Electrochimica Acta 106 (2013) 386–391

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

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

Hierarchical tin-based microspheres: Solvothermal synthesis, chemical conversion, mechanism and application in lithium ion batteries

Danni Lei, Ming Zhang, Baihua Qu, Jianmin Ma, Qiuhong Li, Libao Chen, Bingan Lu, Taihong Wang*

Key Laboratory for Micro-Nano Optoelectronic Devices of Ministry of Education, and State Key Laboratory for Chemo/Biosensing and Chemometrics, Hunan University, China

ARTICLE INFO

Article history:
Received 23 January 2013
Received in revised form 26 May 2013
Accepted 27 May 2013
Available online 2 June 2013

Keywords:
SnS_2
SnO_2
Microsphere
Lithium ion battery

ABSTRACT

Uniform hierarchical SnS_2 structures were synthesized by a facile solvothermal approach. Based on time-dependent experiments results, a possible formation mechanism of the hierarchical SnS_2 architectures was proposed. Mesoporous hierarchical SnO_2 also could be obtained by calcining the corresponding SnS_2 structures. When used as the anode materials of rechargeable lithium-ion batteries, both of them showed high specific capacities and enhanced rate capacities.

1. Introduction

As one kind of energy storage devices, lithium-ion batteries (LIBs) have been extremely important power sources for various portable electronic devices and electric vehicles in modern society [1–5]. To keep pace with the rapid development of integrated circuits and their high energy requirements, new materials with better performance are urgently needed. Among various anode materials, tin-based materials have been extensively studied as possible alternatives for commercially available carbon electrodes due to their high theoretical capacity for battery application (781 mAh g^{-1} for SnO_2; 645 mAh g^{-1} for SnS_2), low cost, low toxicity, and widespread availability [6–13].

Recently, inorganic hierarchical nanostructures with hollow interiors have attracted increasing attention in many fields, because of their extraordinarily high activated surface and roust stability [14–18]. SnS_2 materials have shown good cycling stability as anode for LIBs because of their two-dimensional (2D)-layered structures [19–21]. However, electrochemical performances of such materials still need to be improved. Consequently, the morphology controls of SnS_2 nanomaterials are actively pursued. In particular, much efforts have been devoted to rational and skillful control of hierarchical and complex nanostructures self-assembled with nanosheets [22,23]. Recently, Zai et al. synthesized three-dimensional (3D) architectures with a red-embroidery-ball-like structure, which significantly enhance their lithium storage capacity and improve rate performance [24]. The improvement for such 3D hierarchical structures are related to their structural characteristics, such as large surface area, greater accessibility to electrolyte, faster transportation of Li^+, and accelerated phase transitions. However, there are only a few reports on the synthesis of 3D SnS_2 hierarchical structures. Thus, we have developed an alternative method to prepare SnS_2 with 3D hierarchical structure. On the other hand, SnO_2 materials with hierarchical structure can take both the advantages of the nanometer size effects and the high stability arisen from the micro- or sub-micro-sized assemblies [25–27]. The conventional fabrication procedures of hollow structure generally involved hard templates or soft templates [28–30], which related to tedious synthesis and high cost. Thus, it is of great significance to develop a facile method to synthesize SnO_2 hierarchical nanostructures with hollow interiors from the view of both scientific research and practical application.

In this work, a facile solvothermal approach was developed to fabricate hierarchical SnS_2 microspheres. The formation mechanism of the hierarchical SnS_2 microspheres was proposed based on the systematic study. In addition, mesoporous hierarchical SnO_2 microspheres have been obtained through calcining the corresponding SnS_2 precursors while preserving their original

* Corresponding author.
E-mail address: thwang@aphy.iphy.ac.cn (T. Wang).

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.05.099

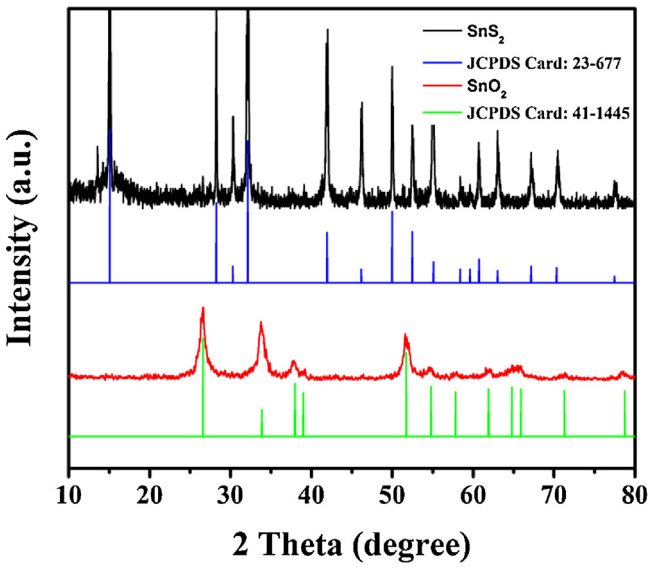

Fig. 1. The typical XRD patterns of the hierarchical SnS_2 microspheres and hierarchical SnO_2 microspheres.

