



Size-controlled monodisperse hydrophobic and hydrophilic magnetite nanoparticles: One-pot synthesis, characterization, and the mechanism study

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ABSTRACT

Depending on whether to add oleic acid in the reaction system, monodisperse magnetite nanoparticles with hydrophobicity and hydrophilicity are prepared by one-step “polyolthermal reaction”. Combined techniques of TEM, XRD, XPS and FTIR are used to characterize the obtained nanoparticles. The diameter of nanoparticles can be tuned easily by a simple change in the reaction time and the concentration of iron precursor. The method proposed here combines all the advantages of the high-temperature thermal decomposition method and the solvothermal process. Details about formation processes of magnetite nanoparticles are studied using UV–vis absorption spectrum. The result shows a different nucleation procedure and nucleation time for oil-soluble and water-soluble nanoparticles due to the presence of oleic acid. Magnetic properties of the prepared magnetite nanoparticles are also measured on vibrating sample magnetometer at room temperature.

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1. Introduction

Magnetic nanoparticles, e.g. Fe_3O_4 have attracted much attention because of their potential application in many advanced technology areas, including magnetic storage media, ferrofluids, magnetic resonance imaging (MRI), magnetically guided drug delivery, medical diagnosis and alternating-current magnetic-field-assisted cancer therapy [1–4]. From the point of these technological and medical applications, it is desired that the nanoparticles are superparamagnetic with sizes smaller than 20 nm and the overall particle size distribution is narrow so that the particles have uniform physical and chemical properties.

Among various chemical syntheses, microemulsion [5], organic solution phase decomposition of the iron precursor at high temperatures and hydrothermal (solvent-thermal) method are the three most successful approaches in creating stable, monodisperse iron oxide nanoparticles with controlled size. However, microemulsion-based syntheses often suffer from the two disadvantages: (I) less crystalline and more polydispersed particles are often generated because of the slow nucleation rate at low reaction temperatures; (II) a large amount of solvent is used to synthesize a very small amount of nanoparticles. Recent reports

about high temperature direct decomposition of FeCup_3 [6], or decomposition of $\text{Fe}(\text{CO})_5$ in the presence of oleic acid and oleylamine [7] or dodecylamine [8] at organic solution phase can lead to high quality magnetic nanoparticles. But they are always followed by oxidation and the samples are mostly $\gamma\text{-Fe}_2\text{O}_3$. An approach to overcome these limitations is first reported by Shouheng Sun's group [9]. They develop a relatively simple method that high temperature reaction of $\text{Fe}(\text{acac})_3$ in the presence of alcohol, oleic acid and oleylamine to produce size-controlled monodisperse Fe_3O_4 nanoparticles. It further extends to other types of magnetic nanoparticles and alloy nanoparticles such as MFe_2O_4 ($\text{M} = \text{Co}, \text{Mn}, \text{Fe}$) [10], FePt [11], and CoNi [12]. However, much more expensive reagents are used in these methods and the produced magnetite nanocrystals are only soluble in nonpolar or weakly polar hydrocarbon solvent due to the capped hydrophobic surfactant ligand, which limits their applications in the biomedical field [13–17]. Recently, in virtue of the advantage of the thermal decomposition method, Yang et al. [18] replaced the commonly used nonpolar high-boiling-point solvents with water-soluble tetraethylene glycol to prepare water-soluble superparamagnetic MnFe_2O_4 nanoparticles. This direct synthesis of water-soluble magnetite nanoparticles can avoid a complicated surface modification for the further applications. Unfortunately, the reaction temperature (295 °C) is always higher than 200 °C, unbeneficial to economic production. Hydrothermal (solvent-thermal) synthesis is a relatively little explored method for the synthesis of magnetic nanoparticles, although it allows the synthesis of high-quality

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nanoparticles. Li et al. [19] reported a generalized hydrothermal method for synthesizing 9 nm of magnetite nanocrystals by a liquid–solid–solution reaction. But the resulted nanoparticles are also always hydrophobic. Later, though they skillfully used the multicomponent reaction mixtures, including ethylene glycol, sodium acetate, and polyethylene glycol, to synthesize monodisperse magnetite crystalline with hydrophilicity, the particles are too large and the size can only be tuned in the range of 200–800 nm [20].

