



# Facile synthesis of stoichiometric zinc ferrite nanocrystal clusters with superparamagnetism and high magnetization



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## ABSTRACT

Stoichiometric  $\text{ZnFe}_2\text{O}_4$  magnetic nanocrystal clusters (MNCs) with an average diameter of 127 nm have been successfully synthesized by using a one-step solvothermal method without any additives, where nitrates ( $\text{Fe}(\text{NO}_3)_3$  and  $\text{Zn}(\text{NO}_3)_2$ ) were used as reactants. Different characterization techniques were used, such as XRD, ICP-AES, TEM, HRTEM, XPS, and SQUID. The results demonstrate that the stoichiometric  $\text{ZnFe}_2\text{O}_4$  is superparamagnetic, and the saturation magnetization ( $35.9 \pm 0.1$  emu/g at 300 K,  $78.0 \pm 0.1$  emu/g at 5 K) is higher than that reported in some references. However, when  $\text{FeCl}_3$  and  $\text{ZnCl}_2$  were used as reactants that replaced the nitrates at the same experimental conditions,  $\text{ZnFe}_2\text{O}_4 \cdot 40\text{Fe}_3\text{O}_4$  was synthesized. The  $\text{NO}_3^-$  decreased the  $\text{Fe}^{2+}$  concentration through oxidation and reduction reactions in the polyol method for the formation of  $\text{ZnFe}_2\text{O}_4$ . A possible mechanism for the stoichiometric  $\text{ZnFe}_2\text{O}_4$  formation was proposed and discussed, based on the time-resolved experiments.

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## 1. Introduction

Spinel ferrites ( $\text{MFe}_2\text{O}_4$ ; M = Fe, Mn, Zn, or Co) have attracted great attention for their applications in various fields as magnetic materials [1–3]. Recently,  $\text{ZnFe}_2\text{O}_4$  has received great interest due to the wide applications in magnetic material, adsorption, photocatalysis, and solar cells [4–10]. There are many methods to synthesize  $\text{ZnFe}_2\text{O}_4$  nanomaterials, such as coprecipitation method [11], reverse micelles [12], mechanical alloying [13], solvothermal method [14], electrochemical synthesis [15], chemical solution deposition method [16], and sol–gel method [17]. Among these different methods for the synthesis of  $\text{ZnFe}_2\text{O}_4$  nanoparticles, solvothermal method was considered as very attractive and advantageous due to a large quantity with high crystallinity and nice compositional control [18].

Superparamagnetic nanomaterials (especially iron series materials) have great potentials in magnetic resonance imaging (MRI), separation and purification, drug delivery, and magnetically induced hyperthermia [19–21]. However, superparamagnetic materials usually show a low magnetization value because of nanosized particles, which limits their practical applications. It is one way to increase the saturation magnetization ( $M_s$ ) by

increasing nanocrystal size [3]. However, the increase of the nanocrystal size usually induces a superparamagnetic–ferrimagnetic transition. Forming magnetic nanocrystal clusters (MNCs) has proved to be an effective way to retain superparamagnetic behavior with high magnetization [18,22]. MNCs consisting of multiple single-domain magnetic nanocrystals that assembled into sub-micrometer scale particles are especially attractive, due to their high magnetic susceptibility as well as low coercive force and superparamagnetism [23]. A polyol method was developed for the preparation of  $\text{ZnFe}_2\text{O}_4$  MNCs through the hydrolysis and reduction of iron chloride and zinc chloride in ethylene glycol at high temperatures [18]. However,  $\text{Fe}_3\text{O}_4$  was the primary component contained in the zinc ferrite [24,25] and this can be demonstrated by our experimental results listed below. The reason may be that some  $\text{Fe}^{3+}$  was reduced to  $\text{Fe}^{2+}$  by ethylene glycol [26,27], and it is more suitable to form of  $\text{Fe}_3\text{O}_4$  than  $\text{ZnFe}_2\text{O}_4$  at this condition. So it is still a challenge for the synthesis of stoichiometric  $\text{ZnFe}_2\text{O}_4$  MNCs by the polyol method. In order to prepare stoichiometric  $\text{ZnFe}_2\text{O}_4$  MNCs, the  $\text{Fe}^{2+}$  concentration should be controlled in the reaction system. According to report [28],  $\text{Fe}(\text{OH})_2$  gel can be oxidized by nitrate ion ( $\text{NO}_3^-$ ) at 90 °C. We propose that  $\text{NO}_3^-$  should be used to decrease the  $\text{Fe}^{2+}$  concentration or prevent the  $\text{Fe}^{2+}$  formation through oxidation and reduction reactions in the polyol method for the formation of  $\text{ZnFe}_2\text{O}_4$ .

In the present work, the chlorates were replaced by the nitrates as the reactants for the preparation of stoichiometric  $\text{ZnFe}_2\text{O}_4$

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**Table 1**

Experimental conditions for the as-prepared samples.

