

Facile and ultra large scale synthesis of nearly monodispersed CoFe_2O_4 nanoparticles by a low temperature sol–gel route

Hongtao Cui · Yanyan Jia · Wanzhong Ren ·
Wenhua Wang

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Abstract Nearly monodispersed cobalt ferrite nanoparticles were synthesized by a low temperature sol–gel route using propylene oxide as a gelation agent. The nanoparticles were obtained by the reaction of FeCl_2 and CoCl_2 in ethanol solution with propylene oxide to form the sol, followed by the boiling of the sol solution. The unique chemistry of this procedure allows the formation of highly homogeneous gel intermediate, resulting in the great reducing of crystallization temperature of ferrites to less than 100 °C without postannealing step. This guarantees the preparation of well defined and non-aggregated ferrite nanoparticles on an ultra-large scale of about 75 g in a single reaction. This large scale synthesis strategy offers important advantages over other conventional routes for the preparation of CoFe_2O_4 nanoparticles, showing the promising application of this route in the industrial production.

Keywords Sol–gel · CoFe_2O_4 · Nanoparticles · Low temperature · Large scale

1 Introduction

Spinel ferrites (MFe_2O_4 , $\text{M}=\text{Fe}$, Co , Ni , Mn , etc.) are very promising magnetic compounds due to their high performance in applications of high density magnetic recording,

microwave device, drug delivery, ferrofluid, magneto-optic, magnetocaloric refrigeration and magnetic resonance imaging [1–6]. Their fascinating properties are the nano-size effects, where their magnetic properties of blocking temperature, saturation, remanent magnetization and coercivity are greatly connected with particle size (size-dependent) [7–9], giving the nanomaterials excellent magnetic properties. When the particle size is reduced to a threshold value, small alternation of size can make their properties greatly change [10, 11], namely size-sensibility. Therefore, monodisperse or narrow size distribution is one of major factors for their magnetic performance, and one of primary objectives in the preparation of nano-magnetic materials.

Due to the asynchrony of the nucleation and phase formation, it is difficult to obtain ferrite nanoparticles with monodisperse state or narrow size distribution through the traditional coprecipitation route [12, 13]. A complicated seed-mediated method was advised to control the crystallization process during coprecipitation, followed by an exhaustive size selection procedure [14] (which is also frequently used by other routes). The crystallization process also can be carefully controlled by a soft reactor (reverse micelle [15], foam [16], etc.) or hard reactor (organic [17] or inorganic matrix [18]) to limit the growth of particles in order to keep their size in a narrow distribution. The non-hydrolytic [8] and decomposition process [19] of metal organic complex offer a much more successful way for the aim of size control due to the better control of nucleation and phase formation. However, their advantages are counteracted by the high reaction temperature in the organic solvent, complicated process and expensive precursors.

Herein, nearly monodispersed cobalt ferrite nanoparticles were successfully synthesized by a recently developed

H. Cui (✉) · Y. Jia · W. Ren · W. Wang
College of Chemistry and Biology, Yantai University,
Yantai 264005, China
e-mail: htcai@ytu.edu.cn

chemical strategy [20–23] on an ultra large, epoxide assisted sol–gel route using propylene oxide as gelation agent. Through the key choosing of iron salts as iron source and optimizing of reaction conditions, the unique chemistry of this route guarantees the lowering of cobalt ferrite crystallization temperature to less than 100 °C. The delicate control of the process without postannealing step results in the nearly monodispersed state and non-aggregation state of the ferrite nanoparticles.

2 Experimental

2.1 Materials

Iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and propylene oxide (PPO) were reagent grade and used as received.

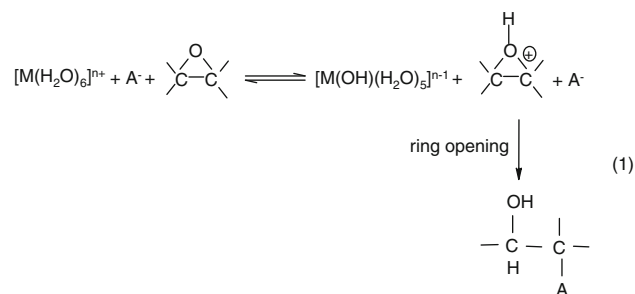
2.2 Preparation of CoFe_2O_4 nanoparticles

All syntheses were performed under ambient atmosphere and same reaction parameters except for the concentration of metal ions and PPO. Stoichiometric $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in a certain amount of ethanol. After the addition of propylene oxide to the solution (molar ratio of propylene oxide and metal ions was kept at 10), the solution became brown with a few minutes. The obtained sol was stirred for 6 h and then boiled around 78 °C for another 15 min. During the boiling of the sol, it gradually became black coloration. The non-aggregated ferrite nanoparticles containing sol solution can be used directly for other applications such as transparent magnetic film and gel, or the boiling of the solution was continued until dry powder was obtained. 75 g CoFe_2O_4 can be produced in a single reaction, where the maximum capacity of production is only limited by the volume of the facilities used for the preparation. As a comparison, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used as iron precursor salts to prepare the nanoparticles, following the same procedure.

