



Combustion synthesized rod-like nanostructure hematite with enhanced lithium storage properties



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ABSTRACT

Fe₂O₃ nanorods are synthesized by combustion method using alcohol as both solvent and fuel, which is a facile and effective strategy for the large-scale and inexpensive fabrication. The Fe₂O₃ nanorods are with the well distributed diameters of 20–30 nm and length ranging from 80 to 100 nm. As an anode material for lithium-ion batteries, the Fe₂O₃ nanorod electrode delivers a high discharge capacity of 761.7 mA h g⁻¹ after 60 cycles at 500 mA g⁻¹, and 727.2 mA h g⁻¹ at a high current density of 2000 mA g⁻¹. The good electrochemical performance is attributed to the sufficient contact of active material and electrolyte, large surface area, and short diffusion length of Li⁺.

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1. Introduction

Nowadays, in order to the success of electric vehicles (EVs), it is key to develop the rechargeable batteries with long cycling life, high capacity, and high rate capability. Among the most popular power sources for portable electronic devices, lithium ion batteries (LIBs), can be successfully used for EVs if their energy density and power density can be enhanced [1]. During the last two decades, extensive efforts have been made to seek for excellent anode materials to satisfy the demand of the better battery performance [2–8]. Poizot et al. firstly proposed transition metal oxides as the new-type anode materials for LIBs [2]. They exhibit much higher theoretical capacities (2 to 3 times) than that of commercial graphite and smaller volume change during the charge–discharge process than that of alloy anodes [9–21]. Among them, hematite (Fe₂O₃) has been extensively investigated as a very appealing host anode material because of its high capacity (1007 mA h g⁻¹), natural abundance, nontoxicity, and low cost [22–26]. During the discharging–charging process, each unit of Fe₂O₃ can react with Li⁺ to form a composite containing Fe nanoclusters embedded in amorphous Li₂O matrix and then it reversibly converts back to Fe₂O₃, which is similar to other transition metal oxides [17,27].

Currently, there are many methods used to synthesize Fe₂O₃ nanostructures, such as hydrothermal method [28–30], temple method [31,32], spray pyrolysis method [33], microwave heating

method [34,35], and so on. However, by using the hydrothermal process, it is difficult to obtain the Fe₂O₃ product in one step, always followed by annealing treatment with energy and time consuming [30,36,37]. And the yield is also disappointing to meet the demand of the industrial production. The use of template can successfully prepare various nanostructures, but it is somewhat cumbersome with a complex elaboration process and rather high production cost. As for the spray pyrolysis and microwave heating method, they both need the special and complicated equipment. Therefore, in order to achieve the practical use of Fe₂O₃, development of a facile and effective strategy for the large-scale and inexpensive fabrication of a high-performance electrode is urgently desirable and of great importance.

Combustion synthesis involves an exothermic and self-sustaining chemical reaction between the metal salts and suitable organic fuel [38]. This method has been successfully used to synthesize many kinds of nanopowder materials [39–42]. In fact, combustion, a very outstanding synthesis process, has attracted a good deal of attention, because it saves the time and energy, requires simple equipment, and cheap reagents, and provides rather high production [43]. It meets the demand of the green and sustainable modern industry. In this present work, we aim to report the Fe₂O₃ nanostructure synthesized by simple and high-efficiency combustion method with ethanol as both solvent and fuel. The effect of ethanol on promoting mixture of the reactants to gain a better performance of the materials has been reported in many other works [42,44]. The as-synthesized Fe₂O₃ nanostructure as the anode material for LIBs, shows greatly enhanced electrochemical performance because of its sufficient contact of

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active material and electrolyte, large surface area, and short diffusion length of Li^+ .

2. Experimental

2.1. Preparation of hematite nanorod

The Fe_2O_3 nanorods were synthesized by a combustion method. Firstly, 30 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 30 mL of ethanol with stirring. Then the resulting solution was poured into a 100 mL corundum crucible. The crucible was put into a chamber furnace which was pre-heated to 500 °C in air, and treated at this temperature for 30 min to obtain the Fe_2O_3 nanorods. To prepare Fe_2O_3 nanoparticles by an annealing method for comparison, the same amounts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and ethanol were used. The solution was firstly dried in an oven at 90 °C. Then it was annealed at 500 °C in air for the same reaction time in the synthesis of Fe_2O_3 nanorods. The average loading of both electrodes was about 1.4 mg cm^{-2} .

2.2. Characterization

The morphology and microstructure of the products were characterized by X-ray diffraction (XRD, Rigaku D/max 2550 PC, $\text{Cu K}\alpha$), field emission scanning electron microscopy (SEM, Hitachi S-4700), and transmission electron microscopy (TEM, JEM 200CX at 160 kV, Tecnai G2 F30 at 300 kV).

The electrode was prepared by mixing the active materials (85 wt%) with carbon black (10 wt%) and polyvinylidene fluoride (5 wt%). The obtained slurry was coated on a copper foil, followed by drying in a vacuum oven at 90 °C for 24 h. The electrochemical tests were performed using a coin-type half cell (CR 2025). Test cells with lithium foil as the counter electrode and a polypropylene (PP) micro-porous film (Cellgard 2300) as the separator were assembled in an argon-filled glove box. Electrolyte consisting of 1 M LiPF_6 in ethylene carbonate (EC)–dimethyl carbonate (DMC) (1:1 in volume) was used. The galvanostatic charge–discharge tests were conducted on a LAND battery program-control test system at certain current densities between 0.01 and 3.0 V at room temperature. Cyclic voltammetry (CV) was performed on a CHI660C electrochemical workstation in the potential from 0 to 3.0 V (vs Li^+/Li) at a scan rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range of 100 kHz–10 mHz by applying an AC signal of 5 mV.

