Preparation and performance of CuFe$_2$O$_4$ and ZnFe$_2$O$_4$ magnetic nanocrystals

Q G Jia$^{1,2,*}$, S H Liang$^1$ and Q X Wang$^3$

$^1$ Xi’an University of Technology, Xi’an, Shaanxi, 710048, People’s Republic of China
$^2$ Xi’an Engineering Technologies Co., Ltd, Xi’an, Shaanxi, 710018, People’s Republic of China
$^3$ Southwest Jiaotong University, Chengdu, Sichuan, 712000, People’s Republic of China

* Author to whom any correspondence should be addressed.
E-mail: jiacrack@163.com

Keywords: inorganic compounds, heat treatment, magnetic properties.

Abstract
Based on the coprecipitation of FeSO$_4$(NH$_4$)$_2$SO$_4$ with CuCl$_2$ and ZnSO$_4$, CuFe$_2$O$_4$ and ZnFe$_2$O$_4$ nanocrystals were successfully synthesized. The morphology and the crystal structures of the nanoparticles were studied via SEM, TEM and XRD, which showed that MFe$_2$O$_4$ samples were formed aggregated nanoparticles with crystal sizes of 16 $\sim$ 20 nm with a narrow dispersion in size. The samples had the typical spinel structures. Magnetic analyses demonstrated that the CuFe$_2$O$_4$ sample had the saturation magnetization ($M_s$) of 10.10 emu g$^{-1}$ with the coercivity of 92.18 Oe, while the ZnFe$_2$O$_4$ sample had the $M_s$ of 8.27 emu g$^{-1}$ with the coercivity of 25.42 Oe at room temperature, respectively.

1. Introduction
The spinel ferrites of AB$_2$O$_4$ have great application in the supercapacitors [1, 2], photocatalysis [3, 4], sensors [5, 6], biomedical applications [7, 8]. The most common combination is A site metal ions are Cu$^{2+}$, Zn$^{2+}$, Ni$^{2+}$ and B site are Fe$^{3+}$, Al$^{3+}$, respectively [9].

Nanoscale ferrite particles have unique optical, electrical, and magnetic properties dependent on their particles size, shape, and dispersion. Many methods e.g., co-precipitation, sol–gel, solid state reaction, microwave and hydrothermal methods have achieved nano/micro structures ZnFe$_2$O$_4$ [10–13] and CuFe$_2$O$_4$ [14, 15] with virous size and shape. However, the expensive and complicated procedure, high reaction temperature can limit its large synthesis. A simple and low-cost route to obtain nanocrystalline MFe$_2$O$_4$ is still important for its application.

It has been reported, the MFe$_2$O$_4$ microstructure assembled by nanoparticles will have more excellent performance in magnetically induced drug delivery, magnetothermal therapy and catalysis at specific sites, which is also vital for applications in various fields [16]. Askari et al. [17] synthesis the rGO on ZnFe$_2$O$_4$ and studied the microstructure of materials on their properties in charge storage. The results show that it was needed to devise nanostructure for specific morphology.

Therefore, it is of great scientific significance to develop a ferrite microstructure with simple preparation process and self-assembly by nanoparticles. The eco-friendliness, and low-cost coprecipitation method is the best choice.

In this work, the nanoparticles of 20 nm were used to form the rod-like CuFe$_2$O$_4$ by self assembly, and cubic-like ZnFe$_2$O$_4$ was obtained by self assembly with nanoparticles of 16 nm via a simple one-step precursor coprecipitation obtained at 300 °C for 1 h. The magnetic properties of rod-like CuFe$_2$O$_4$ and cubic-like ZnFe$_2$O$_4$ are studied.