2.3 Characterization

The XRD patterns of the samples were measured in a Siemens D8 diffractometer using $\text{CuK}\alpha$ radiation. The morphology of the particles was observed using a JEOL 2000 transmission electron microscope working at 200 kV.

3 Results and discussion



During the preparation, the aquo complexes $[\text{M}(\text{H}_2\text{O})_6]^{n+}$ ($\text{M}=\text{Co}, \text{Fe}$) react with propylene oxide (PPO) to form M–OH bonds as shown in equation (1). The hydrolysed ions will undergo condensation, releasing water and forming M–M bonds. The PPO acts as a proton scavenger, reacting with the protons which come from the hydrolysis of the aquo complexes. The protonated propylene oxide is then irreversibly ring-opened.

The XRD patterns of samples prepared with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ are shown in Fig. 1. The samples synthesized with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ present amorphous structure, however, it is very interesting to notice that the samples prepared with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ exhibit a structure of cobalt ferrite (JCPDS 22-1086). This means that the different structures of the final products depend on the reaction kinetic of the three iron salts. Fe^{3+} ions react with propylene oxide to form iron (III) hydroxide which cannot be crystallized to iron oxide just by the boiling of the

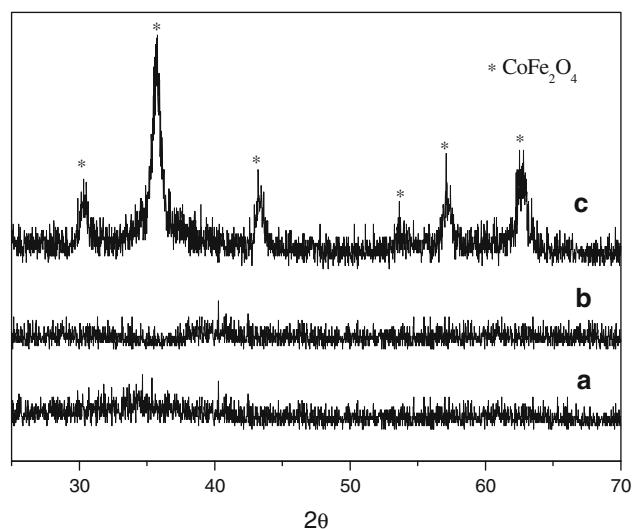


Fig. 1 XRD patterns of samples prepared with $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (a), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (b) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (concentration of iron ions is 0.6 mol l^{-1})

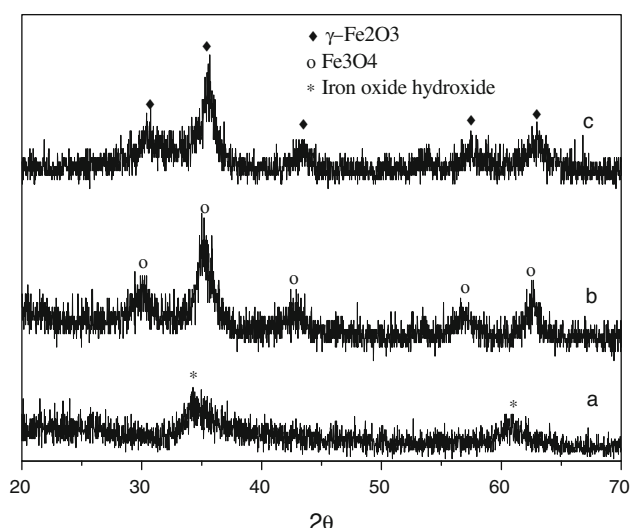


Fig. 2 XRD patterns of the precursor intermediate obtained at room temperature (a), Fe₃O₄ sample prepared by the boiling and vacuum drying of sol solution (b) and γ -Fe₂O₃ sample synthesized by the oxidation of Fe₃O₄ in air atmosphere

ethanol solution. While, the precursor intermediate, which was obtained from the drying of the sol solution (prepared from FeCl₂·4H₂O without adding of CoCl₂·6H₂O) at room

temperature without heat treatment, presents a crystallized phase of iron oxide hydroxide (JCPDS 89-3850) as shown in Fig. 2a. The sample, which was prepared by the boiling and vacuum drying of the same sol solution at room temperature, presents a spinel structure of Fe₃O₄ (Fig. 2b, JCPDS 19-0629). It can be concluded that part of Fe²⁺ ions was oxidized by the oxygen in the solution and crystallized to form mixed valence iron oxide hydroxide during the sol formation process, which was then converted to Fe₃O₄ by the following boiling. This Fe₃O₄ sample can be oxidized easily to γ -Fe₂O₃ (Fig. 2c, JCPDS 39-1346) in the air atmosphere within a few hours. Therefore, it is reasonable to infer that Co²⁺ doped Fe₃O₄ was formed during the boiling process of the sol, which was transformed into spinel CoFe₂O₄ by the oxidization of the Fe²⁺ ions of the Fe₃O₄ to Fe³⁺ in air atmosphere.

