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Synthesis of hollow nickel oxide nanotubes by electrospinning with structurally enhanced lithium storage properties

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ABSTRACT

We report a simple electrospinning synthesis method to prepare hollow NiO nanotubes composed of interconnected nanoparticles. The synthesized NiO nanotubes show diameters of 250–300 nm. As an anode material for lithium-ion batteries, the resultant hollow NiO nanotubes exhibit high capacity and good cycle stability (726 mA hg^{-1} at 0.2C up to 150 cycles), as well as good rate capability. The hollow nanotube structure possesses the following features: high NiO-electrolyte contact area, fast Li ion diffusion and better accommodation of volume change. It suggests that the hollow NiO nanotube is a promising anode material for high energy density lithium-ion batteries.

1. Introduction

Nowadays, great efforts have been devoted to exploring new electrode materials to meet the ever-growing demand for lithium-ion batteries (LIBs) with higher power and energy densities. Transition metal oxides have attracted great attention since Poizot et al. reported the transition metal oxides were a new type of anode materials of LIBs in 2000 [1]. Compared with commercial graphite materials (a theoretical capacity of 374 mAh g^{-1}), transition metal oxides can deliver much higher reversible lithium storage capacity of two to three times higher than that of carbon materials. Among the explored transition metal oxides, NiO is believed to be a promising candidate because of its high theoretical capacity of 718 mAh g^{-1} (according to the reaction $NiO+2Li^{+}+2e^{-}\leftrightarrow Ni+Li_2O$), low cost and excellent chemical stability [2]. However, the commercial application of NiO as LIBs anodes is still hampered by its poor capacity retention and cycling stability arising from large specific volume variation, which inherently accompanies the conversion reaction process and causes pulverization, aggregations and deterioration of active materials during cycling [3]. Until now, two main strategies (coupling with a conductive matrix [4], and construction of various nanostructures [5–7]) have been developed for alleviating the adverse mechanical effects to improve the overall electrochemical performance of NiO anodes. The strategy of nanostructure design has been demonstrated to be an effective approach to improve the electrochemical performance of NiO because of the sufficient contact of active material/electrolyte, large surface area, and short diffusion length of Li^{+} in the nanostructures. In well-designed nanostructures, not only the Li^{+} diffusion is much easier, but also the strain associated with volume change is often much better accommodated. And these merits can lead to significantly improved electrochemical performance. Particularly, nanotube architecture is accepted as a favorable morphology for advanced electrode materials. Recently, NiO nanotubes were prepared via AAO template or biotemplate and enhanced performances were proven in these systems [8,9].

In this work, high-quality hollow NiO nanotubes have been prepared by a facile and scalable electrospinning method without template. The NiO nanotubes consist of interconnected nanoparticles of 30–50 nm. Impressively, the as-prepared NiO nanotubes exhibit superior performance with high specific capacity and excellent capacity retention. The hollow nanotube structure is responsible for the enhanced electrochemical properties.

2. Experimental

In a typical synthesis, 0.8 g of polyacrylonitrile (PAN) was added into 20 mL N,N-dimethylformamide (DMF) and stirred at 60 °C for 8 h. After that, 2.4 g of Nickel(II) acetylacetonate ($Ni(AcAc)_2$) was added into the above solution and stirred continuously for 8 h to yield homogeneous solution. A high-voltage power

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of 20 kV was applied to the needle tip. The flow rate of liquid was set to 1 mL h^{-1}. The humidity level inside the electrospinning chamber was 55 ± 5%. The prepared samples were collected on an aluminum foil collector. The electrospun Ni(AcAc)$_2$/PAN fiber precursor composites were firstly stabilized in the air atmosphere at 300 °C for 1 h. Then the samples were annealed at 500 °C for 3 h in air to obtain the NiO nanotubes.

The morphology and microstructure of the products were characterized by X-ray diffractometer (XRD, Rigaku D/max 2550 PC, Cu Kα), scanning electron microscopy (SEM, Hitachi S-4700 and FESEM, FEI Sirion-100), transmission electron microscopy (TEM, JEM 200CX at 160 kV, Tecnai G2 F30 at 300 kV).

The electrochemical tests were carried out using a coin-type half cell (CR 2025) with pure lithium foil as both the counter and the reference electrodes. The working electrode was made of a mixture containing the active material, conducting acetylene black, and polyvinylidene fluoride (PVDF) in a weight ratio of 85:10:5. The load weight of NiO nanotube is ~1.2 mg cm^{-2}. Test cells were assembled in an argon-filled glove box with the electrolyte of 1 M LiPF$_6$ in ethylene carbonate (EC)-dimethyl carbonate (DME) (1: 1 in volume), and a polypropylene (PP) micro-porous film (Cellgard 2300) as the separator. Cyclic voltammetry (CV) was performed on theCHI660E electrochemical workstation. The galvanostatic charge/discharge tests were conducted on a LAND battery program-control test system at room temperature (25 ± 1 °C).

