



A facile precursor calcination approach to iron oxide micro/nanostructures with a high magnetization



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ABSTRACT

Fe-ethylene glycol (Fe-EG) complex was synthesized using a facile and surfactant-free solvothermal method, and was characterized by field emission scanning electron microscopy (SEM), bright field transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). The obtained Fe-EG complex was an excellent candidate for synthesis of various iron oxides micro/nanostructures by a simple calcination approach. In an air atmosphere, γ -Fe₂O₃, γ -Fe₂O₃/ α -Fe₂O₃ nanocomposites, and α -Fe₂O₃ micro/nanostructures were successfully prepared by controlling the calcination temperature. Fe₃O₄ micro/nanostructures were also synthesized by calcination the Fe-EG complex under an argon atmosphere. The magnetic properties of the obtained series of iron oxides micro/nanostructures were studied, and the saturation magnetisation of the obtained γ -Fe₂O₃ and Fe₃O₄ were 65.91 and 100.20 emu g⁻¹, respectively. The results of the work put forward a simple and effective approach for the synthesis of iron oxides micro/nanostructures with controlled chemical composition and good magnetic properties.

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1. Introduction

Iron oxide is an important metal oxide and usually exists in nature in three phases of magnetite (Fe₃O₄), maghemite (γ -Fe₂O₃) and hematite (α -Fe₂O₃). In the past few decades, nanostructured iron oxide has been at the focus of a remarkable research interest due to their wide variety of properties, and huge potential for applications in the energy [1–3], environment [4–6] and biomedical [7,8] fields. When the size of particles decreased to the nanoscale level, the agglomeration of the nanoparticles turned more and more serious owing to the large surface energy. It is well known that the performance of iron oxide was always depended on their structure. Thus, many efforts have been performed to avoid the agglomeration of the nanoparticles. Among them, the synthesis of three-dimensional (3D) micro/nanostructures has proved to be an excellent strategy to maintain the nanoscale related performance [1–3,5,6].

Up to today, various 3D iron oxide micro/nanostructures have been prepared, including microflowers [5,9], microboxes [1,10],

micro hollow spheres [11–16], micropeanuts [17], microdisks [18], multi-armed nanocrystals [19], microchains [20], etc. The most important preparation methods included directly hydrothermal method and precursor calcination approach [1,5,9,13–15,17]. The precursor calcination method have already utilized for the synthesis of various metal oxides, such as CeO₂, CoO, CuO, Cu₂O, In₂O₃, Fe₂O₃, Fe₃O₄, etc [21]. The reported iron oxide precursors including Fe(acac)₃, Fe(OC₂H₄OCH₃)₃, Fe(OAc)₂, Fe(OAc)₃ and Fe-EG complex [5,9,13–15,21,22]. Among several of iron oxide precursors, Fe-EG complex [5,9,13–15,22] is a very important ones for the synthesis of iron oxide 3D micro/nanostructures. To date, the reported preparation methods of Fe-EG complex was solvothermal method [9,13–15] and refluxing approach [5]. The most used iron sources were anhydrous FeCl₃ [9] and FeCl₃·6H₂O [5,13,14]. On the one hand, sodium dodecylbenzenesulfonate or tetrabutylammonium bromide were utilized as surfactant [5,13,14] when chosen FeCl₃·6H₂O as iron source. With the presence of hexamethylenetetramine, Fe(NO₃)₃·9H₂O can also reacted with EG to form Fe-EG complex [15]. However, the utilization of surfactant always leads to potential process-related hazards or low production efficiency. On the other hand, when using Fe(NO₃)₃·9H₂O as iron source, Fe-EG hierarchical hollow micro/nanostructures can only be

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synthesized with the presence of dimethylformamide [22]. Furthermore, Fe-EG complex also cannot be synthesized with the absence of surfactant when using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as iron source [9]. So, the previous reports suggested that the growth of Fe-EG complex was very sensitive to the small amount crystal water in iron source and also to the presence of surfactant. Thus, it is still a challenge to develop an economical and surfactant-free method for the synthesis of Fe-EG complex.

In this work, using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as iron source, a facile and surfactant-free solvothermal method to synthesize large scale 3D flower-like Fe-EG complex is reported. After calcination in air, $\gamma\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3/\alpha\text{-Fe}_2\text{O}_3$, and $\alpha\text{-Fe}_2\text{O}_3$ micro/nanostructures were successfully prepared by controlling the calcination temperature. In addition, Fe_3O_4 micro/nanostructures were also synthesized under argon atmosphere. The structures of the obtained iron oxides were characterized in detail. More importantly, the magnetic properties of the obtained iron oxides were investigated at room temperature. The saturation magnetisation (M_s) of the prepared $\gamma\text{-Fe}_2\text{O}_3$ micro/nanostructures was 65.91 emu g^{-1} . Furthermore, the M_s of the obtained Fe_3O_4 micro/nanostructures was $100.20 \text{ emu g}^{-1}$, which was higher than the bulk Fe_3O_4 (92 emu g^{-1}), and was about two times larger than the previously reported Fe_3O_4 hollow microspheres. We believe that these iron oxide micro/nanostructures with high saturation magnetization will have important applications not only in advanced magnetic materials, but also in biomedical fields.