The unique chemistry and the low synthesis temperature of this sol–gel route allows the preparation of nanoparticles with very small particle size and narrow size distribution as observed in their TEM micrographs (Fig. 3). The sample, which was prepared with metal ions concentration of 0.3 mol l⁻¹, shows the well defined and non-aggregated CoFe₂O₄ nanoparticles with diameter of about 9 nm (Fig. 3a). When the concentration is increased to

Fig. 3 TEM micrographs of cobalt ferrite samples prepared with concentration of metal ions = 0.3 mol l⁻¹ (a) and 0.6 mol l⁻¹ (b), and the corresponding particle size distribution (c)

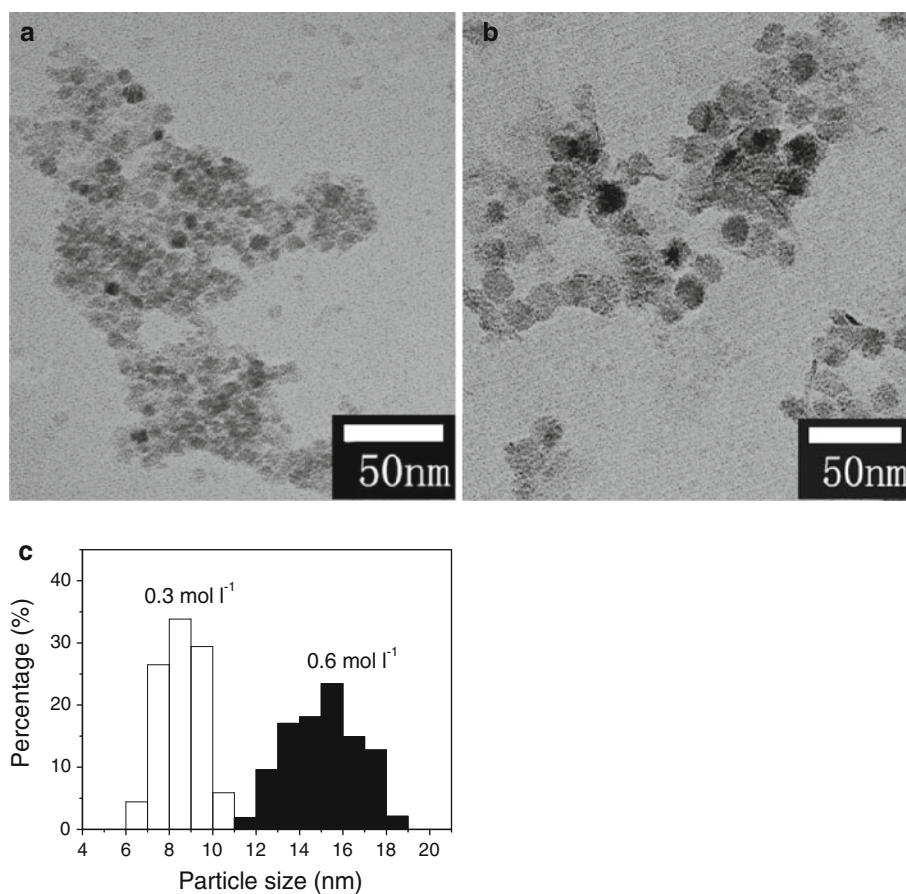
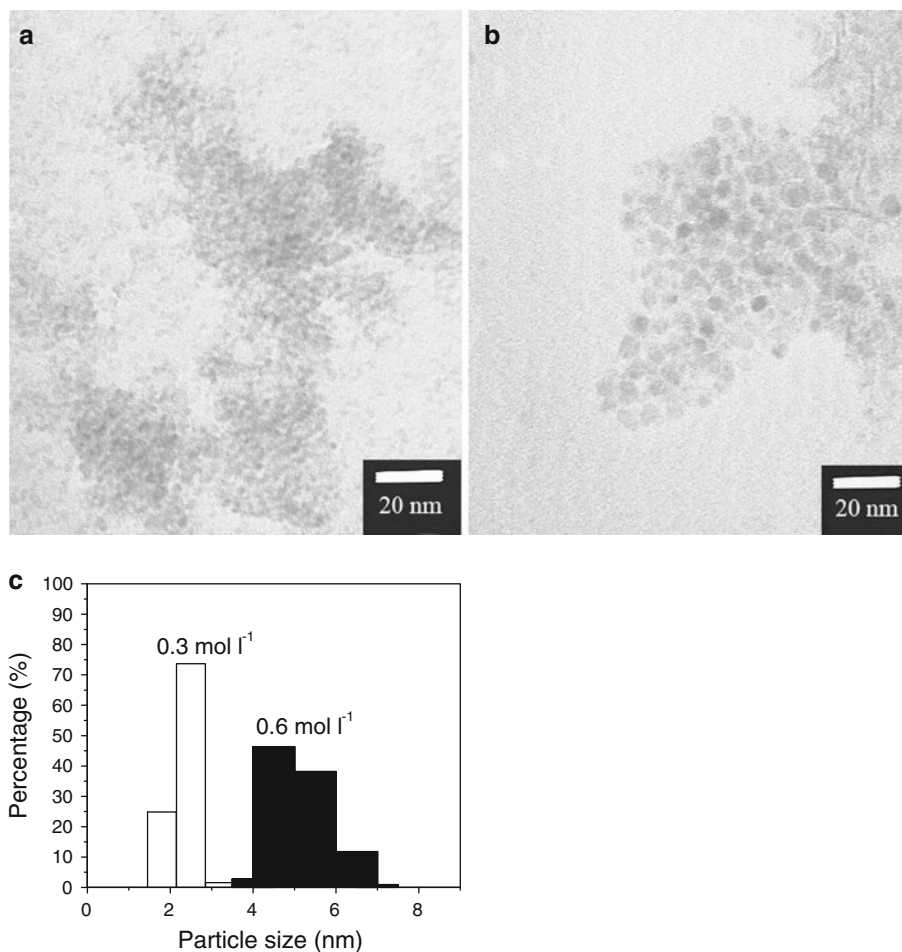