3. Results and discussion

Fig. 1a and b show the SEM images of the as-prepared hollow NiO nanotubes. The synthesized NiO sample exhibits uniform nanotube structure with diameter from 250 to 300 nm. Notice that the NiO nanotube is composed of closely packed nanoparticles of 30–50 nm as primary building blocks (Fig. 1(b)). The tubular morphology is clearly distinguished by TEM image as illustrated in

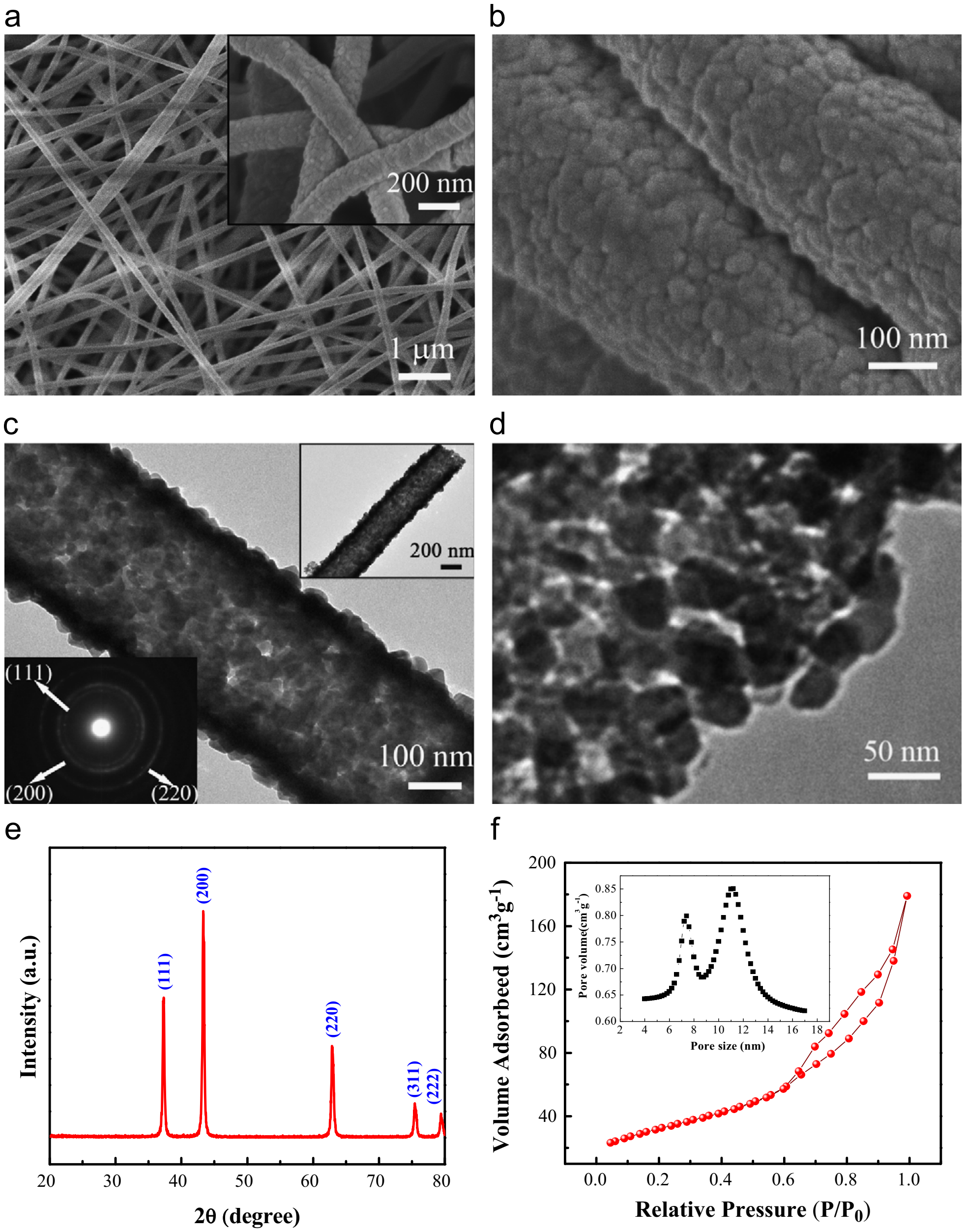

Fig. 1. (a) and (b) SEM and (c) and (d) TEM images of hollow NiO nanotube (SAED pattern in inset); (e) XRD patterns of the hollow NiO nanotubes and (f) BET measurement of NiO nanotube.