Monodisperse Fe₃O₄ spheres: Large-scale controlled synthesis in the absence of surfactants and chemical kinetic process

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ABSTRACT Fe₃O₄ has attracted tremendous interest in vast areas of biomedicine and catalysis as well as environment engineering. However, it is highly desired to fully understand the chemical kinetic process and propose a general, surfactant-free, large-scale synthesis approach for Fe₃O₄ spheres. Herein, we developed a facile scalable solvothermal method in the absence of surfactants to produce Fe₃O₄ spheres with the yield of 5.1 g, which present tunable sizes from 107 to 450 nm by modulated molar ratio of Fe³⁺/COO[−] in the solution. Particularly, it is observed that the reactants undergo a redox process, composed of a precipitation-dissolution equilibrium combined with a coordination reaction (termed as RPC), to the final product based on the LaMer model. It is worth noting that the generation of di-carboxyl group and its coordination with iron cations determine the formation of Fe₃O₄ spheres. This work not only offers a strategy to precisely tailor the particle size in scalable synthesis process, but also gives the insight on the role of dihydric alcohol in the formation mechanism of Fe₃O₄ spheres in the absence of surfactants.

Keywords: Fe₃O₄ spheres, surfactant-free, large-scale synthesis, chemical kinetic process

INTRODUCTION

Fe₃O₄ spheres have been intensively explored in the past few decades due to their unique electronic, magnetic and optical properties, which make them an ideal candidate for catalytic [1,2], biological [3–6] and photonics applications [7,8]. Multi-step self-assembly [9–12] and one-step solution growth [13–22] are main approaches for preparing Fe₃O₄ spheres [23], among which the one-step method is more flexible and efficient. Surfactants applied in the one-step solution growth process play a key role in regulating the morphology of Fe₃O₄ spheres and enhan-

cing their stability, which affect adversely on the magnetic properties. For example, hydrophilic poly(acrylic acid) (PAA) [15] or trisodium citrate (Na₃Cit) [14] are utilized to increase the interfacial hydrophilicity of Fe₃O₄, which eventually reduce the saturated magnetic moment (M_s) of Fe₃O₄ spheres. Thus, it is of great significance to develop a method to synthesize Fe₃O₄ spheres *via* surfactant-free approach.

Furthermore, understanding of the formation mechanism is an essential prerequisite for establishing the scope of synthesis of Fe₃O₄ spheres for broad applications. In previous studies [24–32], polyol has been widely employed as both solvent and reductant while either PAA or Na₃Cit is used as stabilizer. Cheng *et al.* [14] reported that the formation of Fe₃O₄ spheres depended on the balance of surface tension and electrostatic repelling forces of citrate molecules on the surface of nanocrystals. Recently, Gao's group [33] pointed that the crosslinking of the oxidized dihydric alcohols was responsible for forming Fe₃O₄ spheres. However, these mechanisms proposed in the presence of surfactant or stabilizer have not fully presented to us, reducing the reliability of the synthesis processes.

Herein, we developed a facile, scalable and surfactant-free polyol method to fabricate monodisperse Fe₃O₄ spheres whose size can be controlled by adjusting the molar ratio of Fe³⁺/COO[−]. Chemical reaction kinetics was further explored by an *ex-situ* time course study. A redox process, precipitation-dissolution equilibrium combined with a coordination reaction (termed as RPC) formation mechanism is proposed to describe the nucleation and growth process of Fe₃O₄ spheres. This mechanism is expected to open up a deep insight to precisely tailor the particle morphology with narrow size distribution in

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scalable synthesis process.

EXPERIMENTAL SECTION

Chemicals

All the raw materials were used without further purification. Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%) and ethylene glycol (EG, 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium acetate anhydrous (CH_3COONa , NaAc, 99%) was bought from Xi Long Chemical Co., Ltd, Guangdong, China.

