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Controlled synthesis of different types iron oxides nanocrystals in paraffin oil

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ABSTRACT

Monodisperse Fe_3O_4 and FeO nanocrystals (NCs) with different sizes (from 10 nm to 50 nm) and different shapes (cube, sphere, and ellipsoid) were synthesized by simply adjusting reaction temperature or molar ratio of Fe/oleic acid (OA) during the decomposition of FeO(OH) in noncoordinating solvent. The concentration of OA affected the nucleation and growth of NCs by improving the chemical reaction driving force during the syntheses of different types of iron oxide NCs. It has been found that the reaction temperature influenced the reaction activity between FeO(OH) and OA. The structure of Fe oleate complexes was studied using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Raman spectroscopy, and transmission electron microscopy (TEM) were used for structural and chemical characterization of as-prepared iron oxide NCs.

1. Introduction

Magnetic iron oxide nanocrystals (NCs) have gained considerable attention for their broad potential applications including magnetic recording [1,2], magnetic fluids [3,4], magnetic separations [5,6], and magnetic resonance imaging [7,8]. Different types of magnetic oxidation NCs (γ-Fe_2O_3 and Fe_3O_4) and composite magnetic materials ($CoFe_2O_4$, $MnFe_2O_4$, Fe_3O_4/SiO_2, FePt, and CoFe) with sizes ranging from 3 to 50 nm have been world-widely studied in many groups [9–16]. In some cases, every magnetic NC becomes a single magnetic domain and shows superparamagnetic behavior when ambient temperature is above the so-called blocking temperature. Therefore, this feature makes superparamagnetic NCs very attractive for biomedical applications because the risk of forming agglomerates is negligible at room temperature and they are generally stable under air and can be metabolized or degraded *in vivo* [17,18]. Moreover, monodisperse FeO NCs have great potential for catalysis [19] and gas-sensor [20] applications. FeO has a rock-salt structure with Fe and O forming nonstoichiometric Fe_xO ($x = 0.83$–0.96) and Fe vacancies in an ordered distribution. Thermal annealing under an argon atmosphere converted these FeO NCs into composite Fe and Fe_3O_4 NCs, yet Fe tends to accumulate in the particle shell, where it is easily oxidized when the sample is exposed to air and can go undetected [14].

Currently, the most popular method for synthesizing monodisperse iron oxide NCs is high-temperature decomposition of iron compounds with oxygen-containing ligands such as acetylacetonates [21,22], acetates [23], or oleates [24,25] in coordinating and/or noncoordinating solvents. Different sizes and shapes of monodisperse iron oxide NCs were synthesized by adjusting the nucleation and growth temperature, ligands, controllable ratio between Fe and ligands, etc. Herein, we report a facile method to synthesize monodisperse FeO and Fe_3O_4 NCs through high-temperature reductive decomposition of FeO(OH) with oleic acid (OA) in noncoordinating solvent. The formation of iron oxide NCs followed thermodynamics, kinetics theory, and chemical reaction driving force theory in the reaction process. The reaction parameters (such as reaction temperature, time, and Fe/oleic acid molar ratio) have been proven to play important roles in the formation of Fe_3O_4 and FeO NCs. The variation of reaction temperature influenced the activity between FeO(OH) and OA. The OA was not only a reactant, but also a ligand which provide a means of mediating growth and stabilizing the NCs in solution. The concentration of OA influenced chemical reaction driving force, and then different types of iron oxide NCs were formed. To the best of our knowledge, this is the first time that different types of iron oxide NCs were directly synthesized by only adjusting Fe/oleic acid molar ratios through the decomposition of FeO(OH).

2. Materials and methods

2.1. Materials and instrument

FeO(OH) and oleic acid (90%) were obtained from Aldrich. Fe_3O_4 powder and paraffin oil were purchased from Beijing Chemical Reagents Company. Hexanes (⩾97%), methanol (⩾99.5%), and chloroform (⩾99%) were obtained from Tianjing Chemical Reagents Company.

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The X-ray diffraction experiments (XRD) were carried out on a Philips X' Pert Pro diffractometer with Cu$K\alpha$ ($\lambda = 1.54056$ Å) radiation. The size and morphology of NCs were investigated using JEOL 100CX-II transmission electron microscope (TEM) at 100 kV. The nanocrystal samples for TEM were obtained by depositing these solutions onto carbon-coated copper grids. The Raman spectra were recorded at room temperature by a Renishaw 1000 micro-Raman spectrometer with an excitation laser line of 632.8 nm from a He–Ne laser. The integration time for collecting the Raman signal was 60 s. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet AVATAR 360 spectrometer. The samples for FTIR were prepared by evaporating the chloroform solutions of iron oleate complexes on the KBr disks.