Sample	Reactant 1	Reactant 2	Reactant 3	Solvent	Temperature (°C)	Time (h)
ZnN4	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O 12.0 mmol	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 6.0 mmol	CH <sub>3</sub> COONa 18.0 mmol	EG 50 mL	200	4
ZnN6	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O 12.0 mmol	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 6.0 mmol	CH <sub>3</sub> COONa 18.0 mmol	EG 50 mL	200	6
ZnN12	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O 12.0 mmol	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 6.0 mmol	CH <sub>3</sub> COONa 18.0 mmol	EG 50 mL	200	12
ZnN24	Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O 12.0 mmol	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O 6.0 mmol	CH <sub>3</sub> COONa 18.0 mmol	EG 50 mL	200	24
ZnC24	FeCl <sub>3</sub> ·6H <sub>2</sub> O 12.0 mmol	ZnCl <sub>2</sub> ·6.0 mmol	CH <sub>3</sub> COONa 18.0 mmol	EG 50 mL	200	24

MNCs. The ZnFe<sub>2</sub>O<sub>4</sub> MNCs shows high magnetization. The formation mechanism of the ZnFe<sub>2</sub>O<sub>4</sub> MNCs was studied.

## 2. Materials and methods

### 2.1. Materials

All chemicals in this work, such as ferric nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), iron(III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), zinc chloride (ZnCl<sub>2</sub>), sodium acetate (CH<sub>3</sub>COONa), and ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>), were analytical grade reagents from the Sinopharm Chemical Reagent Company and used as starting materials without further purification.

### 2.2. Synthesis of zinc ferrite

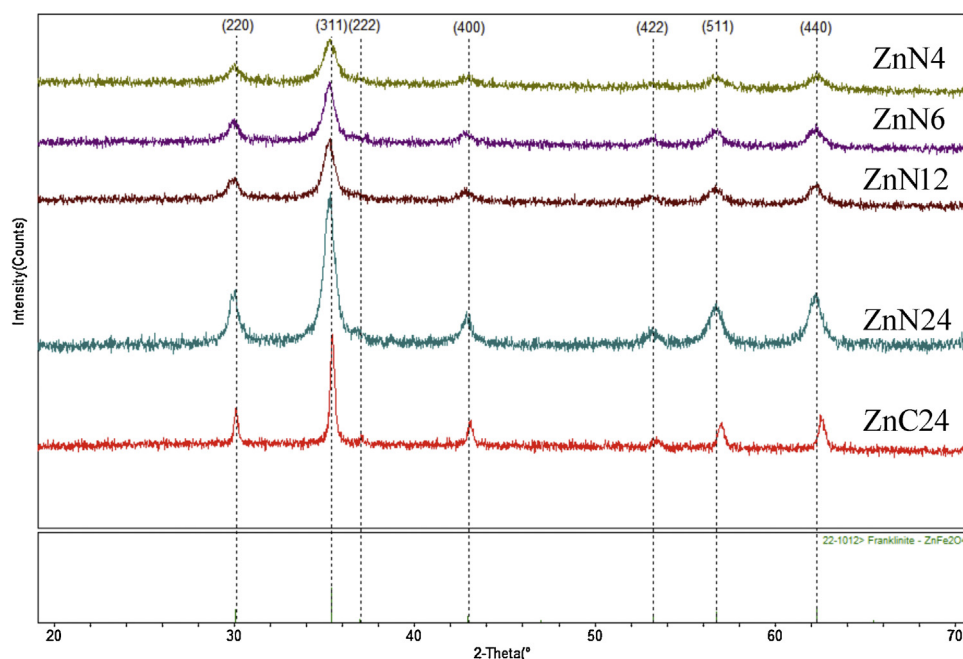
In a typical experiment, 6.0 mmol Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 12.0 mmol Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were dissolved in 50 mL of anhydrous ethylene glycol. Then, 18.0 mmol CH<sub>3</sub>COONa was added into the solution. The whole mixture was stirred vigorously for 5 min to give a homogeneous solution. Subsequently, the solution was transferred into a 50 mL teflon-lined stainless steel autoclave, heated to 200 °C with about a rate of 5 °C/min, and maintained at 200 °C for 24 h. Afterwards, the autoclave was allowed to cool down to room temperature naturally, and the resulting black zinc ferrite was produced. The precipitate obtained by magnetic separation was washed with distilled water and anhydrous ethanol several times, and dried under vacuum at 50 °C for 24 h. 0.01 g of

the resulting sample can be stably dispersed into 20 mL of deionized water as shown in the Supporting information as S1.

Different samples named as ZnN12, ZnN6, and ZnN4 were synthesized at 200 °C for 12, 6, and 4 h, respectively, where Zn represented the zinc ferrite, N the nitrate as reactant, and 12, 6, and 4 experimental intervals. A sample named as ZnC24 was synthesized at 200 °C for 24 h, where chlorates (FeCl<sub>3</sub> and ZnCl<sub>2</sub>) were used as the reactants. The experimental conditions are listed in Table 1.

### 2.3. Characterization

X-ray powder diffraction (XRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The  $2\theta$  range used in the measurement was from 10 to 70°. Standard and high-resolution transmission electron microscopy (TEM and HRTEM) measurements were performed on a JEOL-2010 TEM at an acceleration voltage of 200 kV. Samples were first ultrasonically dispersed in absolute alcohol and drop-cast onto copper grids. The metal ion concentration was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Optima 7300 DV (PerkinElmer). The chemical compositions of the MNPs were determined by the dissolution of 0.2200 g of the sample in 10 mL of 28 wt% HCl solution, followed by the diluting it to 1000 mL. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo VG Thermo Scientific Escalab 250 fitted with a monochromatized X-ray Al K $\alpha$  (1486.8 eV) source. A 150 W X-ray spot of 500  $\mu\text{m}$  in diameter



**Fig. 1.** XRP patterns of the samples.

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