Synthesis of Fe_3O_4 spheres

Fe_3O_4 spheres were synthesized by a modified solvothermal method referring to Li's method [13]. Firstly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.35 g) and NaAc (7.2 g) were dissolved into 20 mL EG, respectively to form a homogeneous solution under magnetic stirring. Then NaAc (in EG solution) was added dropwise to $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (in EG solution) with 1000 rpm magnetic stirring for 1 h. Subsequently, the obtained solution was sealed into a 50-mL Teflon lined stainless autoclave. The autoclave reactor was then put into an oven and heated to 200°C and maintained for 6 h at that temperature. After cooling down to room temperature, the black sediments were collected and washed by deionized water or ethanol for three times to eliminate inorganic and organic impurities. By adjusting the molar ratio of $\text{Fe}^{3+}/\text{COO}^-$ as 1/4.4, 1/6.6, 1/8.8, 1/17.6, 1/35.2, 1/70.4, the obtained samples were named as Fe_3O_4 -*i* (*i* = 1–6).

To investigate the formation mechanism of Fe_3O_4 spheres, we monitored the reaction process after different reaction durations. The reactants were added using the above method with $\text{Fe}^{3+}/\text{COO}^-$ molar ratio at 1/17.6 and divided into six portions. Then these solutions were transferred to Teflon lined stainless autoclaves (50 mL) and reacted for 1, 2, 3, 4, 5, 6 h at 200°C, respectively. The obtained products were named as time-*i* (*i* = 1–6, referred to the reaction time). In addition, the scalability of this technique was illustrated by carrying out the process using a 1-L Teflon lined stainless autoclave where twenty folds of the above reactants were employed.

Characterizations

The transmission electron microscopy (TEM) images were taken on an FEI Tecnai T20 TEM at an acceleration voltage of 200 kV, and the high resolution TEM (HRTEM) images were obtained on a Tecnai-G2-F30 (FEI) transmission electron microscope at 300 kV. Scanning electron microscopy (SEM) characterization was

carried out using a Hitachi S-4800 scanning electron microscope. X-ray diffraction (XRD) studies were done by using a PAN analytical X'Pert³ Powder X-ray diffractometer equipped with Cu-K α radiation (40 kV, 40 mA). XRD scan was performed in the 2θ range of 5°–85°. The FT-IR spectra were taken on PE-spotlight 200 FT-IR microscope with ATR attachment. X-ray photoelectron spectroscopy (XPS) characterization was investigated on Imaging Photoelectron Spectrometer (Axis Ultra DLD, Kratos Analytical Ltd.) with monochromatized Al K α radiation (1486.6 eV) and chamber pressure at 10^{-8} – 10^{-9} torr. The magnetic properties of the samples were recorded on a Physical Property Measurement System (PPMS, Dynacool, Quantum Design) at room temperature. The content of Fe_3O_4 was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

RESULTS AND DISCUSSION

Characterization of Fe_3O_4 spheres with different sizes

The Fe_3O_4 -*i* (*i* = 1–6) spheres were produced by a facile solvothermal method with $\text{Fe}^{3+}/\text{COO}^-$ molar ratio of 1/4.4, 1/6.6, 1/8.8, 1/17.6, 1/35.2, 1/70.4. In Fig. 1a–f, TEM images and the corresponding histograms show the spherical structures of Fe_3O_4 -*is* (*i* = 1–6) with average diameters of 107, 160, 182, 234, 352, and 450 nm, respectively. The representative SEM images of the products are shown in Fig. 1g–l. As the molar ratio of $\text{Fe}^{3+}/\text{COO}^-$ increased in the polyol reaction, the diameter of the resulting Fe_3O_4 spheres gradually increased from about 107 to 450 nm, which was consistent with the TEM results.

The crystal structure and phase composition of the as-synthesized products were confirmed by XRD analysis. In Fig. 2a, the columns at the bottom display the characteristic peaks of standard magnetite phase (PDF #19-0629) [15]. It can be clearly observed that all the diffraction peaks of the Fe_3O_4 -*is* are matched well with the standard PDF card, indicating that the products are pure Fe_3O_4 . XPS analysis was further applied to confirm the valence state of Fe [34]. In Fig. 2b, the high-resolution Fe 2p spectrum of Fe_3O_4 -4 consists of Fe 2p $_{1/2}$ and Fe 2p $_{3/2}$ at 724.3 and 710.6 eV, respectively [35]. Besides, the absence of the satellite peak at about 719.0 eV, which is the characteristic of Fe^{3+} in Fe_2O_3 , affirms that the samples are composed of pure magnetite [36]. Furthermore, the HRTEM images of the Fe_3O_4 -4 (234 nm) in Fig. S1a, b show a lattice spacing of 0.296 nm, corresponding to cubic magnetite (220) facet. It is worth