Fig. 4 TEM micrographs of γ - Fe_2O_3 samples prepared through the same procedure of CoFe_2O_4 with concentration of metal ions = 0.3 mol l^{-1} (a) and 0.6 mol l^{-1} (b), and their corresponding particle size distribution (c)



0.6 mol l^{-1} , its TEM micrograph reveals the particle size of about 15 nm (Fig. 3b). The particle size distributions (Fig. 3c) of the two samples were easily calculated from their TEM micrographs due to the well dispersed state of the nanoparticles. The size distribution demonstrates that the nanoparticles prepared at lower concentration (0.3 mol l^{-1}) are in very narrow size distribution around 9 nm, nearly monodispersed. On the other hand, the higher metal ions concentration of 0.6 mol l^{-1} not only results in the increase of particle size to about 15 nm but also makes the size distribution a little wider than the former.

As a comparison, γ - Fe_2O_3 nanoparticles was prepared by the boiling of FeCl_2 resulted sol solution with the same synthesis procedure of CoFe_2O_4 , which is described in our previous work [23]. The sample produced with metal ions concentration of 0.3 mol l^{-1} presents 2.3 nm of particle median diameter (Fig. 4a) and a very narrow size distribution (Fig. 4c). With the increase of metal ions concentration to 0.6 mol l^{-1} , the median diameter of particles also increases to 5.1 nm (Fig. 4b) with slightly wider size distribution (Fig. 4c) than that of former. This indicates that

Co^{2+} ions promote the increase of particle size even in the exactly same reaction conditions with synthesis of γ - Fe_2O_3 .

4 Conclusions

In this work, cobalt ferrite nanoparticles were prepared on an ultra-large scale of about 75 g in a single reaction by a low temperature sol–gel route using simple procedure and cheap precursors. The unique chemistry of this route results in the crystallization of CoFe_2O_4 at low temperature, leading to the preparation of small and nearly monodispersed nanoparticles without aggregation. The phase formation of CoFe_2O_4 was achieved by the boiling of the sol solution for some minutes and the obtained particles containing solution can be used directly for some applications such as ferrofluid or the preparation of transparent film and gel.

As compared with the well known synthetic methods such as decomposition of organometallic and metal complexes in high boiling point solvent [8, 19], this epoxide

assisted sol–gel route provides important advantages for the large scale production of ferrites nanoparticles. First, the maximum production capacity is only limited by the volume of the facilities used for the preparation. Second, inexpensive reagents and solvent are used with the characteristic of non-toxicity, and there is almost no waste released during the process. Third, the procedure that is carried under mild reaction conditions is quite facile and economical. These guarantee the promising application of this route in the industrial preparation.

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