TiO_2) is probably the most widely studied semiconducting metal oxide due to its great application potential in many fields, such as photocatalysis, sensors, solar cells, and lithium-ion batteries. Nanostructured TiO_2 has been widely investigated as a key material for Li-insertion, because it is not only a low-voltage insertion host for Li^+, but also a fast Li-insertion/extraction host. These characteristics render it a potential anode material for lithium-ion batteries [5–7].

Recently, nanotubular TiO_2, nanostructured TiO_2 nanorods, and TiO_2 (B) nanowires have been studied by many researchers. They always mixed the TiO_2 nanoparticles and high concentrations NaOH solution, and added the mixture into Teflon-lined autoclave to be autoclaved at 110–200 °C for 24–72 h [8–13]. In this paper, we propose a novel, simple, rapid, inexpensive and improved process to synthesize anatase TiO_2 nanowires as an anode material for lithium-ion batteries.

2. Experimental

2.1. Synthesis and characterization

Anatase TiO_2 nanowires were synthesized by adding 12 g of titanium sulfate into de-ionized water until it was completely dissolved. An aqueous solution of NH_4OH (30 wt.%) was then added to form white hydrated titanium oxide. After aging for a period of time, hydrated titanium oxide gel was filtered and washed with distilled water until no sulfate ions were detected in the solution. Distilled water (100 ml) was then added to the hydrated titanium oxide, the white gel cake, in the 250 ml beaker. After stirring for 5 min, 20 g of 30 wt.% H_2O_2 solution was added into the beaker and ammonia solution (12.5 wt.%) was added into the beaker to maintain pH value near 10. After about 40 min, the white slurry was dissolved to form a yellow-green solution, and then transferred to a 1000 ml Beaker. After that, 400 g of 5 wt.% NaOH solution was added into the beaker, and then boiled to boiling point under vigorous stirring in an oil bath. One hour later, the white slurry was formed and filtrated. The obtained precipitate was washed 2 times with 2 wt.% HNO_3 solution, then washed with de-ionized water several times. Finally, the white product was dried at 120 °C for more than 8 h and the precursor nanowires were obtained. Further, the dried precursor was calcined at 500 °C for 3 h in air, anatase TiO_2 nanowires were formed.

The precursor nanowires and TiO_2 nanowires were analyzed using inductively coupled plasma emission spectroscopy (ICP, IRIS intrepid XSP, Thermo Electron Corporation). The SEM images of the particles were observed with scanning electron microscopy (SEM, JEOL, JSM-5600LV). The powder X-ray diffraction (XRD, Rint-2000, Rigaku) using CuKα radiation was employed to identify the crystalline phase of the precursor nanowires and TiO_2 nanowires. The elements on the

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* Corresponding author. Tel./fax: +86 731 88836633.
E-mail address: feixiang0929@163.com (X. Li).

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surface of samples were identified by energy-dispersive X-ray spectroscopy (EDS).

2.2. Electrochemical measurement

The electrochemical performance was performed using a two-electrode coin-type cell (CR2025) of Li $LiPF_6$ (EC:EMC:DMC = 1:1:1 in volume) TiO_2. The working cathode was composed of 80 wt.% TiO_2 powders, 10 wt.% acetylene black as conducting agent, and 10 wt.% poly (vinylidene fluoride) as binder. After being blended in N-methyl pyrrolidinone, the mixed slurry was spread uniformly on a thin copper foil and dried in vacuum for 12 h at 120 °C. A metal lithium foil was used as the anode. Electrodes were punched in the form of 14 mm diameter disks, and the typical positive electrode loading was about 1.95 mg/cm^2. A polypropylene micro-porous film was used as the separator. The assembly of the cells was carried out in a dry argon-filled glove box. The cells were charged and discharged over a voltage range of 1.0–3.0 V versus Li/Li^+ electrode at room temperature.

3. Results and discussion

3.1. Morphology and structure of the materials

Fig. 1. shows SEM images of the precursor (a and b) and as-prepared TiO_2 (c and d). From Fig. 1 (a and c), porous spherical particles or microspheres with a diameter of 500–700 nm and rough surface are observed obviously chestnut-like morphology. Two enlarged images of the particles of the precursor and as-prepared TiO_2 indicate that the spherical particles or microspheres are composed of aggregations of nanowires (Fig. 1 (b and d)). The precursor is calcined at 500 °C for 3 h to as-prepared TiO_2. As shown in Fig. 1, the morphology images of the precursor and as-prepared TiO_2 are the similar nanowires structure. These nanowires are of diameter 20 nm and can extend up to 250 nm in length. Compared with other nanostructured TiO_2, this unique morphology would make the active material contact with electrolyte more sufficiently, which improves the electrochemical property.

