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## Fabrication and characterisation of Fe<sub>3</sub>O<sub>4</sub> nanowires via an ethylenediamine-assisted route

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In this article, Fe<sub>3</sub>O<sub>4</sub> nanowires were synthesised from iron chloride, using ethylenediamine (EN)–water mixed solvent as the medium. The as-prepared powders were characterised in detail by conventional techniques, such as X-ray powder diffraction, selected area electron diffraction, transmission electron microscope and field-emission scanning electron microscopy. An EN is a bidentate ligand and it can react with metal ions to form relatively stable metal complexes which plays important roles in the formation of the products in the process. And their magnetic properties were evaluated on a vibrating magnetometer. The sample exhibits a high first discharge capacity of 902 mAh/g, which enables it to be used for a lithium-ion battery.

**Keywords:** magnetic materials; nanostructure; magnetic properties; electrochemical properties

### 1. Introduction

Magnetic nanoparticles have been widely studied because of their fascinating properties and wide range of potential applications in ferrofluids, information storage and medicine [1]. Among magnetic particles, iron oxides (Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>) have been extensively investigated. Various methods have been reported in the literature for the preparation of ultrafine particles of Fe<sub>3</sub>O<sub>4</sub>, such as: reduction of hematite by CO/CO<sub>2</sub> [2] or H<sub>2</sub> [3], co-precipitation of the solution of ferrous/ferric mixed salt [4], microwave plasma synthesis [5], microemulsion methods [6] and ultrasound irradiation [7]. Among them, hydrothermal process has been widely used to prepare single crystal and ceramic powder. In the past 10 years, it has been employed to generate novel oxides [8], polyanion clusters [9] and zeolite materials [10]. Considerable attention has been drawn towards one-dimensional (1D) nanostructured materials, including nanotubes, nanorods and nanowires, because of both their interesting physical properties and their wide range of potential applications in nanodevices. Much effort has been made to understand the magnetic, electronic and optical properties of these nanostructures because they exhibit

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novel physical and chemical properties, differing from those of their bulk counterparts, due to their reduced size and large surface-to-volume ratios [11–13]. In this article,  $\text{Fe}_3\text{O}_4$  nanowires have been prepared by a one-step hydrothermal procedure from ferric chloride ( $\text{FeCl}_3$ ), diamine hydrate ( $\text{H}_4\text{N}_2 \cdot \text{H}_2\text{O}$ ) and sodium hydroxide ( $\text{NaOH}$ ) in ethylenediamine (EN)–water mixed solvent.

## 2. Experimental

All reagents were of analytical purity from Shanghai Chemistry Co. and were used without further purification. Distilled water was used for the preparation of an aqueous solution of  $\text{Fe}^{3+}$  ions (0.2 mol/L). In a typical procedure, 30.0 mL  $\text{Fe}^{3+}$  solution and 10 mL EN were put into a Teflon-lined stainless autoclave, sodium hydroxide (0.6 g) was dissolved into 5.0 mL  $\text{H}_4\text{N}_2 \cdot \text{H}_2\text{O}$  and then the mixture was slowly dropped into the Teflon-lined stainless autoclave. Then, the autoclave was put into an oven, kept at  $150^\circ\text{C}$  for 6 h, then cooled to room temperature naturally. The products were filtered and washed several times with distilled water and absolute ethanol, and finally dried in vacuum oven at  $40^\circ\text{C}$  for 12 h.

The samples, which were recorded at a scanning rate of  $0.05^\circ/\text{s}$  with the  $2\theta$  range from  $10$  to  $70^\circ$ , were characterised by X-ray powder diffraction (XRD) using an X-ray diffractometer with high-intensity Cu- $\text{K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The morphologies of the samples were examined by transmission electron microscopy (TEM, Hitachi, Model H-800) and field-emission scanning electron microscopy (FESEM, JEOL-7500B). Their magnetic properties were measured on a BHV-55 vibrating sample magnetometer at room temperature.

