Materials Science and Engineering B 189 (2014) 32–37

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Short communication

Facile synthesis of Zn-doped SnO_2 dendrite-built hierarchical cube-like architectures and their application in lithium storage

Tiekun Jia[a,*], Jian Chen[a], Zhao Deng[b], Fang Fu[a], Junwei Zhao[a], Xiaofeng Wang[a], Fei Long[c]

[a] Department of Materials Science and Engineering, Luoyang Institute of Science and Technology, Luoyang 471023, PR China
[b] State Key Lab of Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, PR China
[c] School of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, PR China

ARTICLE INFO

Article history:
Received 2 April 2014
Received in revised form 8 July 2014
Accepted 22 July 2014
Available online 2 August 2014

Keywords:
Zn-doped SnO_2
Dendrites
Hierarchical architectures
Hydrothermal synthesis
Lithium storage capacity

ABSTRACT

Zn-doped SnO_2 dendrite-built hierarchical cube-like architectures were successfully synthesized by a facile hydrothermal approach without the use of any surfactants or templates. The as-prepared samples were characterized by the X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), and Raman spectroscopy. The observation of FESEM and HRTEM showed that Zn-doped SnO_2 hierarchical cube-like architectures were composed of numerous oriented dendrites. Each dendrite is assembled by a pronounced trunk with highly ordered branches distributing on the both sides. The as-prepared Zn-doped SnO_2 dendrite-built hierarchical cube-like architectures were used as anode materials for Li-ion battery, and a stable capacity of 488.3 mA h g^{-1} was achieved after 50 cycles. The results of electrochemical measurements indicated that the as-prepared Zn-doped SnO_2 dendrite-built hierarchical cube-like architectures have potential application in Li-ion battery.

1. Introduction

It is well known that the properties and applications of complex hierarchical architectures are strongly dependent on the size, morphology, shape, chemical composition and surface property [1–5]. Thus, great efforts have been devoted to synthesizing functional materials with complex hierarchical architectures [1–9]. The dendrite-built hierarchical architecture has been considered to be one of the most important categories because of the large surface area and good stability [4]. Nowadays, dendrite-built hierarchical architectures have attracted increasing attentions due to their unique properties in the fields of solar energy conversion, field electron emission, gas sensing and photocatalysis [6–9]. So far, a variety of dendrite-built hierarchical architectures, including Zn-doped NiO, CuSe, lead chalcogenides, Fe_2O_3, Cu-doped Fe_2O_3, Co, SnO_2, have been successfully synthesized for pursuing excellent properties [10–15].

SnO_2, as an n-type semiconductor with a band gap of 3.6 eV, has numerous applications inoptoelectronic devices, dye-sensitized solar cells, secondary lithium batteries, electrode materials, transistors, gas sensors, and catalyst supports [15–20]. In order to meet increasing demands under more complicated and harsh conditions, many investigations have been made on the modification of SnO_2, e.g., element doping and heterostructure constructing [19–26]. In the previous study [21], SnO_2 nanoparticles were synthesized by a molten-salt decomposition method. The product was used as anode materials for lithium ion battery and the specific capacity was 402 mA h g^{-1} after 40 cycles. Liu et al. prepared SnO_2 hollow microspheres via a hydrothermal-annealing method and investigated the elecrochemical property. The specific capacity was 374.2 mA h g^{-1} after 100 cycles [22]. All the above experimental procedure was complicated and the results were not satisfied. Generally, doping is considered to be a simple and effective approach to enhance the properties of oxide semiconductors. Up to now, several types of Zn-doped SnO_2 nanostructures have been synthesized and exciting results have been obtained in the previous studies [23–27]. However, the design and synthesis of Zn-doped SnO_2 hierarchical architectures with desired morphology assembled by one-dimensional nanobuilding blocks are still a challenge. Therefore, one-step surfactant-free approach is strongly desirable for the synthesis of Zn-doped SnO_2 dendrite-built hierarchical architectures. Moreover, there are few studies focused on the synthesis and electrochemical properties of Zn-doped SnO_2 dendrite-built hierarchical architectures.

* Corresponding author at: Wangcheng Road 90#, Luoyang City, Henan Province, PR China. Tel.: +86 379 65928196; fax: +86 379 65928196.
E-mail addresses: tiekunjia@126.com, tkjia@whut.edu.cn (T. Jia).

