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Highly water-soluble nanocrystal powders of magnetite and maghemite coated with gluconic acid: Preparation, structure characterization, and surface coordination

Xiucheng Wei, Zhiwei Wei, Liping Zhang, Yingqi Liu, Deyan He *

School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, China
Key Laboratory of Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, Lanzhou 730000, China

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ABSTRACT

A simple method was developed to prepare highly water-soluble nanocrystal powders of magnetic iron oxides with different oxidation degree from magnetite (Fe_3O_4) to maghemite (γ-Fe_2O_3) coated with gluconic acid (GLA). X-ray diffraction and transmission electron microscopy measurements show that the products have a narrow size distribution, and the cores are inverse spinel iron oxides and completely crystallized. Vibrating sample magnetometry measurements reveal that all the samples exhibit superparamagnetic behavior at room temperature. Fourier transform infrared (FTIR) and Raman spectra were used to identify the products. It is shown that GLA molecules are immobilized on the nanoparticle surface by chemical bonding and the carboxyl is asymmetrically bound to the surface iron atom, and the vacancies in the γ-Fe_2O_3 cores are disordered. Compared with FTIR, Raman spectrum analysis is a rapid, simple, and accurate method for identifying inverse spinel iron oxides. The chemical stability and the high solubility of the products are explained in terms of the proposed coordination modes of the surface iron atom with GLA.

1. Introduction

The magnetic iron oxides, magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), have been receiving continuous attention in fundamental researches for their structural characteristics and physicochemical properties [1–14]. In recent years, the preparation of water-soluble magnetic nanocrystals has evoked increasing interest for their applications in magnetic resonance imaging [15,16], wastewater and oil pollution treatments [17–19], thermal therapy [20,21], separation or purification of DNA or protein [22,23], and gene carriers or drug delivery [24–28], etc.

Although a great amount of work has been done on the magnetic oxide irons, some problems remain to be addressed. (1) It is a general view that stable water-soluble nanoparticles modified with small organic molecules are instable, especially in an alkaline or acidic environment [29]. This view limits the researches and applications of this type of nanoparticles. The structures of small organic molecules are varied, and the researches on the preparation, properties, and surface coordination of nanoparticles modified with special structured small molecules are worthy of further exploration. (2) What exactly is the component of the magnetic nanocrystals? Is it Fe_3O_4, γ-Fe_2O_3, or partially oxidized Fe_3O_4? If the nanocrystals are γ-Fe_2O_3, then, are the cation vacancies in them ordered or disordered? These materials are difficult to be identified because of their similarities in structure and properties, especially in their nano state. Some identification methods have been reported, such as X-ray diffraction (XRD) [30–32], X-ray absorption spectroscopy (XAS) [33], X-ray photoelectron spectroscopy (XPS) [34,35], Mössbauer spectra [36,37], and Fourier transform infrared (FTIR) spectra [30]. Each of these methods has its advantages and disadvantages. γ-Fe_2O_3 can be identified by XRD if the vacancies in it are ordered, but the component (Fe_3O_4 or γ-Fe_2O_3) is difficult to be identified if the vacancies are disordered. Furthermore, it is well known that γ-Fe_2O_3 superstructures are difficult to be detected using Cu Kα radiation, because the K-absorption edge of iron (λ = 1.7435 Å) is longer than Cu Kα radiation wavelength (λ = 1.5418 Å) [38–40]. XAS, XPS, and Mössbauer spectra can determine the difference between Fe_3O_4 and γ-Fe_2O_3 to a certain extent, but cannot determine whether the vacancies are ordered. FTIR is not precise enough to determine the oxidation degree of Fe_3O_4. Thus, new identification methods are worthy of exploration.

Preparation of iron oxide nanoparticles coated with gluconic acid (GLA) by a co-precipitation method has been reported before [41], but the core structure and surface coordination are not clear. In the present work, we successfully prepared stable water-soluble Fe_3O_4, partially oxidized Fe_3O_4, and γ-Fe_2O_3 nanocrystal powders, coated with GLA, a small molecule of polyhydroxy carboxylic acid. It is shown that the vibrational spectra (FTIR and Raman) analyses can be used to identify the inverse spinel iron oxides (Fe_3O_4 or γ-Fe_2O_3). Compared with FTIR which is suitable for the

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* Corresponding author at: School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, China.

E-mail address: hedy@lzu.edu.cn (D. He).

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determination of the vacancies ordering of γ-Fe_2O_3, Raman spectrum measurement is a rapid, simple, and accurate method for the determination of the oxidation degree of Fe_3O_4. The possible coordination modes of the surface iron atom with GLA were suggested, which well explain the chemical stability and the high solubility of the products.

2. Materials and methods

2.1. Materials

Ferric chloride ($FeCl_3{\cdot}6H_2O$) and ferrous chloride ($FeCl_2{\cdot}4H_2O$) were purchased from Tianjin Shuangchuan Chemical Reagent Factory (Tianjin, China). Hydrochloric acid (37 wt.% HCl) and sodium hydroxide (NaOH) were purchased from Baiyin Chemical Reagent Factory (Baiyin, Gansu, China) and Tianjin Chemical Reagent Factory (Tianjin, China), respectively. Sodium gluconate was purchased from Shanghai Reagent Company (Shanghai, China). All the chemicals used are of AR grade except as noted. Deoxygenated distilled water was used for the preparation of all the aqueous solutions.

