

Full paper

In situ analysis of SnO₂/Fe₂O₃/RGO to unravel the structural collapse mechanism and enhanced electrical conductivity for lithium-ion batteries

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ABSTRACT

Herein, we describe a microwave-assisted hydrothermal process to synthesize α -Fe₂O₃ nanotubes/SnO₂ nanorods/reduced graphene oxide (FNT/S/RGO) for application as a high-performance anode in lithium-ion batteries (LIBs). The composite products exhibit anisotropic growth because of heteronucleation and the preferred orientation of SnO₂. SnO₂ nanorods on the FNT surfaces are converted into Sn metal during the alloying/dealloying reaction, which offers improved electrical conductivity. The FNT/S/RGO show substantially enhanced electrochemical properties because of the reduced volume expansion effect, which improves the electrical and Li-ion conductivity and provides a large surface area. As a consequence, the FNT/S/RGO anode delivers a high reversible capacity of 883 mA h g⁻¹ even at a current density of 200 mA g⁻¹, with a capacity retention of 90% between the 1st and 220th cycles, excellent high-rate capacity (382 mA h g⁻¹ at 4320 mA g⁻¹), and long-term cycle durability (maintaining 629 mA h g⁻¹ at 1000 mA g⁻¹ for 1000 cycles). The presented FNT/S/RGO electrodes are the most efficient SnO₂- and Fe₂O₃-based anode electrodes reported thus far for LIBs. The origin of the synergistic effect and the reaction mechanism of the FNT/S/RGO was thoroughly investigated using various *in situ* transmission electron microscopy, electrochemical impedance spectroscopy, and X-ray diffraction analysis methods.

1. Introduction

Iron oxide and tin oxide are considered promising anode materials because of their high theoretical capacity (Fe₂O₃ and SnO₂: ~1005 and ~781 mA h g⁻¹), eco-friendly materials, and natural abundance, which can be much higher than that of a commercial graphite anode (372 mA h g⁻¹) [1,2]. However, one of the serious drawbacks of metal oxides, including Fe₂O₃ and SnO₂, for LIBs is their low electrical conductivity and severe volume expansion during the insertion and extraction of Li ions, which can result in the detachment of the metal oxide anode from the current collector. This issue is directly related to a large initial capacity drop, poor rate capability, and insufficient cycle performance [3]. Various groups have suggested solutions to these serious problems by designing structures such as nanorods, nanotubes, nanocubes, nanoparticles, 3d porous structures, hollow shells, and epitaxial growth structures; however, all these solutions provide unsatisfactory rate capacity and long-term cyclability [4–9].

Because the high rate capacity and long-term cyclability remain unsatisfactory, hollow nanostructures to prevent volume expansion and provide high rate capability for metal oxide anodes have attracted

considerable interest because of their excellent resistance to volume expansion and short diffusion lengths for Li ions [10]. Nevertheless, one of the drawbacks of preparing hollow structures is the formation of a hard template during preprocessing, which is a tedious task because of the difficulty in obtaining a hollow nanostructure. The hard template from the hollow nanostructure is difficult to remove while keeping the hollow nanostructure intact. Synthesis without a template by calcination is favorable. Therefore, in this study, we investigate the hollow nanostructure of template-free α -Fe₂O₃ nanotubes/SnO₂/RGO (FNT/S/RGO) prepared using a microwave-assisted hydrothermal process to maximize the practical use and large-scale processability of Fe₂O₃ nanotubes and SnO₂ nanorods as anode materials for LIBs.

Recently, SnO₂-Fe₂O₃ composites have been reported to exhibit better cycling characteristics than pristine SnO₂ or Fe₂O₃ due to the presence of metallic components during conversion reaction [5,11]. However, the electrochemical performance of simply mixed SnO₂-Fe₂O₃ composites is unsatisfactory because of the huge volume changes and low electrical conductivity in SnO₂ and Fe₂O₃ during the reaction [5,8,12]. In the present work, the unique hybrid structure of FNT/S/RGO is proposed to overcome these drawbacks. To reduce the volume

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change, α - Fe_2O_3 nanotubes were fabricated with the free space of a hollow structure, which can offer superior and stable cyclability. The Fe_2O_3 and SnO_2 structure was synthesized as hollow α - Fe_2O_3 (wall thickness of ~ 20 nm) and SnO_2 nanorods (rod diameter of ~ 10 nm) to apply electric vehicle, hybrid electric vehicle and energy storage systems, which can provide high rate performance [12]. In addition, the RGO provides advantages such as improved electrical conductivity, a buffer effect, and a large surface area to accommodate Li ions [13,14]. Therefore, the synergistic improvement provided by RGO and FNT/S compared to pristine α - Fe_2O_3 and SnO_2 enables high capacity retention, enhanced rate capability, and good cycle durability.