2. Experimental details

2.1. Preparation of the Fe-EG complex

All of the chemical reagents purchased from Shanghai Chemical Reagents Company, were of analytical grade and used without purification. In a typical synthesis process for the precursor, 1.01 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 100 mL EG to form a clear solution, followed by the addition of 2.4 g of urea. The mixture was stirred vigorously for 10 min until it became homogeneous, sealed in a Teflon-lined stainless-steel autoclave, and then heated to 200°C for 10 h. After cooling to room temperature naturally, emerald green products were obtained by centrifuging. Then the products were sequentially rinsing with deionized water and ethanol for several times, dried in oven at 60°C overnight, and then the final yellow-green products were obtained.

2.2. Preparation of 3D iron oxides micro/nanostructures

3D flower-like $\gamma\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3/\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ micro/nanostructures were obtained by heating the Fe-EG complex in air to 200, 300, 400 and 500°C at a rate of 2°C min^{-1} and maintaining at this temperature for 1 h. For the synthesis of Fe_3O_4 hollow micro/nanostructures, the obtained Fe-EG complex powder was put in a quartz boat, and then inserted in the center of a quartz tube reactor. Argon (99.999%) was introduced into the quartz tube reactor. After 20 min, the quartz tube reactor was heated under Ar atmosphere to 500°C . After 1 h, the system was allowed to cool down to room temperature in argon atmosphere. Then, Fe_3O_4 hollow micro/nanostructures were obtained.

2.3. Characterization

The as-prepared products were characterized by field emission scanning electron microscopy (SEM, FEI Sirion 200 FEG, operated at 10 kV), bright field transmission electron microscopy (TEM, JEOL-2010, operated at 200 kV), X-ray diffraction (XRD, X'Pert ProMPD, Cu $K\alpha$ radiation, wavelength 1.54056 \AA), thermal gravimetric

analysis (TGA, Pyris 1, heating rate 5°C min^{-1}), X-ray photoelectron spectroscopy (XPS, VG ESCALAB MKII spectrometer, Mg KR X-ray source, 1253.6 eV, 120 W) analyses, and Fourier transform infrared spectroscopy (FTIR, Nicolet Analytical Instruments, NEXUS-870 infrared spectrophotometer with the KBr pellet technique). Nitrogen adsorption–desorption measurements for the products were performed using a Micromeritics ASAP 2020 M + C instrument with a degassing temperature of 300°C , and using Barrett–Emmett–Teller (BET) calculations for surface area and Barrett–Joyner–Halender (BJH) calculations for pore size distribution of the obtained iron oxides. The magnetic properties of the samples were conducted on a Magnetic Property Measurement System (MPMS, XL5) at 300 K.

3. Results and discussions

Fig. 1a and b are the SEM images of the obtained yellow-green products. It is clear that flower-like micro/nanostructures with a diameter $1\text{--}2 \mu\text{m}$ were synthesized. The obtained products were obviously composed of several nanoplates, which were also confirmed by the bright field TEM images shown in Fig. 1c and d. In addition, the obtained micro/nanostructures present a hollow structures, as shown in Fig. 1c. The thickness of the nanoplates was about $30\text{--}40 \text{ nm}$, as shown in Fig. 1d.

The obtained micro/nanostructures were also characterized by XRD, and the results are shown in Fig. 2a. The most intense peak located at about 11.19° (d spacing of 7.9077 \AA) is the typical characteristic of Fe-EG complex [9,13,14]. Fig. 2b presents the FTIR spectrum of the obtained products. The wide absorption band centered at about 3410 cm^{-1} is assigned to physically absorbed water. The peaks between 2500 and 3000 cm^{-1} are attributed to the C–H stretching mode. The peaks below 1500 cm^{-1} can be attributed to C–C, C–O, $-\text{CH}_2-$ and Fe–O bonds [13]. To further investigate the structure, thermal properties of the Fe-EG complex was investigated, and the results are shown in Fig. 2c. The obtained Fe-EG complex was quite stable with the temperature low than 200°C . However, with increasing temperature, a large weight loss in the range of 200 and 250°C was observed. The total weight loss is 42.85%, which was very closer to the previous reports [15]. The weight loss was resulted from the decomposition and removal of the organic constituent in the Fe-EG complex during heat treatment. To reveal the valence state of iron, the obtained Fe-EG complex was characterized by XPS, and the Fe2p spectrum is shown in Fig. 2d. The $\text{Fe}2p_{3/2}$ and $\text{Fe}2p_{1/2}$ peaks are located at 710.1 and 723.3 eV , respectively. No obvious satellite peaks were observed at higher binding energies, suggesting the presence of ferrous ions [23–25]. The formation of ferrous ions should be resulted from the reduction of Fe(III) ions with the presence of EG at high temperature [15]. However, the binding energy of $\text{Fe}2p_{3/2}$ is higher than that of Fe^{2+} in FeO and Fe_3O_4 , and at the same time, is lower than the ones of NiFe_2O_4 and $\text{Fe}_3\text{O}_4/\alpha\text{-FeOOH}$ [23,24]. Furthermore, by using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as iron source, the color of the product was changed from yellow to yellow-green, and finally to completely green [5]. Herein, the color of the original obtained products were emerald green, suggesting that most the iron ions in the products were Fe(II) ions. However, in the rinsing and drying process, the color of it turned to yellow-green. Furthermore, when dispersing the products in water for long time, the yellow-green Fe-EG complex turned red brown gradually. The red brown products should be resulted from the oxidation of Fe(II) ions to Fe(III) ions by the dissolved oxygen in water. So, the iron ions in the final products should be a mixed Fe(II) and Fe(III) ions.

It is well known that the metal-EG complexes are very important precursor for the synthesis of metal oxide via a simple thermal treatment method [5]. Herein, series of iron oxides were prepared

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