The positive electrodes were fabricated by pasting slurries of the as-prepared  $\text{Fe}_3\text{O}_4$  crystallites (85 wt%), carbon black (Super P, 10 wt%), and polyvinylidene (PVDF, 5 wt%) dissolved in *N*-methylpyrrolidinone (NMP) on Al foil strips by the doctor blade technique. Then the strips were dried at  $160^\circ\text{C}$  for 24 h in an air oven, pressed under 20 MPa pressure, and kept at  $120^\circ\text{C}$  for 12 h in vacuum. The electrolyte was 1 M  $\text{LiPF}_6$  in a 1:1 mixture of ethylene carbonate (EC)/diethyl carbonate (DEC); the separator was Celgard 2500. The cells were assembled in the glovebox filled with highly pure argon gas. The cyclic voltammetry (CV) test was carried out on an automated LK98BII electrochemical measurement system with metal lithium anode. The cells were galvanostatically cycled in the 0.5–3 V range at a current density of  $0.1 \text{ mA}/\text{cm}^2$ .

## 3. Results and discussion

XRD pattern (Figure 1) of the prepared product can be clearly seen and indexed to the face-centered cubic spinel structure of pure  $\text{Fe}_3\text{O}_4$  with a lattice parameter of  $a = 8.393 \text{ \AA}$  (JCPDS card no. 85-1436), which is close to that reported in the previous literature [14]. No peaks of metal hydroxides or other impurities were detected, suggesting the complete formation of  $\text{Fe}_3\text{O}_4$ . The strong and sharp peaks revealed that  $\text{Fe}_3\text{O}_4$  particles were well crystallised.

The FESEM images of the as-prepared products are shown in Figure 2, which reveal that the synthesised products consist of a large quantity of nanowires. A low magnification image (Figure 2(a)) shows that the obtained nanowires have typical lengths in the range of several to several tens of micrometres. Magnified FESEM images (Figure 2(b)) reveal that

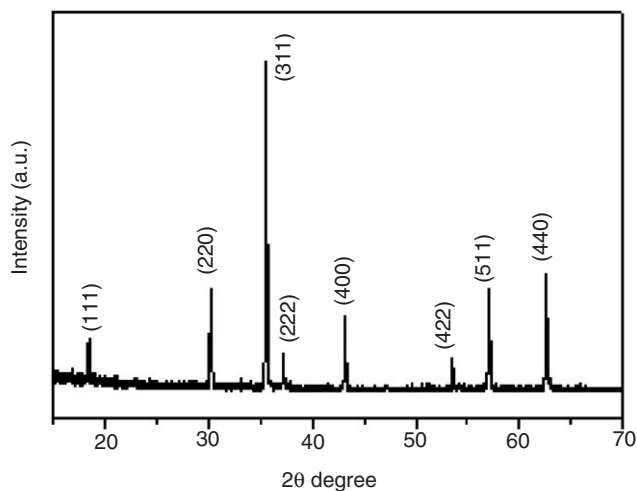


Figure 1. XRD pattern of the sample.

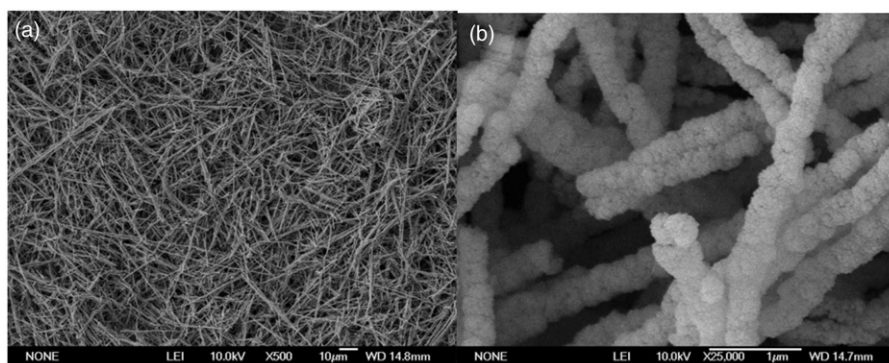


Figure 2. (a) A typical FESEM image of  $\text{Fe}_3\text{O}_4$  nanowires. (b) Typical high-magnification FESEM image.