Figure 1 (a–f) TEM images and the corresponding histograms of the particle size distribution (inset images), (g–l) SEM images of the as-prepared Fe_3O_4 -*i* spheres with molar ratio of $\text{Fe}^{3+}/\text{COO}^-$ as 1/4.4, 1/6.6, 1/8.8, 1/17.6, 1/35.2, 1/70.4. The average sizes of spheres are (a, g) 107 nm, (b, h) 160 nm, (c, i) 182 nm, (d, j) 234 nm, (e, k) 352 nm, and (f, l) 450 nm.

noting that the selected area electron diffraction (SAED) pattern of the Fe_3O_4 -4 in Fig. S1c displays a polycrystalline structure, indicating misalignments among the primary nanocrystals. In Fig. S1d–f, energy dispersive spectrometer (EDS) chemical mapping images are also recorded to detect the elements distribution, which clearly displays that the product is composed of Fe and O.

In order to explore the surface properties of the as-synthesized Fe_3O_4 spheres, FT-IR and XPS analyses were further conducted. The FT-IR spectra (Fig. 2c) of Fe_3O_4 spheres show absorptions centered at 1557 and 1419 cm^{-1} , which are attributed to the vibrations of the symmetric and asymmetric stretching of the COO^- group [37]. Besides, the absorption peaks at 1044 cm^{-1} ($\nu_{\text{as}}(\text{C}-\text{O})$) and 885 cm^{-1} ($\delta(\text{O}-\text{H})$) reveal the existence of EG. Meanwhile, the products show strong absorption at 538 cm^{-1} owing to the $\nu(\text{Fe}-\text{O})$ of the magnetite spheres [38], which agrees well with the XRD and XPS analyses. The high-resolution C 1s spectrum (Fig. S2a) of the Fe_3O_4 spheres displays three peaks at 288.7, 286.2 and 284.8 eV, corresponding to the aliphatic $-\text{C}=\text{O}$ groups, $-\text{C}-\text{OH}$ groups, and $-\text{C}-\text{C}$ bonds, respectively. The O 1s spectrum (Fig. S2b) displays three peaks at 531.2, 530.7 and 530.0 eV, which can be assigned to the oxygen in three different environments as $-\text{O}-\text{H}$, $\text{O}-\text{C}=\text{O}$ and $\text{Fe}-\text{O}$, respectively [4,36].

The magnetic properties of the Fe_3O_4 spheres were accessed by PPMS. The as-synthesized products exhibit super-paramagnetic behaviors at room temperature. And the saturation moments are found to be 76, 79, 81, 83, 85 and 89 emu g^{-1} for Fe_3O_4 -*i* (*i* = 1–6), respectively (Fig. 2d). The values of M_s decrease slightly with the reduced sphere size, due to the lack of full alignment of the surface atoms and decreased crystallinity of the magnetite samples [25,39]. The element content of Fe in Fe_3O_4 -*i* was detected by ICP-AES analysis. It is found that the weight percentage of Fe_3O_4 -*i* (*i* = 1–6) are more than 95%, which is far beyond the ones with surfactant as reported [14,19].

Furthermore, the scalable synthesis of the Fe_3O_4 spheres was also explored. 5.1 g Fe_3O_4 spheres (Fig. S3b) with good dispersity (Fig. S3c) can be obtained at one time with 1-L Teflon lined stainless autoclaves (Fig. S3a). Besides, the crystallinity (Fig. S3d) and saturated moments (Fig. S3e) are almost the same as the product synthesized by 50-mL Teflon lined stainless autoclaves, which demonstrates the scalability of this method.

