



Zinc ferrite nanorods coated with polydopamine-derived carbon for high-rate lithium ion batteries



Xiayin Yao, Junhua Kong, Chenyang Zhao, Dan Zhou, Rui Zhou, Xuehong Lu*

School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

ARTICLE INFO

Article history:

Received 3 August 2014

Received in revised form 22 August 2014

Accepted 27 August 2014

Keywords:

zinc ferrite nanorods
polydopamine
carbon
anode
lithium-ion battery

ABSTRACT

Zinc ferrite (ZnFe_2O_4) nanorods are synthesized using a facile and scalable method, i.e., decomposition of oxalate precursors which are obtained through a polyvinyl alcohol-assisted aqueous precipitation reaction. The ZnFe_2O_4 nanorods are further coated with carbon by self-polymerization of dopamine on the surfaces of the ZnFe_2O_4 nanorods followed by carbonization. The carbon layer on the ZnFe_2O_4 nanorods is homogeneous with the thickness of 3 to 5 nm. The polydopamine-derived carbon coating greatly improves the electrochemical performances of the ZnFe_2O_4 nanorods, especially rate capability and cycling stability. When galvanostatic discharging/charging at 0.5 and 2 A/g, the ZnFe_2O_4 /carbon nanorod anode can deliver reversible capacities of 805 and 504 mAh/g, respectively, whereas the ZnFe_2O_4 nanorod anode only delivers the capacities of 616 and 154 mAh/g, respectively. Besides, the ZnFe_2O_4 /carbon nanorod anode shows excellent cycling stability; no obvious capacity fading is observed at the current density of 1 A/g for 100 cycles. The improved electrochemical performances could be attributed to the enhanced electron conductivity of the ZnFe_2O_4 nanorods with the carbon layer, which is confirmed by electrochemical impedance spectroscopy measurements and scanning electron microscopic studies of the cycled electrodes.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Zinc ferrite (ZnFe_2O_4), a typical ferrite spinel, is currently considered as a promising alternative anode material (to graphite) for lithium-ion batteries (LIBs) because of its non-toxicity, environmentally friendly, good structural stability and low cost [1–6]. It has been reported that ZnFe_2O_4 can react with nine Li ions per formula unit with a theoretical specific capacity of about 1000.5 mAh/g [3,5]. However, ZnFe_2O_4 anode materials usually suffer from low rate capability resulting from poor electric conductivity as well as kinetic limitations and poor cycling stability caused by electrode pulverization induced by large volume changes and severe agglomerations of active materials during repeated lithiation/delithiation processes.

Generally, these problems can be partly solved by using nanostructured electrode materials [7,8]. A number of works focused on the synthesis and properties of nanostructural ZnFe_2O_4 with controllable size and shape have been reported [9–14]. Among these nanostructured materials, one-dimensional (1D) nanostructured electrodes have attracted much attention as they can

provide short pathways and high kinetics for lithium ion insertion/extraction [15], while also facilitating electron transport along the longitudinal direction of the 1D nanostructures if they have adequate electrical conductivities. Up to now, several methods have been reported to synthesize 1D ZnFe_2O_4 nanomaterials, such as a template method [16], an electrospinning strategy [14,17], a microemulsion method [18] and a hydrothermal approach [19]. Teh et al. [14] prepared nanowebbs consisting of interwoven ZnFe_2O_4 nanofibers by an electrospinning technique. The obtained nanowebbs, employed as anodes for LIBs, show good cyclability and rate capability. However, the aforementioned fabrication methods for 1D ZnFe_2O_4 generally require relatively complicate procedures and are therefore unsuitable for mass production of the anode materials.

Another useful strategy to improve electrochemical performances of transitional metal oxide electrodes is to prepare metal oxide/carbon nanocomposite electrodes [20], in which the carbonaceous materials can buffer the volume expansion as well as increase the electrical conductivity of the metal oxides. Dopamine, a synthetic compound that contains catechol and amine functional groups, can self-polymerize under basic aqueous conditions to form coatings on various substrates. And this mussel-inspired biomimetic polydopamine (PDA) conformal coating process has been considered to be an ideal route for coating a thin layer of

* Corresponding author. Tel.: +65 6790 4585; fax: +65 6790 9081.
E-mail address: asxhlu@ntu.edu.sg (X. Lu).