the wires were composed of individual finer particles. Further analyses of as-prepared samples are analysed by TEM and selected area electron diffraction (SAED) procedures. From TEM images (Figure 3(a)), all the products consisted of straight nanowires with average diameters of about 500 nm. The SAED pattern (inset in Figure 3(a)) of the as-prepared products shows diffuse rings, indicating the  $\text{Fe}_3\text{O}_4$  wires are polycrystalline.

It is well known that solvent plays an important role in determining the crystal morphology. Solvents with different physical and chemical properties can influence the solubility, reactivity and diffusion behaviour of the reactants [15,16], in particular, the polarity and coordinating ability of the solvents can influence the crystal morphology of the final product.

In this EN-assisted route, the addition of EN is the key factor to the morphology of the products. Without the addition of EN the final products are all particles in un-ordered

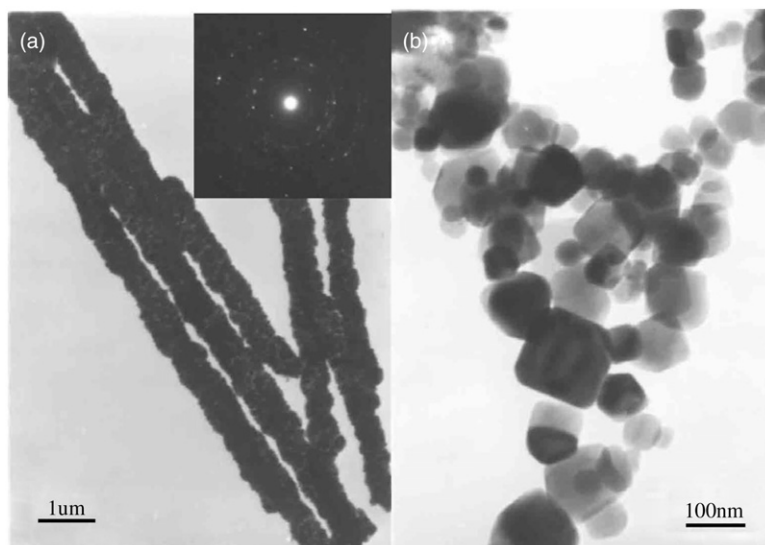


Figure 3. (a) A typical TEM image of sample and the corresponding ED pattern (inset). (b) TEM image of the sample prepared without EN.

shapes (Figure 3(b)) even when other experimental conditions are kept all the same. The result fits well with the reference reported before [17]. The N-chelating behaviour makes EN a strong donor ligand, and it plays an important role in the formation of 1D nanowires. EN can react with antimony ions to form relatively stable antimony complexes, which may serve as molecular templates in control of the crystal growth [18]. Moreover, the formation of the complexes can reduce the concentration of free  $\text{Fe}^{3+}$  in the solution, and slows the reaction rate, which is favourable for the growth of  $\text{Fe}_3\text{O}_4$  nanowires [19]. To improve the understanding of the effect of EN, we substituted EN with ammonia, diethylamine and pyridine. Unfortunately,  $\text{Fe}_3\text{O}_4$  nanowires cannot be obtained. Experiments show that EN is an excellent additive to control the morphology of as-prepared sample.

Magnetic measurements on thus-prepared nanowires were conducted and magnetisation–hysteresis ( $M$ – $H$ ) loops are presented in Figure 4. Figure 4 shows magnetic hysteresis curves for the samples investigated at room temperature. The hysteresis loop of the products shows ferromagnetic behaviour with saturation magnetisation ( $M_s$ ) and coercivity ( $H_c$ ) values of about 55 emu/g and 254 Oe, respectively, and the values are different from those reported for  $\text{Fe}_3\text{O}_4$  prepared by other methods [18] and bulk  $\text{Fe}_3\text{O}_4$  [20]. Although the detailed reasons are not clear, they may be concerned with the size effect and morphologies of the fractal nanocrystals.