3. Results and discussion

Fig. 1 shows typical XRD patterns of the two powders. All the diffraction peaks confirm that both the crystal structures are in agreement with the standard values for the rhombohedral phase of Fe_2O_3 [JCPDS card No. 33-0664]. No impurity is detected from the XRD patterns of the two samples, indicating that they both have a single-phase rhombohedral crystal structure.

The comparison on the morphologies of the two products is shown in Fig. 2. The Fe_2O_3 product synthesized by combustion method exhibits a uniform rod-like morphology (Fig. 2(a)). The relatively high magnified SEM image shows that the Fe_2O_3 nanorods are with the well distributed diameters of 20–30 nm and length ranging from 80 to 100 nm (Fig. 2(b)). Fig. 2(c) and (d) shows the morphology of Fe_2O_3 nanoparticles with the non-uniform size of 50–200 nm due to the inhomogeneous precipitation in the drying process. With the combustion method, in such a short reaction time, the raw materials reacted more homogeneously in ethanol solution. The structural features and detailed morphological of the powders are also examined by TEM.

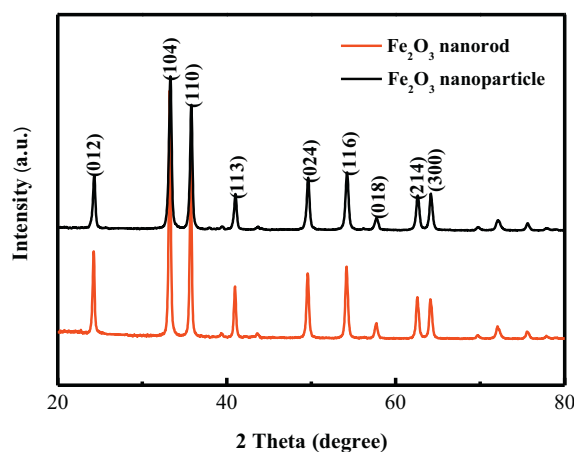


Fig. 1. XRD pattern of Fe_2O_3 nanorods and nanoparticles.

Fig. 3(a) further confirms the rod-like structure of Fe_2O_3 synthesized by combustion method. The HRTEM examination of a Fe_2O_3 nanorod shown in Fig. 3(b) shows the nanorod has perfect crystallinity with a distinct set of visible lattice fringes. The inter-planar spacing is 0.25 nm, corresponding to the (110) plane of rhombohedral Fe_2O_3 . The Fe_2O_3 nanoparticles are also observed in Fig. 3(c) and (d). From the HRTEM (Fig. 3(d)), the space between the adjacent planes is 0.37 nm, corresponding to the (012) plane of Fe_2O_3 . Fig. 4 shows the nitrogen adsorption and desorption isotherm and the Barrett–Joyner–Halenda (B–J–H) curves of the Fe_2O_3 nanorod and Fe_2O_3 nanoparticle. At the relative pressure range of 0.5–1.0, the isotherm exhibits a hysteresis loop, which is an indication of the existence of the porosity in the samples. For Fe_2O_3 nanorod, the B–J–H curve consists of two peaks. One is around 17 nm which may be the pore in the nanorod. The other peak around 360 nm indicates the interspaces between the nanorods. The Brunauer–Emmett–Teller (B–E–T) surface area of the Fe_2O_3 nanorod is calculated to be $15.84 \text{ m}^2 \text{ g}^{-1}$. The relatively large specific surface area can offer large contact area between active material and the electrolyte, and promotes Li-ion diffusion. However, the B–E–T surface area of the Fe_2O_3 nanoparticle is only $7.96 \text{ m}^2 \text{ g}^{-1}$, much smaller than that of the Fe_2O_3 nanorod.

In view of the potential application of Fe_2O_3 as an anode in LIBs, we investigated their ability to reversibly insert/release lithium. Fig. 5 shows the CV curves of the two Fe_2O_3 electrodes for the first three cycles at the scan rate of 0.1 mV s^{-1} in the potential range from 0 to 3.0 V (vs Li/Li^+). The observed CV curves of the two electrodes are very similar. As shown in Fig. 5(a), in the first cathodic scan for the Fe_2O_3 nanorod, there is a sharp reduction peak at about 0.57 V, which can be attributed to the reduction of Fe^{3+} to Fe^0 and the irreversible reaction with the electrolyte. And the anodic peak at about 1.70 V corresponds to the reversible oxidation of Fe^0 to Fe^{3+} , which agrees well with previous works [19,33,45]. During the charging process, both the peak current and the integrated area of the anodic peak are decreased. In this step, the conversion of Fe_2O_3 to Fe and the formation of insulated Li_2O are responsible for the irreversible capacity. Compared to Fe_2O_3 nanoparticle, however, the peak current and areas of all CV peaks of the Fe_2O_3 nanorod electrode are larger and the CV curves are more stable after the second cycle, indicating that the Fe_2O_3 nanorod electrode has higher reactivity and capacity. The uniform Fe_2O_3 nanorod with much larger surface area results in a more adequate reaction and higher electrode utilization.

The first two galvanostatic charge–discharge curves for the Fe_2O_3 nanorod and nanoparticle electrodes at a current density of 500 mA g^{-1} within a voltage range of 0.01 to 3.0 V are shown in

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