



Short communication

Controlled synthesis of α -Fe₂O₃ nanostructures and their size-dependent electrochemical properties for lithium-ion batteriesYanna NuLi^{a,b}, Rong Zeng^a, Peng Zhang^a, Zaiping Guo^{a,*}, Huakun Liu^a^a Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia^b Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

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ABSTRACT

Highly crystalline hematite α -Fe₂O₃ nanostructures were selectively synthesized by a simple hydrothermal method. By carefully tuning the concentration of the reactants, reaction time and pressure, a series of α -Fe₂O₃ nanocuboids, nanospheres, nanosheets, nanorods and nanowires can be obtained. Based on the evidence of electron microscope images, a formation mechanism for nanowire-structured hematite is proposed. The electrochemical performance of these hematite nanostructures as anode materials for lithium-ion batteries was further evaluated by cyclic voltammetry, electrochemical impedance and charge–discharge measurements. It was demonstrated that both the morphology and the particle size have an influence on the performance. The results showed that the nanospheres displayed the highest discharge capacity and superior cycling reversibility, which may result from the high surface area and small and uniform grain size.

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1. Introduction

It is well known that particle size is an important parameter that strongly influences the properties of powders, especially when the particle size is decreased to the nanometer scale. Three-dimensional (3D) nanomaterials, two-dimensional (2D) layered nanostructures and one-dimensional (1D) nanorods, nanowires and nanotubes have attracted much attention because of their unique properties and potential applications [1,2]. The main objective of nanoscale science and technology has been to synthesize nanomaterials with controlled size and shape, as well as search for new properties that are not realized in microscale morphologies [3]. Among the various nanomaterials, nanostructured metal oxides play an important role in physics, chemistry and material science [4].

As the most stable iron oxide, hematite (α -Fe₂O₃), based on hexagonal close packing of oxygen with iron in 2/3 of the octahedral vacancies, has been extensively used in the production of pigments, catalysts, gas sensors, magnetic recording media and raw materials for hard and soft magnets, due to its low cost, environmental friendliness and high resistance to corrosion [5]. Furthermore, it has also been shown to act as a rechargeable conversion electrode material that reacts with six Li per formula unit, exhibiting higher capac-

ity than carbonaceous substances (e.g., maximum of 372 mAh g⁻¹ for graphite) used currently in commercial lithium-ion batteries. A mechanism for the reduction and oxidation of metal nanoparticles, accompanied by the formation and decomposition of Li₂O has been proposed [6]. Iron oxides with large particles have been considered too difficult to be used anode materials for lithium-ion batteries due to their irreversible phase transformation during the reaction [7]. There have been reports, however, on the effects of particle size on the lithium reaction with α -Fe₂O₃, which reached the conclusion that nano- α -Fe₂O₃ has better electrochemical performance than micro-sized α -Fe₂O₃ [8–10].

Because of its excellent properties, considerable efforts have been focused on the properties and synthesis of hematite nanomaterials with controllable size and shape [11], such as nanocrystals [12], nanoparticles [13], nanocuboids [14], nanospindles [15], nanoflakes [16], nanorods [17], nanowires [18], nanobelts [19] and nanotubes [20]. Several methods, such as a template method [21], a sol–gel strategy [17], gas–solid reaction techniques [22] and a hydrothermal approach [20,23] have been developed for the synthesis of hematite nanostructures.

Among the methods mentioned above, hydrothermal synthesis has been shown to be advantageous over other methods in terms of homogeneous nucleation and grain growth of hematite nanocrystals [24]. It has been shown that the preparation conditions, such as concentrations, reaction temperature and reaction time are the main factors in determining the structures and morphologies of the α -Fe₂O₃ nanocrystals [25–27]. Nevertheless, it still remains a

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challenge to develop simple hydrothermal approaches to synthesize α -Fe₂O₃ nanostructures with tunable sizes and shapes, which will facilitate our understanding of the size-dependent properties of α -Fe₂O₃.

Herein, we describe an easy route to synthesize α -Fe₂O₃ nanocuboids, nanospheres, nanosheets, nanorods and nanowires via a low-temperature hydrothermal method and report on a study of their properties as attractive anode materials for lithium-ion batteries. Poly(ethylene glycol), with an average molecular weight of 600, was employed as a soft template. PEG is a typical non-toxic, non-immunogenic, non-antigenic and protein-resistant polymer reagent with long polymer chains [28], and the PEG-600 used here plays multiple roles in the synthesis process. It acts as a coordination and linking reactant, as a stabilizer, and as a structure-directing agent [29]. By changing the concentration of the reactants, reaction time and pressure, highly crystalline nanocuboids, nanospheres, nanosheets, nanorods and nanowires can be obtained. Their shape-dependent electrochemical properties as anode materials for lithium-ion batteries have been systematically investigated, using cyclic voltammetry, electrochemical impedance and galvanostatic methods. It was found that as-prepared nanospheres, characterized by uniform size and shape with a high specific surface area, exhibited superior electrochemical activity, with an initial discharge capacity of 1248.1 mAh g⁻¹ and capacity retention of 61.1% after 30 cycles at an ambient temperature.