The discharge curve of the sample is shown in Figure 5. The sample delivered a large discharge capacity of 902 mAh/g at a current density of  $0.1 \text{ mA/cm}^2$  in the voltage range 3.0–0.5 V, corresponding to the reaction of 7.8  $\text{Li}^+$  per  $\text{Fe}_3\text{O}_4$ . The discharge capacity includes two parts, (i) Fe(II)–Fe(0) and (ii) Fe(III)–Fe(0), which are consistent with the voltage plateaus at ca 1.0 and 0.85 V (Figure 5), respectively. The sample exhibits a higher first discharge capacity than that of  $\text{Fe}_3\text{O}_4$  octahedrons prepared by the EDTA-assisted hydrolysis method (884 mAh/g) [21]. The improved electrochemical performances of the

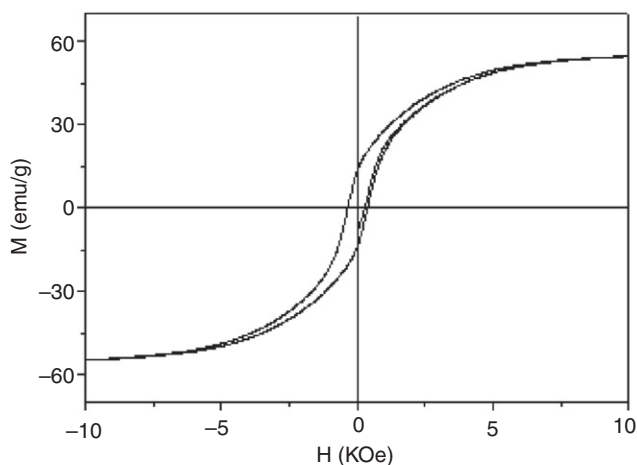


Figure 4. M–H loops of as-prepared samples measured at room temperature.

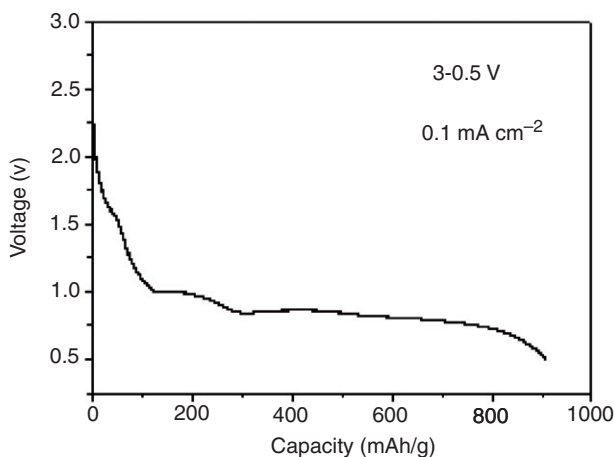


Figure 5. Discharge curve for the obtained magnetite sample at a voltage window of 3.0–0.5 V.

as-prepared  $\text{Fe}_3\text{O}_4$  nanowires may be ascribed to the unique microstructure and smaller particle size achieved by the present synthesis procedure. With decreasing particle size, an increasing proportion of the total number of atoms lies near or on the surface, making the electrochemical reactivity of the particles more and more important and facilitating the intercalation/deintercalation of lithium ions.

#### 4. Conclusions

In conclusion, we have succeeded in synthesising  $\text{Fe}_3\text{O}_4$  nanowires using an EN-assisted route under mild conditions. EN plays important roles in the formation of the products

in the process. This method can be easily controlled and is expected to be applicable for the preparation of other metal oxides with special morphologies. The sample exhibits a high first discharge capacity of 902 mAh/g, which enables it to be used for a lithium-ion battery.

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