Ex-situ chemical kinetic process exploration of Fe_3O_4 spheres

The formation mechanism of the Fe_3O_4 spheres has been exploited by an *ex-situ* time study. TEM and SEM images of the products collected after different reaction times (time-*i*, *i* = 1–6) are shown in Fig. 3 and Fig. S4. The TEM image of 1 h presents an aggregated granular morphology composed of tiny grains. Subsequently, sheet-like structure with a small amount of rough spherical particles (diameter of 40 nm) emerged in Fig. 3b from the margin

Figure 2 (a) XRD patterns, (b) XPS high-resolution of Fe 2p, (c) FT-IR spectra, (d) room-temperature magnetization curves. The samples were obtained by adjusting the molar ratio of $\text{Fe}^{3+}/\text{COO}^-$ as (i) 1/4.4, (ii) 1/6.6, (iii) 1/8.8, (iv) 1/17.6, (v) 1/35.2, (vi) 1/70.4.

of the matrix. The content of sheet-like structure decreases while both of the amount and the diameter of the spherical particles increase (Fig. 3c, d). Consequently, the products display spherical particles without sheet-like structures, whose diameter increases slightly from 200 nm (Fig. 3e) to 230 nm (Fig. 3f). In addition, the HRTEM images of the product collected after 2 h reaction (time-2) in Fig. S5a and b display the lattice fringes of 0.296 and 0.216 nm, corresponding to Fe_3O_4 (220) facet and Fe_2O_3 (101) facet. HRTEM image of the product in 2 h (Fig. S5b) shows an amorphous structure, which can be confirmed by SAED (Fig. S5c). This pre-aligned clusters were deemed as direct precursors of iron crystal and the alignment was hypothesized based on the anisotropic structural features within the short-range structure of the clusters [31].

Furthermore, the crystalline nature and the surface state of the *ex-situ* products were investigated *via* XRD

and FT-IR. The XRD patterns of the isolated powders obtained after different durations are shown in Fig. 4a. The product obtained at 1 h presents strong peak at 21.2° , in accord with the (110) planes of FeOOH (PDF #29-0731). As the time goes on, the dehydration of FeOOH starts and FeOOH transforms to $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (PDF #13-0092). The magnetite peaks are clearly detected at 4 h, which indicates the products are the mixture of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and Fe_3O_4 . After 5 h, the product completely transforms to well-crystallized Fe_3O_4 (PDF #19-0629). Fig. 4b shows the FT-IR-ATR spectra of the products prepared after different reaction times. At 1 h (time-1), the characteristic bands at about 1571 and 1444 cm^{-1} correspond to the symmetric and asymmetric stretching of the COO^- group, coming from the absorption of NaAc. Meanwhile, the band at 1054 cm^{-1} is attributed to the C–O stretching of COO^- group. It is worth noting that the samples in Fig. 4b (ii–iv) show two obvious peaks at 2902

Figure 3 TEM images of the products prepared after different reaction durations: (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, and (f) 6 h.

and 2885 cm^{-1} , which are assigned to the vibrations of the symmetric and asymmetric stretching of the C–H group in aldehyde group, and the intensities of these signals decrease with time going on, demonstrating the glycol oxidation to glyoxal. In addition, the absorptions centered at 1535 and 1414 cm^{-1} in Fig. 4b (v, vi) are attributed to the vibration of COO^- group. Particularly, the vibration band of C=O shifts to lower wavenumber than Fig. 4b–i due to the formation of di-carboxyl group [33]. The absorption peaks at 1043 cm^{-1} ($\nu_{\text{as}}(\text{C}-\text{O})$) and 885 cm^{-1} ($\delta(\text{O}-\text{H})$) reveal the existence of EG. Besides, the absorption band below 700 cm^{-1} is attributed to the vibration of $\nu(\text{Fe}-\text{O})$, and the peak at 537 cm^{-1} in Fig. 4b (v, vi) indicates the formation of Fe–O bond in Fe_3O_4 spheres.

Formation mechanism of Fe_3O_4 spheres

On the basis of the above analyses, it is evident that the transformation from glyoxal to oxalic acid and the coordination between Fe^{3+} and di-carboxyl in oxalic acid play an important role in forming magnetite spheres. The formation mechanism of magnetite spheres can be summarized as the following equilibriums:

Figure 4 (a) XRD patterns and (b) FT-IR spectra of products prepared after different reaction durations: (i) 1, (ii) 2, (iii) 3, (iv) 4, (v) 5, and (vi) 6 h.