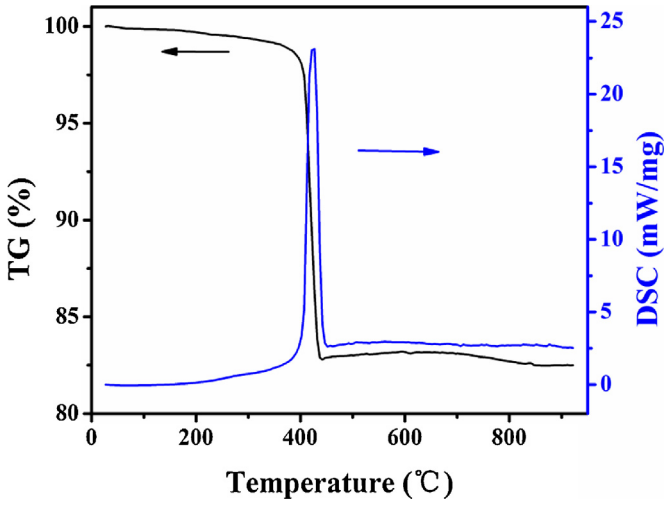

Fig. 2. TGA and DSC curves of the SnS_2 sample.

morphologies. When they were used as the anode for LIBs, these unique hierarchical tin-based microspheres can significantly enhance their lithium storage capacity, respectively.

2. Experimental

2.1. Preparation of hierarchical SnS_2 and SnO_2 microspheres

All the chemicals were of analytical grade and used as received without further purification. In a typical procedure, 1.4 g tetrachlorostannane pentahydrate ($SnCl_4{\cdot}5H_2O$), 1.2 g thioacetamide (TAA) was dissolved in 100 mL ethanol to obtain the homogenous solution. After being stirred for several minutes, the clear solution was transferred into a 130 mL Teflon-lined autoclave and maintained at 180 °C for 24 h, then cooled to room temperature naturally. The precipitate was collected by centrifugation after being washed with distilled water and ethanol several times. Finally, the product was dried completely in vacuum at 80 °C. The mesoporous SnO_2 superstructures could be obtained by annealing the as-prepared SnS_2 in a muffle furnace at 500 °C in air with heating rate of 2 °C min^{-1}.

2.2. Characterization

The crystal structure of the products were determined by X-ray powder diffraction (XRD, Cu Kα radiation; λ = 1.5408 Å) with a SIEMENS D5000 X-ray diffractometer. Scanning electron microscope (SEM) images were performed with a Hitachi S-4800 microscope. Thermogravimetry analysis was carried out on a Netzsch STA449C (at a heating rate of 10 °C min^{-1} in flow air).

2.3. Electrochemical measurement

The electrochemical properties of products were measured using CR 2025-type coin cells. In a process of fabricating the LIBs, The anode electrode consisted of 80 wt% active material, 10 wt% conductive carbon black, and 10 wt% binder (carboxyl methyl cellulose) on a copper foil. One molar $LiPF_6$ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl

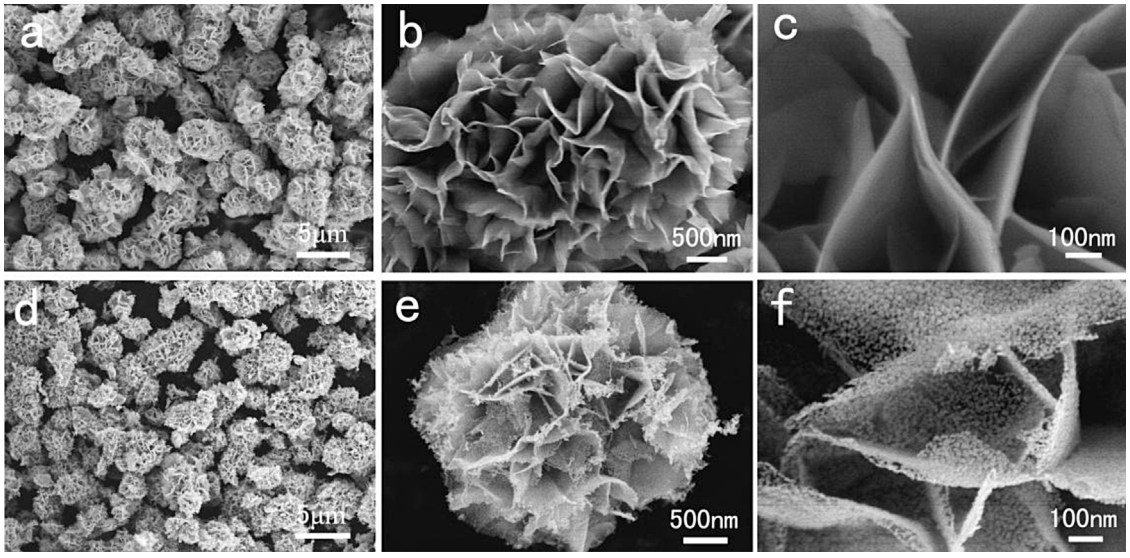

Fig. 3. (a–c) SEM images of hierarchical SnS_2 microspheres; (d–f) SEM images of hierarchical SnO_2 microspheres.