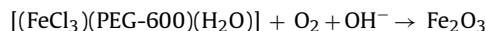
2. Experimental

2.1. Preparation of α -Fe₂O₃ nanomaterials

All the chemical reagents were analytically pure and used without further purification. The α -Fe₂O₃ nanomaterials were prepared by a PEG-precursor route. In a typical experimental procedure, an aqueous solution of FeCl₃ (BDH Laboratory Supplies, England) was added dropwise to PEG-600 (Aldrich) methanol solution with equivalent molar number under continuous stirring at room temperature to obtain a homogeneous solution. The solution was kept at 50 °C for 12 h to form crystals, which were collected as precursors. Stoichiometric proportions of the precursors and NaOH aqueous solution (4 M) were added under stirring to a Teflon-lined autoclave, which was filled to one-third by volume. The autoclave was sealed, heated to 160 °C, and maintained at this temperature in an oven for a given period (shown in Table 1). After the reactions, the autoclaves were cooled down naturally. The resulting products were separated by centrifugation, washed with ethanol and distilled water, and then dried under vacuum at 80 °C for 4 h. The detailed preparation conditions of the formed powders are shown in Table 1.

Here, the reaction process of Fe₂O₃ may be similar to that of MnO₂ synthesized using MnSO₄, PEG-6000 and NaOH [29]. Fe³⁺ might produce a relatively stable complex once PEG-600 has been added into the aqueous solution of FeCl₃. Then, Fe(OH)₃ was precipitated

after mixing with NaOH. At auto-generated vapour pressure and high temperature, Fe₂O₃ was obtained by reaction with oxygen in air. At the same time, PEG-600 was pyrolyzed to form low-molecular-weight products [30]. Although the exact mechanism is not clear to date, it is reasonable to believe that the PEG-600 mainly controls the size of the as-synthesized crystallites. The chemical equation for this reaction could be expressed as follows:



2.2. Sample characterizations

X-ray powder diffraction (XRD) analysis was conducted on a Philips 1730 X-ray diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) with 2θ ranging from 20° to 80° to analyse the structure of the resultant products. A JEOL JSM 6460A scanning electron microscope (SEM) was employed to examine the morphology.

For electrochemical measurements, a typical slurry was obtained by grinding a mixture of α -Fe₂O₃, carbon black and poly(vinylidene fluoride) (PVDF) dissolved in *N*-methyl-2-pyrrolidinone (NMP) with a weight ratio of 70:15:15. It was then spread onto a piece of copper foil (1 cm²) to form an electrode. After the electrode was dried at 100 °C for 4 h under vacuum, it was compressed at a rate of about 150 kg cm⁻² and then weighed. The cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany). The charge-discharge measurements were examined via CR2025 coin-type cells with lithium metal counter electrode, Celgard 2400 membrane separator and electrolyte of 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) at an ambient temperature on a multi-channel battery cycler in the voltage range between 0.01 V and 3.0 V at a current density of 20 mA g⁻¹. Cyclic voltammetry (CV) and electrochemical impedance measurements were performed on three-electrode cells with lithium foils both as the counter and reference electrodes using a CHI instrument. The scanning rate for CV was 0.1 mV s⁻¹ and the amplitude of the ac voltage in impedance measurements was 5 mV over the frequency range between 10⁵ Hz and 0.1 Hz. The electrochemical impedance measurements were performed at the open-circuit voltage (OCV) before and after the CV experiments.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of as-synthesized powders prepared using the hydrothermal method under different conditions. It can be observed that the positions of the characteristic peaks of the products are consistent with the standard values for the hexagonal α -Fe₂O₃ phase (JCPDS number 33-0664),

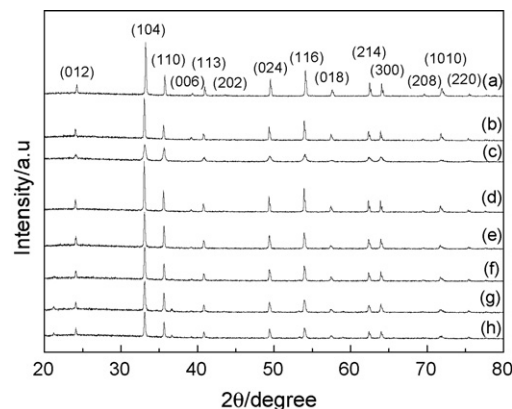


Fig. 1. XRD patterns of as-prepared α -Fe₂O₃ samples: (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7 and (h) 8.

Table 1
Experimental condition for the preparation of the α -Fe₂O₃ nanomaterials

Sample no.	The concentration of PEG-600 (mol L ⁻¹)	The concentration of FeCl ₃ (mol L ⁻¹)	The capacity of autoclave (mL)	Reaction time (h)
1	0.4	1	15	12
2	0.4	1	15	24
3	1	1	15	24
4	1	1	15	48
5	1.5	1	50	24
6	2	1	15	24
7	2	2	15	24
8	2	4	50	24

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