2.2. Sample preparations

2.2.1. Preparation of cationic colloid of magnetite nanocrystals

The bare Fe_3O_4 nanocrystals were prepared by the well-known Massart's method [42] with some modifications [43,44] which consists of Fe^{3+} and Fe^{2+} co-precipitation in alkaline solutions:

$$2Fe^{3+} + Fe^{2+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$$

Briefly, an aqueous solution of Fe ions with a molar ratio of $Fe^{3+}/Fe^{2+} = 2$ was prepared by dissolving 10 mmol $FeCl_3{\cdot}6H_2O$ and 5 mmol $FeCl_2{\cdot}4H_2O$ powders in 10 ml of aqueous acid. The aqueous acid was obtained by combining 9.5 ml water with 0.5 ml of 12 M HCl. The resulting solution was added dropwise into 50 ml of 1.5 M NaOH solution with vigorous mechanical stirring under the protection of argon (99.9%). A black precipitate formed instantly. The obtained reaction mixture was further stirred for 30 min at room temperature (~17 °C) and 2 h at 70 °C in succession. After that, the precipitate was isolated by centrifugation (3000 rpm, 10 min), and the supernatant was removed from the precipitate by decantation. After rinsing with water (acetone was added as needed) four times, the precipitate was dispersed in 100 ml H_2O (with a pH value of ~2) in an ultrasonic bath for 30 min to neutralize the anionic charges on the nanocrystals. A clear and transparent cationic colloid (hydrosol) was finally obtained after a little precipitate was removed by centrifugation (3000 rpm, 10 min).

2.2.2. Preparation of cationic colloids of magnetic iron oxides with different oxidation degree

The oxidation of Fe_3O_4 was carried out by heating its cationic colloid in water-bath under aeration (with air). The hydrosol solution of Fe_3O_4 was heated in air at 80 °C with reflux condensation. Aliquots of solution were taken out after certain periods of time (0.5, 1, 2, 3, 4, 5, and 6 h, respectively) and cooled immediately with ice water to quench the reaction [13]. After ultrasonic treatment (10 min) and the removal of a little precipitate by centrifugation (3000 rpm, 10 min), a clear transparent oxidized Fe_3O_4 colloid was obtained.

2.2.3. Preparation of water-soluble iron oxides nanocrystal powders

The cationic colloid of iron oxides with different oxidation degree (20 ml) was added dropwise to 10 ml of water containing 0.5 g of sodium gluconate and 0.5 g of NaOH. The reaction mixture was stirred for 4 h at room temperature. The precipitate was isolated by centrifugation and rinsed with ethanol and acetone three times, and dried in air at 80 °C for 5 h. And then, the water-soluble iron oxides nanocrystal powders (S1–S8) were obtained in different oxidation degree (see Table 1).

2.2.4. Preparation of maghemite reference sample

The maghemite reference sample (S9) was prepared by heating S1 in a furnace for 2 h at 250 °C [45].

2.3. Characterizations

The identification of crystalline phase of the synthesized particles was performed by a Philips X'Pert Pro diffractometer (Cu Kα radiation, $\lambda = 1.5418$ Å), operating at 40 kV and 40 mA. Each sample was analyzed between 20° and 70° 2θ with a step size of ca. 0.005° 2θ and a counting time per step of ca. 20 s. The morphologies and microstructures of the samples were observed on a FEI Tecnai F30 high-resolution transmission electron microscope (HRTEM). FTIR spectra were recorded from a KBr pellet on a Nicolet FTIR 360 spectrometer. Raman spectra were collected at room temperature using a JY-HR800 Raman spectrometer with laser excitation at 532 nm. The magnetic hysteresis loops were measured on a vibrating sample magnetometer (VSM, Lakeshore Model 7304) with a powder sample packed in a capsule at room temperature.

3. Results and discussion

3.1. The apparent performance of the products

Fig. 1a shows photographs of the as-prepared products. It can be seen that S1 is pure black and the others (S2–S8) are brown. The longer oxidation time, the lighter color is observed. The bare or partially protected Fe_3O_4 nanoparticles are very easy to be oxidized in air [43]. The fact that the colors of samples S1–S8 remain intact after drying in air at 80 °C for 5 h indicates that the products are fully protected by GLAs. This makes it possible to be stored in air for a long time without further oxidation. Thus, the samples can be characterized by Raman, FTIR, and other instruments without considering their structural and property changes during storage and testing [46]. Fig. 1b–e are the photographs of S1 and S7 in a magnetic field and in aqueous solution, respectively. The results show that the products are magnetic materials, and have high water solubility. The relatively dilute aqueous solutions have obvious Tyndall scattering effect, which indicates that the products have a particle size of 1–100 nm.

3.2. TEM and XRD analyses

Magnetite has a cubic inverse spinel structure with space group Fd $\bar{3}$m and structural formula $Fe^{3+}_{8\mathbf{t}}[Fe^{2+}_{8}Fe^{3+}_{8}]_{\mathbf{o}}O_{32}$ (**t** = tetrahedral, **o** = octahedral), in which Fe ions occupy both tetrahedral and octahedral sites [47]. Maghemite has a structure similar to that of Fe_3O_4, only differs in that all or most of the Fe ions are in the trivalent state. Cation vacancies compensate for the oxidation of Fe^{2+} cations, with structural formula $Fe^{3+}_{8\mathbf{t}}[Fe^{3+}_{5.3}\bullet_{2.7}Fe^{3+}_{8}]_{\mathbf{o}}O_{32}$ (• = vacancies). The basic space group of γ-Fe_2O_3 is $P4_332$, whereas the ordered distribution of the cation vacancies results in symmetry

Table 1
Water-soluble nanocrystal powders of magnetic iron oxides with different oxidation degree, obtained by heating Fe_3O_4 cationic colloids for 0–6 h at 80 °C under aeration, then coating with GLA and drying in air at 80 °C for 5 h.

Samples	S1	S2	S3	S4	S5	S6	S7	S8
Oxidation time (h)	0	0.5	1	2	3	4	5	6