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Ultrasonic-assisted preparation of monodisperse iron oxide nanoparticles

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Abstract

Monodisperse iron oxide nanoparticles with 5–20 nm can be synthesized by an inexpensive and simple ultrasonic-assisted method at low temperature. This is based on the decomposition of iron pentacarbonyl in cis–trans decalin. The high energy emitted by ultrasonic irradiation at a short time can promote the crystallization process simultaneously. At low temperature, these crystalline nucleuses can grow to monodisperse nanoparticles. Effects of ultrasonic treatment, the concentration of surfactant and the refluxing time on the size and size distribution of iron oxide nanoparticles were investigated. The morphology and crystal structure of iron oxide nanoparticles obtained at different conditions were characterized by high-resolution transmission electron microscope, X-ray diffraction and selected area electron diffraction.

Keywords: Iron oxide nanoparticles; Ultrasonic; Monodisperse; Magnetic materials

1. Introduction

The synthesis of nanoparticles with controlled size and composition is of fundamental and technological interest. The synthesis of monodisperse nanocrystals (size variation $<5\%$) is of key importance, because the properties of these nanocrystals depend strongly on their dimensions [1–3]. For example, the semiconductor nanocrystals showing size-tunable optical properties have been integrated into exploratory optical and electronic devices [3–6]. The study of nanoscale magnetic materials domains is of both fundamental and pressing technical interest as the grain size of advanced recording media is rapidly shrinking to dimensions where magnetic properties depend strongly on nanocrystal size [7–10]. In recent years, various synthetic methods have been reported to prepare monodisperse magnetic nanomaterials, including Fe [11,12], Co [13,14], γ-Fe_2O_3 [15,16], Fe_3O_4 [17] and ferrimagnetism [17]. Since the 1980s, ultrasound, in the frequency range from 20 kHz to 1 MHz, has been widely used in chemical synthesis because it leads to an increase in the rate of many chemical reactions: organic, inorganic, organic composite, etc [18]. The value of ultrasonic irradiation to organic chemists lies in its ability not only to accelerate known reactions, particularly those that are heterogeneous in the solvent systems of interest, but also in its ability to generate new chemistry that is not available using existing methodologies because an ultrasonic wave can generate a very extreme reaction environment as it passes through a liquid [19]. Many research groups have used ultrasound in the synthesis of polymers and composites, and have obtained striking results [20,21]. In the present work, we found that ultrasonic irradiation could greatly enhance the crystallization of iron oxide nucleus at 190 °C, after the react solution was refluxed at this temperature, monodisperse γ-Fe_2O_3 nanocrystals could be obtained.

2. Experimental

In a typical experiment, 15 ml cis–trans decalin and 2.2 ml oleic acid were mixed in a three-neck round-bottomed flask and heated to 100 °C at a rate of 5 °C/min, then 0.3 ml iron pentacarbonyl ($Fe(CO)_5$) was added into the flask quickly. The

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mixture solution was heated at a rate 2 °C/min under an argon flow, when the temperature reached 190 °C, a probe equipped on a high-intensity ultrasonic horn (Branson 184 V, 20 kHz, 900 W) was dipped into the solution, ultrasonic irradiation time was 10 min. The mixture was then refluxed at 190 °C for 30–90 min under mechanic stirring and argon atmosphere. After reaction, the solution was placed in air for 12 h, iron oxide nanoparticles were precipitated by adding ethanol to the reaction solution. The supernatant was discarded after centrifugation. The precipitate was redispersed in 10 ml hexane with a few drops of oleic acid. The molar ratio of oleic acid to $Fe(CO)_5$ was changed from 1:1 to 6:1 by increasing oleic acid from 2.2 ml to 13.2 ml in the reaction solution.

Transmission electron microscopy (TEM JEOL-2010) samples were prepared by dipping the dispersion onto a carbon coated copper grid. X-ray powder diffraction (XRD) measurements were performed using a Rigaku D/MAX-2550PC X-ray powder diffractometer with Bragg–Brentano geometry using Cu K_α irradiation in the range of 25–70°, a step of 0.02° and 2 s per step. Fourier transform infrared (FTIR) measurements were carried out with a resolution of 2 cm^{-1} and 32 scans.

3. Results and discussions

Iron oxide nanoparticles were prepared by ultrasonic-assisted method as shown in Fig. 1a. These monodisperse nanoparticles have an average grain size of 9.6±0.2 nm. Grain size distribution was estimated by counting about 300 nanoparticles and characterized by a log-normal function (solid line) (Fig. 1d). SAED pattern of iron oxide nanoparticles in Fig. 1b is indexed by a cubic γ-Fe_2O_3 (PCPDF #872334), the diffraction rings are attributed to the (220), (311), (400), (422), (511) and (440) planes, respectively. The high-resolution TEM image in Fig. 1c shows the internal crystallinity for an iron oxide nanocrystal. The particle appears to be a single crystal and exhibits a 0.24 nm d-spacing for the (311) reflection. The surface of iron oxide nanoparticles was wrapped by oleic acid, which can be detected from the FTIR pattern in Fig. 1e. The pattern was obtained from the sample as shown in Fig. 1a. The peaks that appear at 1565–1487 cm^{-1} are attributed to the characteristic absorption of the –COO– group on the surface of iron oxide nanoparticles. The effects of surfactants and their concentrations, ultrasonic irradiation and refluxing time on the size and size distribution of iron oxide nanoparticles were studied systematically.