In this paper, we develop a one-step “polyolthermal reaction” to synthesize size-controlled monodisperse Fe₃O₄ nanoparticles. The method proposed here is of great significance and combines all the advantages of thermal decomposition method and hydrothermal (solvent-thermal) method. Similar to the Yang’s method [18], diethylene glycol is chosen as the reaction medium instead of phenyl ether, and 1,2-hexadecanediol or 1,2-dodecanediol [10] is also need not to add because of the reducing property of diethylene glycol itself. The whole reaction is proceeded in Teflon-lined stainless autoclave at 180 °C, a comparatively lower temperature. It should be noted that in our present study, monodispersed magnetite nanoparticles with hydrophobicity and hydrophilicity can both be prepared depending on whether to add oleic acid in the reaction system, and the diameters of the prepared oil-soluble and water-soluble magnetic nanoparticles both can be tuned easily by a simple change in the reaction time and the concentration of Fe(acac)₃. The results of UV–vis absorption spectrum demonstrate that the processes underlying the formation of nanocrystals are different for the two systems arising from the existence of oleic acid, in that iron-oleate, a necessary intermediate, is generated before the formation of Fe₃O₄ phase, resulting in an alternant reaction mechanism compared with the system for synthesizing water-soluble magnetite nanoparticles. In addition, the magnetic properties of the prepared magnetite nanoparticles are also discussed.

2. Materials and methods

2.1. Chemicals and materials

Iron(III) acetylacetonate (Fe(acac)₃) (99.9%) and oleic acid (90%) were purchased from Sigma–Aldrich. Diethylene glycol, hexane, ethanol and ethyl acetate were purchased from Beijing Chemical Co. The above chemicals without denotation are of analytical grade reagents and used as received without further purification.

2.2. Preparation of magnetite nanoparticles

A typical procedure for preparation of oil-soluble magnetite nanoparticles is briefly described as follows: first, 20 mL of diethylene glycol, 0.70 g (2 mmol) of iron (III) acetylacetonate, and 1.06 mL (3 mmol) of oleic acid were mixed in a 50 mL

Teflon-lined stainless autoclave while magnetically stirring. Then, the autoclave was put into oven, kept at 180 °C for 5 h. After cooled to room temperature naturally, 40 mL ethanol was added to yield a black precipitate. The black Fe₃O₄ precipitate was separated by centrifuging at 10,000 rpm for 20 min, and re-dispersed in 10 mL of hexane or dried at 60 °C under vacuum for 24 h. (The as-prepared product was donated as SO1.) The as-synthesized Fe₃O₄ colloid in hexane is hydrophobic and stable for nearly a year, while the dried Fe₃O₄ sample can be stable for several months.

The synthesis of water-soluble magnetite nanoparticles was carried out only by reacting an iron precursor, iron (III) acetylacetonate (Fe(acac)₃), in the polyol medium (diethylene glycol) without oleic acid under the same reaction conditions. After cooling down to room temperature, 40 mL of ethyl acetate was added to the reaction solution resulted in a black precipitation of magnetite nanoparticles which was then separated from the solution by centrifuging at 10,000 rpm for 20 min. After washed with ethyl acetate for three times, the precipitation was re-dispersed in polar solvents such as ethanol and water for further investigation. The Fe₃O₄ solid productions could also be obtained by drying the precipitation at 60 °C under vacuum for 24 h. (The as-prepared product was donated as SW1.)

To vary the particle size, the concentration of the Fe(acac)₃ and the reaction time were varied, keeping the amount of diethylene glycol, the volume of the autoclave, and the reaction temperature constant. For example, six other samples (SO2–SO4 and SW2–SW4) were obtained, the preparation conditions of which were summarized in Table 1.

2.3. Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku-Dmax 2500 diffractometer at a scanning rate of 15°/min in the 2θ range from 10 to 80°, with graphite-monochromatized Cu Kα radiation (λ = 0.15405 nm). Transmission electron microscopy (TEM) images were performed using JEOL JEM-2010 electron microscope with a tungsten filament at an accelerating voltage of 200 kV. In the case of the oil-soluble colloidal samples for the TEM characterizations, the nanoparticles were first dispersed in hexane, and then were dropped on a copper grid and allowed to dry in air at room temperature. A similar procedure was employed for the water-soluble iron oxide nanoparticles except that the water was employed as the solvent. Particles’ surface element binding energy and chemical composition were characterized by a VGESCALAB MKII X-ray photoelectron spectrometer. Fourier transform infrared (FTIR) spectra were recorded on a BIO-RADFTS135 Fourier transform infrared spectrometer. Magnetic measurements were carried out using Lakeshore 7300 vibrating sample magnetometer at room temperature. UV–vis absorption spectra were measured using Cary 300 UV–vis Spectrometer.

Table 1

Summary of the experiment conditions and the corresponding average particle size of the samples (all samples are treated at 180 °C).

Samples	Polyol (mmol)	Fe(acac) ₃ (mmol)	Oleic acid (mmol)	Time (h)	Average size ^a (nm)
SO1	20	2	2	5	3.0
SW1	20	2	0	5	2.0
SO2	20	2	2	7	5.2
SW2	20	2	0	7	4.5
SO3	20	2	2	24	7.3
SW3	20	2	0	24	6.6
SO4	20	1	2	5	6.2
SW4	20	1	0	5	5.5

^a Estimated from TEM images.

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