At first, “self-nucleation” occurs at a rate called “effectively infinite” [24] according to LaMer model. Three main reactions are happening at this stage, which are, the hydrolysis of acetate (Equation (1)), the formation of $\text{Fe}(\text{OH})_3$ (Equation (2)) and FeOOH (Equation (3)). In stage II (0.5–1.5 h), there is a burst of nucleation of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ through dehydration reaction of FeOOH (Equation (4)). At the same time, a redox process happens by oxidation of glycol (Equation (5)) and partial reduction of $\text{Fe}(\text{III})$ (Equation (6)), which is in agreement with the XRD and FT-IR analysis. In next stage (stage III), $\text{Fe}(\text{OH})_2$ forms (Equation (7)) and nucleation essentially stops. Meanwhile, Fe_3O_4 is formed through the reaction between $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ or $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Equations (8) and (9)). It should be noted that Fe_3O_4 nanoparticles grow to spheres structure by the strong coordination of iron cations and carboxylate group on the magnetite surface in the dissipation of pre-aligned $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ precursor. Finally, after a reaction of 6 h, pure Fe_3O_4 spheres with high crystallinity are obtained. Particularly, the initial concentration of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in the solution plays a key role in the size control of the monodispersed Fe_3O_4 spheres *via* a precipitation-dissolution equilibrium. As the initial concentration of Fe^{3+} increases, the size of Fe_3O_4 spheres grows gradually. Thus, an RPC (refers to redox process, precipitation-dissolution equilibrium and coordination reaction, separately) mechanism based on LaMer model is proposed and schematically elaborated in Fig. 5. This scheme clearly depicts the redox reaction in

Figure 5 Schematic illustration of the formation mechanism of Fe₃O₄ spheres based on the laMer model.

the solution, the morphology evolution in solid state and the coordination structure of Fe³⁺ with di-carboxyl group over the process time.

Fe₃O₄ spheres have extraordinary catalytic activity, Li/Na ion storage capability and biological applicability owing to their unique structure, magnetic properties and good biocompatibility [40–44]. In catalysis, Fe₃O₄ microspheres are ideal support materials as a result of their porous structure, rigid framework and short diffusion lengths of surrounding solutes, which ensure that the catalyst can maintain its original structure and catalytic activity [45–47]. Besides, in the biological field, microspheres can be conveniently separated from the solution mixture and the spheres are water-soluble, which is important for biomolecular separation, targeted drug delivery, hyperthermia treatment of cancer and magnetic resonance imaging [48–50].

CONCLUSIONS

In this work, we investigated the chemical kinetics of forming Fe₃O₄ spheres, which were obtained by a scalable surfactant-free solvothermal method. Fe₃O₄ spheres ranging from 107–450 nm can be addressed by tuning the molar ratio of Fe³⁺/COO[−] in the reaction solution. Furthermore, a RPC mechanism is proposed based on LaMer model and the coordination structure of di-carboxyl group with iron cations to interpret the nucleation and growth process of Fe₃O₄ spheres. This work figures out the formation mechanism of Fe₃O₄ spheres and offers a reliable synthetic method to produce large amount of Fe₃O₄ spheres for potential applications.

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无表面活性剂条件下大规模可控制备单分散 Fe_3O_4 及其化学动力学过程研究

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摘要 Fe_3O_4 微球被广泛应用于生物医药、催化和环境工程领域. 理解 Fe_3O_4 微球的化学动力学过程并发展一种通用的、无表面活性剂的大规模合成 Fe_3O_4 微球的方法成为当前的迫切需求. 本文提出了一种简单的无表面活性剂的方法用于大规模合成 Fe_3O_4 微球, 通过调节溶液中 $\text{Fe}^{3+}/\text{COO}^-$ 的比例, 合成了直径为 107 到 450 nm 的 Fe_3O_4 微球. 研究表明, 反应物通过氧化还原反应、沉淀溶解平衡和配位过程形成最终反应产物. 其中, 二羧基基团和铁离子的配位促进了 Fe_3O_4 微球的形成. 本文不仅提供了一种在大规模合成反应过程中调控产物尺寸的方法, 而且详细研究了在无表面活性剂条件下合成 Fe_3O_4 微球过程中醇起到的特殊作用.