http://dx.doi.org/10.1016/j.mseb.2014.07.006
0921-5107/

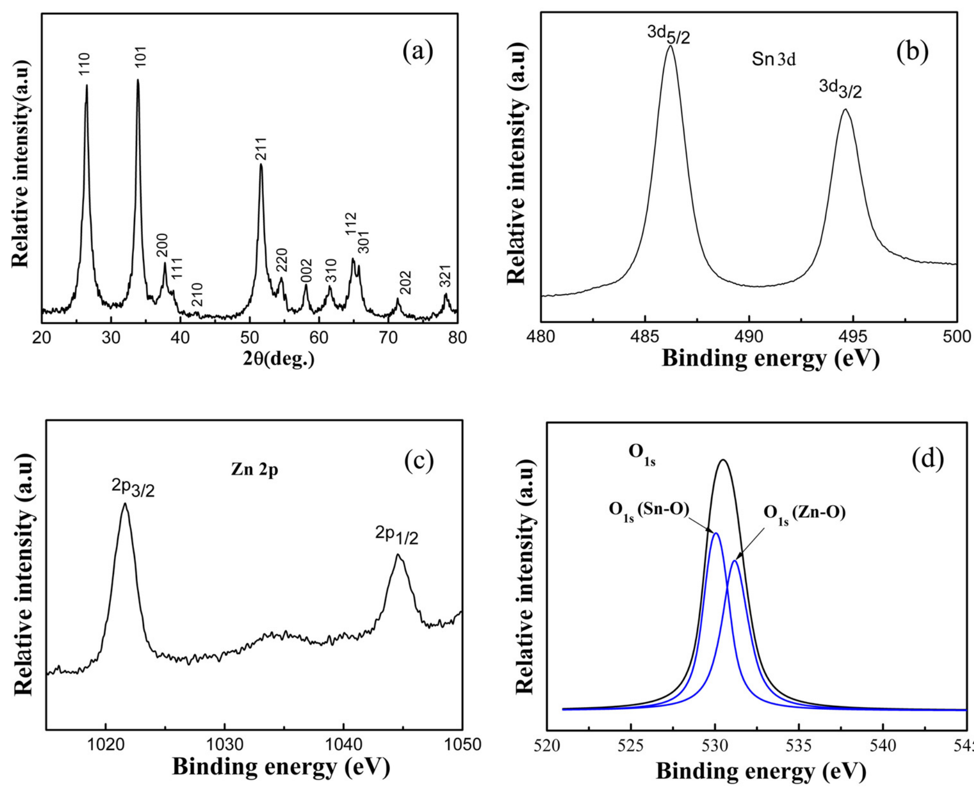

Fig. 1. (a) XRD pattern, and high-resolution XPS spectra of (b) Sn 3d and (c) Zn 2p and (d) O 1s of the as-prepared Zn-doped SnO_2 dendrite-built hierarchical cube-like architectures.

Herein, we present a facile and reliable hydrothermal approach for preparing Zn-doped SnO_2 dendrite-built hierarchical cube-like architectures without the use of any templates or surfactants. The electrochemical properties of the as-prepared samples used as anode materials for Li-ion battery were also investigated.

2. Experimental

2.1. Preparation of Zn-doped SnO_2 dendrite-built hierarchical cube-like architectures

All the reagents were analytically pure (Shanghai Chemical Industrial Co.) and used as received. In a typical procedure, 1.2 g of $SnCl_4{\cdot}5H_2O$ and 0.168 g of $Zn(NO_3)_2{\cdot}6H_2O$ were dissolved in 60 mL distilled water. Then, 100 mL of NaOH aqueous solution (0.6 M) was added dropwise into the solution under vigorous stirring. After stirring for 30 min, the mixture was transferred into a Teflon-lined stainless steel autoclave, and maintained at 200 °C for 20 h. After the hydrothermal procedure, the autoclave was cooled naturally down to room temperature. The resultant products were centrifuged and washed with distilled water and ethanol for several times, followed by drying in vacuum at 60 °C for 12 h. For comparison, pure SnO_2 nanoparticles were prepared via the similar approach without using zinc source.

2.2. Characterization

X-ray diffraction (XRD) pattern was collected using a Rigaku ultimaIII diffractometer equipped with Cu Kα radiation (λ = 0.15406 nm). Scanning electron microscopy (SEM) images were taken on an Hitachi S-4800 field emission scanning electron microscope. High-resolution transmission electron microscopy (HRTEM) images were performed on a JEM 2010FEF transmission electron microscope. X-ray photoelectron spectroscopy (XPS) measurement was carried out on a VG Multilab 2000X X-ray photoelectron spectrometer. Raman spectra were recorded with a Renishaw/invia Raman microscope at the room temperature with an Ar^+ laser of 514 nm line as the excitation source. The nitrogen adsorption and desorption isotherms were measured at 77 K using a Quantachrome NOVA 2000e sorption analyzer after the sample was vacuum-dried at 473 K overnight.

2.3. Electrochemical measurements

Electrochemical measurements were carried out by using two-electrode cells with lithium metals as the counter and reference electrodes. The assembly of the lithium cells has been reported in the previous literature [28]. The electrodes were fabricated by compressing a mixture of the active material including Zn-doped SnO_2, conductive material (acetylene black), and binder (polytetrafluoroethylene) with a weight ratio of 82:8:10. The electrode was dried at 80 °C for 1 h and cut into a disk of 1.0 cm in diameter. The cells were assembled in a glove-box filled with pure argon. The electrolyte was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethylmethyl carbonate (EMC) (1:1:1 by weight). An appropriate amount of electrolyte was added before sealing. The newly assembled cells were measured by a galvanostatic discharge–charge method in a multichannel battery tester (model Land CT2001A) in the potential range of 0.005–2.5 V (vs. Li^+/Li). Typically, a working electrode of 1 cm^2 was prepared with the active material mass loading of 1.95 mg.

3. Results and discussion

3.1. Phase structure

Fig. 1a shows the XRD pattern of Zn-doped SnO_2 dendrite-built hierarchical cube-like architectures. All the diffraction peaks can be