3.1. Effect of surfactant concentration on size and size distribution of iron oxide nanoparticles

The concentration of surfactant has a drastic effect on the size distribution of iron oxide nanoparticles in this work as shown in Fig. 2. The obtained iron oxide nanoparticles in Fig. 2a, b and c correspond to the molar ratio (oleic acid to $Fe(CO)_5$) of 1:1, 3:1 and 6:1, respectively. The average sizes are 9.5±1.2 nm, 9.6±0.2 nm and 5.4±0.1 nm, respectively. We find that higher concentration of oleic acid can get smaller size and narrower size distribution of iron oxide nanoparticles as reported in Ref. [9]. When the molar ratio is 1:1, only polydispersed nanoparticles can be observed, which suggests that, at low concentration, oleic acid is ineffective at stabilizing the iron oxide particles. When the ratio reaches 3:1, monodisperse nanoparticles are obtained as shown in Fig. 2b, but the size is not smaller than that obtained at 1:1, the reason is that the size is an average statistic value from 300 particles. Keeping on increasing the concentration of oleic acid in the solution, monodisperse iron oxide particles with smaller size are obtained, as shown in Fig. 2c, which can be explained that higher concentration of surfactant can wrap iron oxide particles and can prevent the growth of nanoparticles more easily.

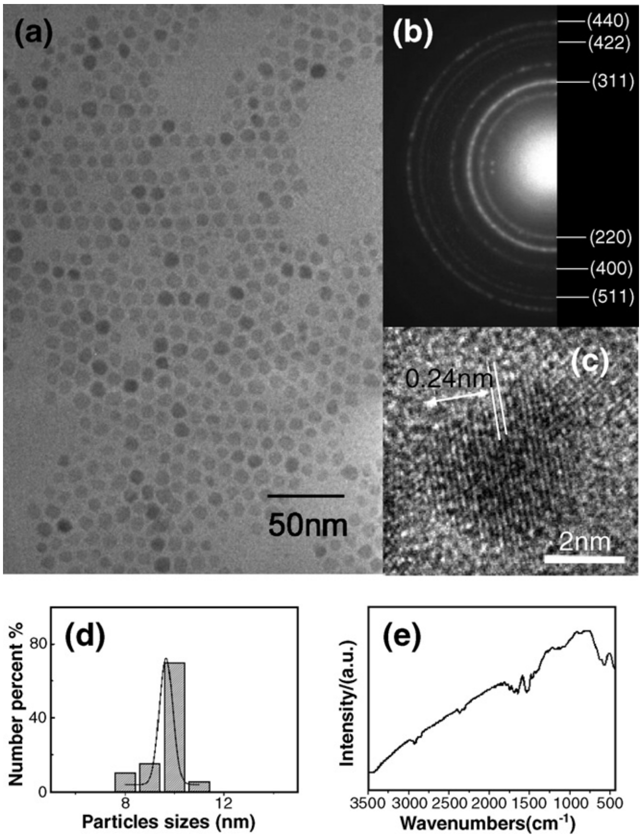

Fig. 1. Iron oxide nanoparticles prepared by ultrasonic-assisted method, the molar ratio of oleic acid to $Fe(CO)_5$ is 3:1, ultrasonic irradiation time is 10 min, refluxing time is 30 min. (a) Low magnification TEM image of monodisperse iron oxide nanoparticles. (b) SAED pattern of iron oxide shown in (a), the diffraction rings are attributed to the (220), (311), (400), (422), (511) and (440) planes, respectively. (c) High-resolution TEM image of a single iron oxide nanoparticle, the d-spacing is 0.24 nm corresponding to the (311) fringes of cubic γ-Fe_2O_3. (d) Size distribution of iron oxide nanoparticles obtained from counting 300 nanoparticles. (e) FTIR pattern of iron oxide nanoparticles shown in (a).

3.2. Effect of refluxing time on iron oxide nanoparticles

Fig. 3 shows TEM images of iron oxide nanoparticles obtained with oleic acid:$Fe(CO)_5$ ratio of 3:1 at 190 °C for a refluxing time that varies from 30, 60 and 90 min. The average sizes of iron oxide nanoparticles are 10, 15 and 20 nm, which correspond with XRD patterns (Fig. 3d). The diffraction peaks are attributed to the (220), (311), (400), (422), (511) and (440) planes of cubic γ-Fe_2O_3, the smaller the size of the nanoparticles, the broader of the peaks. It appears that the larger nanoparticles have relatively higher crystallinity.

3.3. Effect of ultrasonic irradiation on iron oxide nanoparticles

Many researchers have investigated the effect of ultrasound on chemical reactions and have suggested some proposed explanations, such as the “hot spot” explanation [18], the “electrical explanation”