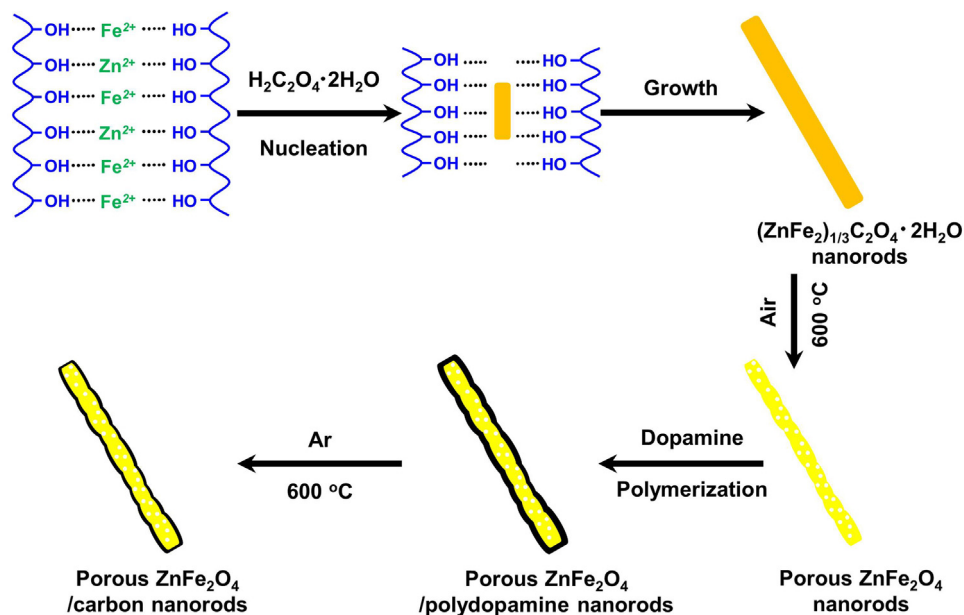


Fig. 1. Schematic illustration of the synthesis route for ZnFe₂O₄/carbon nanorods.

carbon source on inorganic nanomaterials in order to improve their electrochemical performances [21]. Kong et al. used PDA as the carbon precursor for preparation of SnO₂/carbon nanocomposites and significantly enhanced electrochemical performance was realized [22]. N-doped carbon coated Fe₃O₄ nanoparticles were also synthesized using PDA as the carbon precursor [23]. The Fe₃O₄/carbon electrodes showed excellent electrochemical performance for lithium ion batteries in term of cyclic performance and rate capability. However, there is no prior report regarding the effects of the PDA-derived carbon coating on electrochemical performances of 1D binary transition metal oxide nanostructures as LIB anodes. It is believed that the carbon coating on 1D nanostructures may improve electron conduction of the system more pronouncedly and hence significantly enhance the electrochemical performances.

In this article, we present a facile route for large-scale preparation of carbon-coated ZnFe₂O₄ nanorods. (ZnFe₂)_{1/3}C₂O₄·2H₂O nanorods were synthesized through polyvinyl alcohol (PVA)-assisted co-precipitation of an aqueous solution containing metal cations, which were then converted to ZnFe₂O₄/carbon nanorods by decomposition of (ZnFe₂)_{1/3}C₂O₄·2H₂O, coated with PDA and carbonized. Both the inorganic and organic synthesis steps are conducted in aqueous media at room temperature and ambient pressure, making the process simple, cost-effective and scalable. The obtained ZnFe₂O₄/carbon nanocomposites exhibit excellent high-rate capability and cycle life as anode materials in LIBs, demonstrating a facile procedure for realizing large-scale production of high-performance LIB anode materials.

2. Experimental

2.1. Synthesis of (ZnFe₂)_{1/3}C₂O₄·2H₂O and ZnFe₂O₄ nanorods

All chemicals were analytical grade and used as received without further purification. (ZnFe₂)_{1/3}C₂O₄·2H₂O precursors were firstly prepared through a solution-based precipitation process using polyvinyl alcohol (PVA, with the degree of polymerization DP = 1750 ± 50) as surfactant. In detail, 15 g of 33.3 wt % zinc

sulfate heptahydrate and iron sulfate heptahydrate (with a molar ratio of 1:2) aqueous solution was firstly mixed with 30 g PVA aqueous solution under stirring at room temperature. The concentrations of PVA aqueous solution were set at 0.0, 0.3 and 1.0 wt%, respectively. Then, equivalent amount of 20 wt % H₂C₂O₄·2H₂O aqueous solution was introduced into the above solution. Yellow precipitates appeared immediately. After being stirred for 30 min, the (ZnFe₂)_{1/3}C₂O₄·2H₂O precipitate formed was centrifugalized, washed with deionized water and dried in vacuum. Finally, the obtained (ZnFe₂)_{1/3}C₂O₄·2H₂O precursors were calcined at 600 °C at a heating rate of 2 °C min⁻¹ for 2 h in air to obtain ZnFe₂O₄ particles or nanorods.

2.2. Preparation of ZnFe₂O₄/carbon nanorods

The obtained ZnFe₂O₄ nanorods were dispersed in water with stirring. Then, certain amounts of dopamine and Tris-buffer were added into the suspension at the concentration of 0.8 mg/ml and 1.21 mg/ml, respectively. The solution was stirred for 6 hours at room temperature for the polymerization of dopamine. After that, the product was centrifuged and washed with deionized water for five times and then dried. Finally, the sample was calcined at 600 °C at a heating rate of 5 °C min⁻¹ for 2 h under Ar atmosphere to obtain ZnFe₂O₄/carbon nanorods.

2.3. Characterization

Scanning electron microscopy (SEM) images were acquired with a JEOL-6340F field emission scanning electron microscope. X-ray diffraction (XRD) patterns were obtained on a D8 Discover GADDS (Bruker AXS, Germany) powder diffractometer. Thermogravimetric analyses (TGA) were performed with a TGA Q500 under an air flow of 60 ml/min between 80 to 700 °C. Transmission electron microscopy (TEM) experiments were performed on a JEOL 2100 transmission electron microscopy at an accelerating voltage of 200 kV. The Brunauer-Emmett-Teller (BET) test was determined via a Micromeritics Tristar II-3020 nitrogen adsorption apparatus. Pore size distribution plot was obtained by the Barrett-Joyner-Halenda (BJH) method.

Download English Version:

<https://daneshyari.com/en/article/6612780>

Download Persian Version:

<https://daneshyari.com/article/6612780>

[Daneshyari.com](https://daneshyari.com)