2.2. A typical experiment for the synthesis of 10 nm Fe_3O_4 NCs

FeO(OH) (0.178 g, 2.00 mmol) was added to the mixture containing paraffin oil (5 mL) and OA (1.13 g, 4.00 mmol) in a three-necked flask. The mixture was heated to 150 °C for 15 min under nitrogen, and then heated to 320 °C for another 30 min after it was heated to 340 °C for 5 min under nitrogen flow. During this time, the solution turned from turbid black to clear reddish-brown as the iron source material dissolved. Ultimately, the obtained clear black solution was cooled to room temperature slowly. A mixture of hexane (10 mL) and methanol (100 mL) was added to the mixture to precipitate the NCs. The NCs were separated by centrifugation and then washed for three times with the mixture of hexane and methanol. These NCs can be easily redispersed in various organic solvents, such as hexane, octane, toluene, etc.

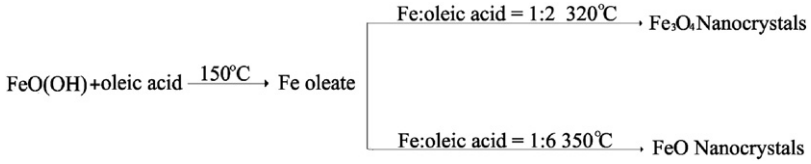
2.3. A typical experiment for the synthesis of 35 nm FeO NCs

FeO(OH) (0.178 g, 2.00 mmol) was added to the mixture containing paraffin oil (5 mL) and OA (3.39 g, 12.00 mmol). The mixture was heated to 150 °C for 15 min under nitrogen, and then heated to 350 °C for another 60 min after it was heated to 370 °C for 5 min under nitrogen flow. The FeO NCs were easily purified using similar method which was used for 10 nm Fe_3O_4 NCs purification.

3. Results and discussion

We have explored the synthesis of iron oxides over a range of compositions based on an underlying reaction scheme that relied on the decomposition of simple salts or organometallic precursors of Fe in high boiling point solvents with the help of suitable ligands. The ligands affected the chemistry of the decomposition and controlled the nucleation and growth by reducing the surface energy of the crystal [14]. This type of approach has been well established in NCs syntheses. By optimizing the reaction parameters such as the Fe/oleic acid molar ratio and reaction temperature, different types of iron oxide NCs with sizes ranging from 10 to 50 nm were synthesized successfully.

As illustrated in Scheme 1, the reaction of FeO(OH) with OA at higher temperatures led to monodisperse iron oxide NCs. In the first stage, Fe oleate formed at 150 °C. In the second stage, different types of iron oxide NCs were synthesized from the decomposition of Fe oleate in noncoordinating solvent at certain temperatures and Fe/oleic acid molar ratios. In fact, the complex structure of Fe oleate may have influence on the formation of iron oxide NCs with different size and shape [26]. Fig. 1 presents the FTIR spec-



Scheme 1. Possible reaction routes for FeO(OH) with OA to synthesize monodisperse iron oxide nanocrystals.

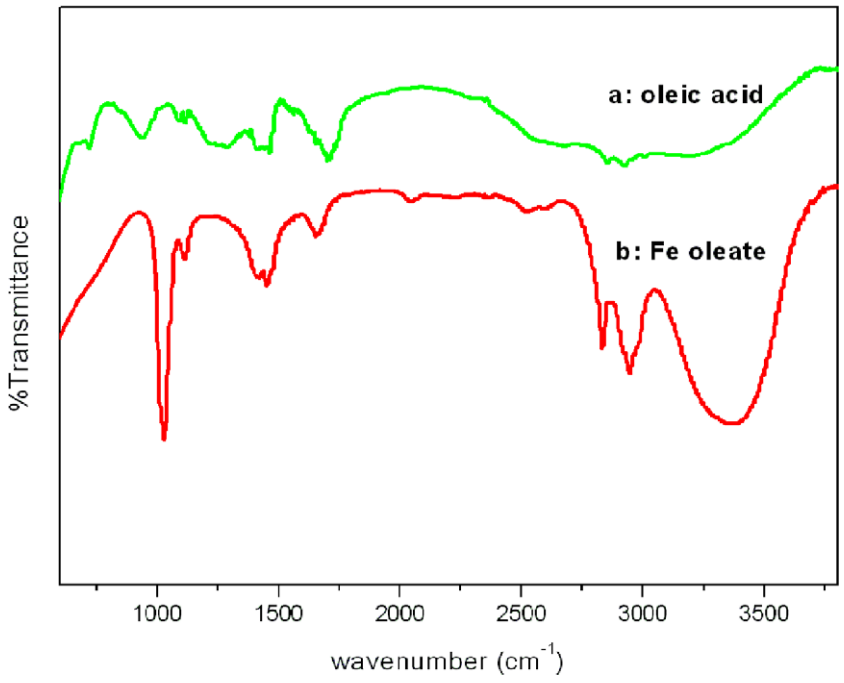


Fig. 1. FTIR characterization of oleic acid (a) and iron oleate complex (b).