The electrochemical performance of an anode, such as its cyclability, rate capability, and coulombic efficiency, are strongly related to the charge transfer and ion diffusion behavior at the electrode surface [15]. The formation of the solid electrolyte interface (SEI) on a complicated shape and the co-relationship between the collapse mechanism and the structural strain of the multi-metal oxide, which is generated from the shape, remain difficult to define. Recently, *in situ* TEM conducted using a bias-controlled *in situ* TEM holder revealed structural changes during lithiation; however, examining both the behavior of the decomposed electrolytes and the practical structural failure due to the use of a solid-type electrolyte or ionic liquid is difficult [16–18]. Therefore, FNT/S/RGO electrodes were characterized using stacked graphene sheets that

contained a liquid electrolyte; the advantages of this approach are easy fabrication, applicability to any conventional transmission electron microscope, and similarity to a realistic measurement environment because of the liquid electrolyte [19,20]. Furthermore, the electrochemical characterization during cycling strongly affects the electron conductivity, conversion mechanism, and structural integrity. Therefore, various *in situ* analysis techniques (TEM, electrochemical impedance spectroscopy (EIS), and XRD) were used to examine the cycle mechanism of α - Fe_2O_3 and SnO_2 . Profound insights of the reaction behavior and conversion mechanism of Fe_2O_3 nanotubes and SnO_2 nanorods were obtained.

2. Experimental section

2.1. Preparation of α - Fe_2O_3 nanotubes (FNTs)

All chemicals in this study were of analytical reagent grade. The FNTs were fabricated using a microwave-assisted hydrothermal process (MARS 6, CEM Co.). $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and Na_2SO_4 were mixed in 40 ml of deionized (DI) water, and the resulting solution was transferred to a Teflon vessel and heated at 220°C for 30 min. After the synthesis was complete and the mixture was cooled to room temperature, the precipitate was centrifuged with DI water and dried in an

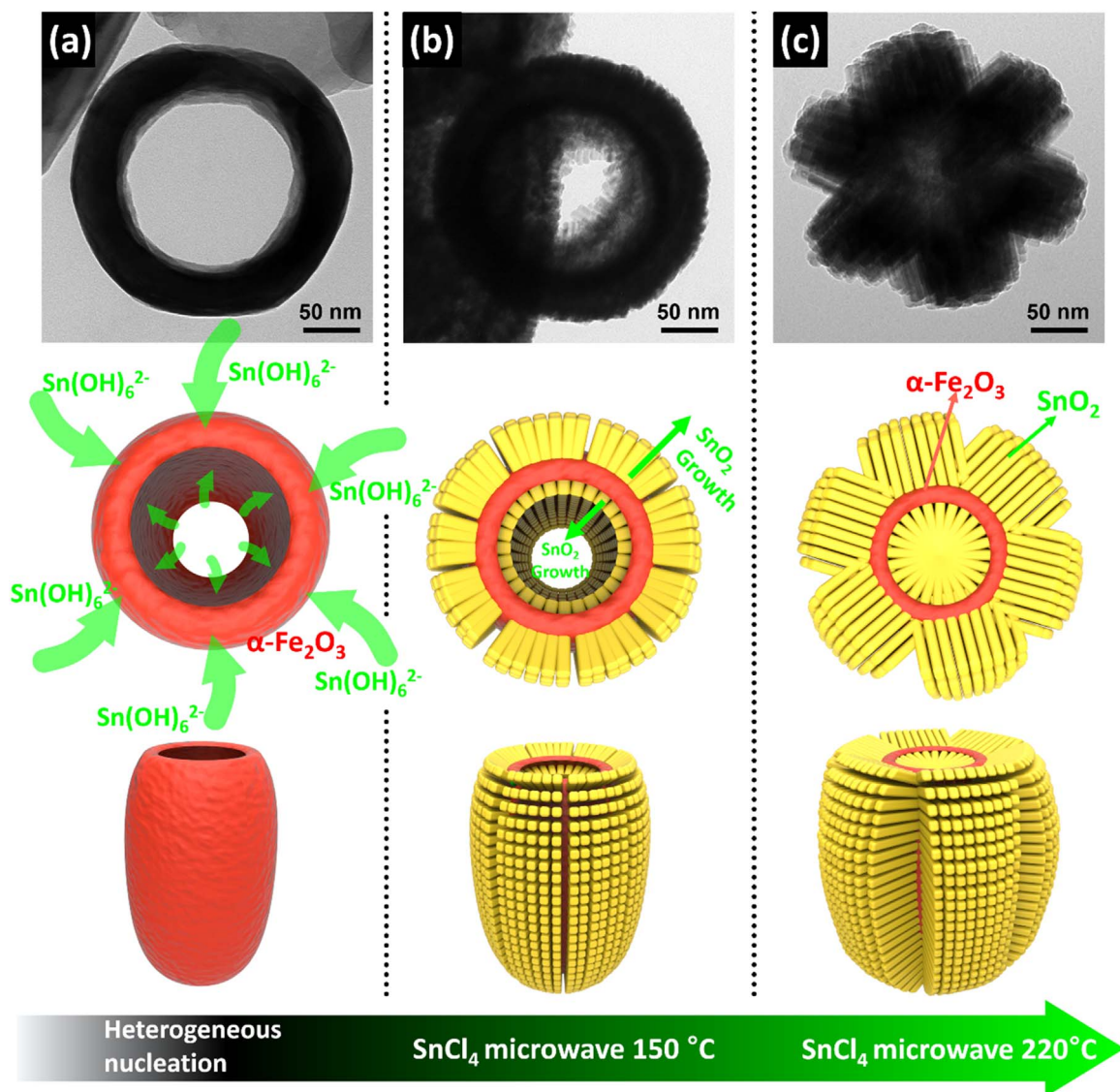


Fig. 1. TEM images and schematics of the microwave-assisted hydrothermal synthesis process of (a) FNT at 220°C , (b) FNT/S at 150°C , and (c) FNT/S at 220°C .

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