Fig. 2 shows the XRD patterns of the precursor and as-prepared TiO_2. According to Ma's report, all the peaks can be readily indexed to a lepidocrocite-type titanate phase (e.g., orthorhombic $H_xTi_{2-x/4}\gamma_{x/4}O_4 \cdot H_2O$, here $x \approx 0.7$, γ: vacancy, $a = 0.3783$ nm, $b = 1.8735$ nm and $c = 0.2978$ nm) [14]. The broad peaks at $2\theta = 8.85°$, 24.1°, 27.8°, 48.3° and 61.7° correspond well with (0 2 0), (1 1 0), (1 3 0), (2 0 0) and (0 0 2) reflections of the lepidocrocite titanates. Fig. 2 (b) displays the different diffraction peaks of as-prepared TiO_2 from the precursor nanowires. The as-prepared TiO_2 with high crystallinity is well ascribed to the diffraction peaks of anatase TiO_2. The anatase nanostructured TiO_2 which facilitates the insertion/extraction of Li^+ during discharge/charge would exhibit excellent electrochemical performance. ICP analysis reveals that Na and other impurity elements are not detected in the as-prepared TiO_2. EDS pattern of as-prepared TiO_2 is shown in Fig. 2 (c). As shown, Na and other impurity elements are absent in the as-prepared TiO_2, which is consistent with the ICP results.

3.2. Electrochemical performance

Fig. 3 (a) shows the initial three potential-capacity profiles of anatase TiO_2 nanowires at the charge/discharge current density of 20 mA g^{-1}. There are distinct potential plateaus at 1.77 and 1.89 V for

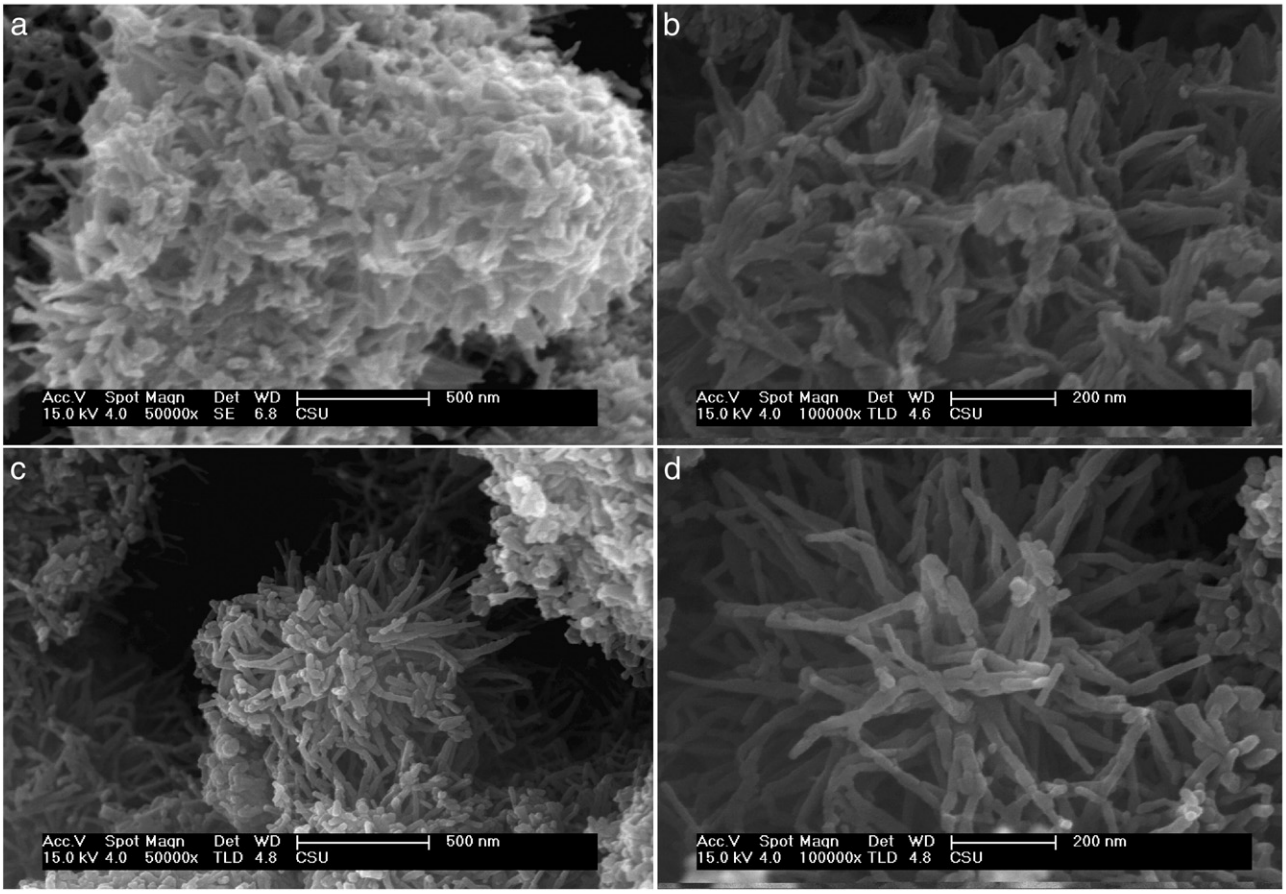

Fig. 1. SEM images of the precursor (a, b) and as-prepared TiO_2(c, d); the enlarge images of the precursor (a) and as-prepared TiO_2 (c).