



Original article

The fabrication of hollow magnetite microspheres with a nearly 100% morphological yield and their applications in lithium ion batteries



Yong-Tao Zuo^a, Jun Peng^a, Gang Li^a, Li Liu^a, Zhi-Song Han^a, Gang Wang^{a,b,c,*}

^aSchool of Chemistry and Chemical Engineering, Shihezi University, Shihezi 832003, China

^bEngineering Research Center of Materials-Oriented Chemical Engineering of Xinjiang Production and Construction Corps, Shihezi 832003, China

^cKey Laboratory of Materials-Oriented Chemical Engineering of Xinjiang Uygur Autonomous Region, Shihezi 832003, China

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ABSTRACT

Hollow Fe₃O₄ (H-Fe₃O₄) microspheres were fabricated through a facile one-step solvothermal synthesis, which was performed in an ethylene glycol (EG)–diethylene glycol (DEG) mixed solvent using polyethylene glycol (PEG) as the stabilizer. The addition of DEG increased the viscosity of the system, which caused the Fe₃O₄ primary crystal to aggregate slower and the morphological yield to approach nearly 100%. The as-prepared hollow Fe₃O₄ microspheres show promise for application in lithium ion battery anodes and showed a reversible specific capacity of 453.3 mAh g⁻¹ after 50 cycles at 100 mA g⁻¹.

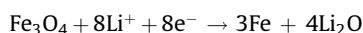
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1. Introduction

For the last few decades, graphite has been the most used commercial anode material in lithium-ion batteries (LIBs) with a theoretical capacity of 372 mAh g⁻¹ [1]. With the increasing demand of LIBs as power sources in electric vehicles (EV) and hybrid electric vehicles (HEV), much attention has been paid to alternative anode materials [2–5]. A major breakthrough for LIB anodes, made by Tarascon *et al.* in 2000, is the development of transition metal oxides as anode materials, which exhibit a much higher theoretical specific capacity than traditional graphite electrodes [6]. Iron oxide, Fe₃O₄, is one of the few transition metal oxide materials that possesses both a high theoretical capacity (926 mAh g⁻¹) and a high electronic conductivity (2 × 10⁴ S m⁻¹), in addition to the advantages of nontoxicity, natural abundance, and low cost [7,8].

The electrochemical conversion reaction of Fe₃O₄ with Li⁺ is shown in the reaction [9,10]:



Each formula unit of Fe₃O₄ can react with eight Li⁺ to form a composite containing Fe nanoclusters embedded in an amorphous

Li₂O matrix, which reversibly converts back to Fe₃O₄ on charging process. The quite reversible reaction ensures excellent coulombic efficiency and high reversible capacity of Fe₃O₄.

However, the large volume variation (>200%) that inherently accompanies the conversion reaction process and severe destruction of the electrode hamper the use of Fe₃O₄ as an anode material in LIBs. This holdback can partially be solved by fabricating nanostructured materials. Hollow nanomaterials of transition metal oxides (SnO₂ [11–13], Co₃O₄ [14], Fe₂O₃ [15], Ni(OH)₂ [16], Co(OH)₂ [17], and TiO₂ [18]) have been the research focus as promising high-energy electrode materials for next-generation lithium-ion batteries for a long time. The results from these previous works prove that construction of hollow nanostructures is an effective strategy to improve the cyclability, resulting from the large surface area, the sufficient contact of active material/electrolyte, and the short diffusion length of Li⁺. Inspired by this, we attempt to produce hollow nanostructured Fe₃O₄. The synthesis strategies of hollow Fe₃O₄ [19–21] have been reported in many ways, however, a tiny change in experimental parameters or operations leads to the morphological transformation from hollow to solid [22], resulting in bad repeatability. Therefore, there is an urgent need for a new synthesis strategy of H-Fe₃O₄ microspheres which is more repeatable.

Herein, we report a facile one-step solvothermal synthesis of H-Fe₃O₄ microspheres based on oriented aggregation and Ostwald ripening mechanisms. The synthesis is performed in an ethylene glycol (EG)–diethylene glycol (DEG) mixed solvent

* Corresponding author at: School of Chemistry and Chemical Engineering, Shihezi University, Shihezi 832003, China.

E-mail address: wanggang@shzu.edu.cn (G. Wang).

using polyethylene glycol (PEG) as the stabilizer. Significantly, the approach is suitable for the high-yield mass production of H-Fe₃O₄ microspheres with nearly 100% morphological yield. Benefiting from the hollow nanostructures, when used as the anode material in lithium-ion batteries, not only is the Li⁺ diffusion is much easier, but also the strain associated with Li⁺ intercalation and the volume expansion of active materials are often better accommodated, resulting in significantly improved electrochemical performance.

2. Experimental

2.1. Preparation of H-Fe₃O₄ microspheres

The synthesis of H-Fe₃O₄ microspheres was performed in an EG–DEG mixed solvent. Typically, FeCl₃·6H₂O (1.35 g) and PEG 20000 (1.5 g) were dissolved in EG (20 mL) and DEG (20 mL), respectively. After mixing the two solutions, NaAc (3.6 g) was added. The mixture was stirred vigorously for 60 min at 50 °C and then sealed in a 50 mL Teflon-lined stainless steel autoclave. The autoclave was treated in an air-flow electric oven at 200 °C for 24 h. After cooling down naturally, the precipitate was collected using a centrifuge and was washed with ethanol. The washed products were dried in vacuum at 60 °C overnight. The synthesis of S-Fe₃O₄ microspheres is performed in an EG solvent, then followed by the same conditions and procedures applied in the synthesis of H-Fe₃O₄ microspheres.

2.2. Characterization techniques

The morphologies of the samples were examined by scanning electron microscopy (SEM; Zeiss Supra 40 FE) and transmission electron microscopy (TEM; FEI Tecnai G20 and Hitachi H600). The crystal phases of the samples were characterized by X-ray diffraction analysis (XRD) recorded on a powder diffractometer (Bruker D8 Advanced Diffractometer System) with Cu-K α (1.5406 Å) source.

2.3. Electrochemical measurements

The electrochemical measurements were carried out on coin-type half cells using a Land battery system (CT2001A). To prepare the working electrode, 80 wt% of the active material, 10 wt% carbon black and 10 wt% Polytetrafluoroethylene (PTFE) dissolved in *N*-methylpyrrolidone (NMP) were mixed to form a slurry. The slurry was pasted on the Ni foil and dried in a vacuum oven for 12 h. The loading of the working electrodes was typically in the range of 1–2 mg (6 mg cm⁻²). Li foil was used as both the counter and reference electrodes. 1 mol L⁻¹ LiPF₆ in ethylene carbonate and diethyl carbonate (EC/DEC, v/v ¼ 1:1) solution was used as the electrolyte. Galvanostatic charge and discharge measurement was carried out in the voltage range between 3.0 and 0.05 V at a current density of 100 mA g⁻¹. The impedance spectrum measurements were carried out in the frequency range from 100 kHz to 0.01 Hz.

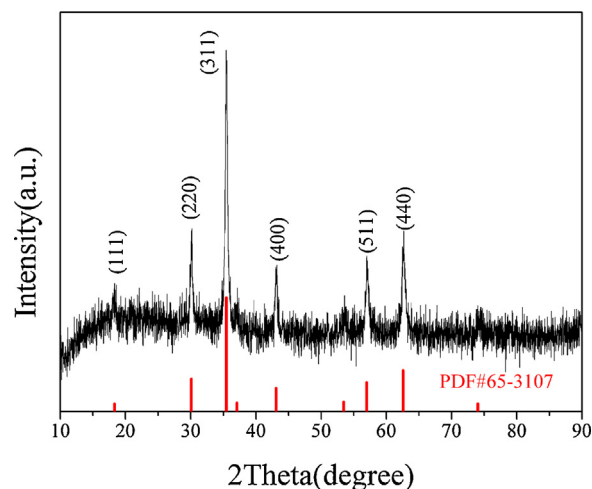


Fig. 1. XRD pattern of H-Fe₃O₄ microspheres after solvothermal treatment for 24 h.

3. Results and discussion

Fig. 1 shows the XRD pattern of the H-Fe₃O₄ microspheres after solvothermal treatment for 24 h at 200 °C. The reflections of the H-Fe₃O₄ microspheres can be mainly attributed to the face-centered cubic structural (Fd3m space group) magnetite Fe₃O₄ (JCPDS card No. 65-3107). Fig. 2a shows the TEM image of the monodispersed H-Fe₃O₄ microspheres at low magnification obtained at 200 °C for 24 h via a solvothermal route with diameters of 400–500 nm. Through the clear variation in contrast, the porous and hollow nature of the microspheres was confirmed. The TEM image of a single Fe₃O₄ microsphere was shown in Fig. 2b and c. Most pores were channel-like, connecting the central hollow interior and the outside space. According to our understanding, this structure represents an ideal candidate for LIBS anode material. For example, the hollow interior could act as a good container for Li⁺, while the interstitials between primary crystals, which enable Li⁺ diffusion, could work as “nanochannels” for material exchange between the interior and exterior of the spheres. To achieve more detailed crystallographic information of the constituent nanocrystals, a high resolution TEM image was taken at the conjunction of two constituent Fe₃O₄ nanocrystals, which was shown in Fig. 2d. Interestingly, both nanocrystals shared one common crystallographic orientation. The lattice fringe calculated from the HRTEM image was 0.25 nm, fitting well with the (3 1 1) planes of a cubic Fe₃O₄ structure.

In order to investigate the growth mechanism of such hollow microstructures, we carried out time-dependent experiments, as shown in Fig. S1a–d in Supporting information. The first capture of the discrete nanocrystals layer was after solvothermal treatment for 12 h (Fig. S1a). With a synthesis time up to 16 h (Fig. S1b), the discrete nanocrystals layer became slightly thicker, and the partial Fe₃O₄ microspheres transformed from solid to hollow, which could

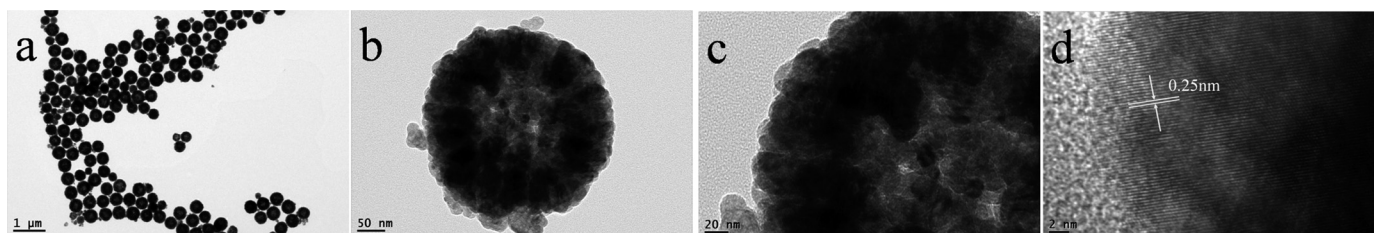


Fig. 2. (a and b) Representative TEM images of microspheres of H-Fe₃O₄ after solvothermal treatment for 24 h; (c and d) HRTEM images of a Fe₃O₄ sphere.

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