2. Experimental

2.1. Materials
In this paper, the MFe$_2$O$_4$ was prepared by the coprecipitation process with CuCl$_2$·2H$_2$O ($\geq$99%, Xi’an chemical reagent factory), ZnSO$_4$·7H$_2$O ($\geq$99%, Xi’an chemical reagent factory), FeSO$_4$(NH$_4$)$_2$SO$_4$·6H$_2$O ($\geq$99%, Xi’an...
chemical reagent factory) and H2C2O4·2H2O (>99.5%, Tianjin chemical reagent factory) as the starting materials.

2.2. Synthesis procedure
In a typical process, FeSO4·(NH4)2SO4·6H2O (10 mmol), CuCl2·2H2O (5 mmol), and ZnSO4·7H2O (5 mmol) were first added into 20 ml of de-ionized water under vigorous stir at room temperature for 40 min to get a well-dissolved solution. Then, 30mL of 0.5 M H2C2O4 solution was mixed to the above solution to obtain the solid precursor. The precipitation was collected by filtration and washed with de-ionized water and ethanol for several times. The sample was dried in air at 60 °C. To transfer from the precursor solid to the product, the dried precursor was heated in air at 300 ~ 500 °C for 1 h with a heating rate of 10 °C/min.

2.3. Characterization
The thermogravimetric-differential thermal analysis (TG-DTA) was used to tested the thermal decomposition and weight loss of the products by (Pyris Diamond TG-DTA, Perkin Elmer Instrument, USA). The crystal phases of the precursor and the product particles were measured by x-ray Diffraction (XRD) using an x-ray diffractometer (Rigaku D/Max-IIIC, Japan) with Cu-Kα radiation (λ = 0.15406 nm). The microstructure of the calcined products were characterized by scanning electron microscopy (SEM, JSM-6700F, JEOL, Japan) and the transmission electron microscopy (TEM, JEM-3010, JEOL, Japan). The magnetic properties of the products were tested by a vibrating sample magnetometer (VSM, VSM 7403, Lake Shore, USA). Moreover, the MeH loop was subtracted as the background signal to get the substrate contribution.
3. Results and discussion

3.1. XRD and FESEM analysis of MFe₂O₄ precursors

XRD was used to characterize the MFe₂O₄ precursor powders. Figure 1(a) shows the XRD pattern of the precursor powders for copper compound, which was identified as the CuC₂O₄·H₂O (JCPDS NO: 21–0297) and FeC₂O₄·2H₂O (JCPDS NO: 23–0293). Figure 1(b) shows the XRD pattern of zinc compound precursor powder, which was formed with ZnC₂O₄·2H₂O (JCPDS NO: 25–1029) and FeC₂O₄·2H₂O (JCPDS NO: 23–0293).

The microstructure of the ferrite precursor powders was observed by SEM. Figures 2(a) and (b) show the rod-like morphology of the CuFe₂O₄ precursor with an average diameter of 1.0 ~ 4.0 μm and a length of 6.0 ~ 8.0 μm. Figures 2(c) and (d) show the cubic morphology of the ZnFe₂O₄ precursor with the size of 5.0 μm.

---

Figure 2. SEM micrographs of the MFe₂O₄ precursor powders. (a), (b) CuFe₂O₄ and (c), (d) ZnFe₂O₄.

Figure 3. TG-DTA curve of the obtained (a) CuFe₂O₄ and (b) ZnFe₂O₄ precursor.
3.2. Thermal behavior

The thermal behavior was obtained by the TG-DTA analysis in the air with a fixed heating rate of 5 °C min⁻¹, shown in figures 3(a) and (b). The DTA curve of the sample shows the exothermic peaks at around 178 and 184 °C which correspond to the sharp weight losses on the TG line, which maybe possibly the removal of water trapped in the precursors. The DTA curve also shows the endothermic peaks at around 258, 295 and 243 °C on the TG line. These high-temperature peaks are probably associated with the thermal decomposition of oxalic acid salt. From figure 3(b), no more weight was lost above 300 °C, showing that the decomposition for precursor was completed at 300 °C with the formation of crystalline MFe₂O₄ product.

3.3. XRD and FESEM studies of MFe₂O₄

The products calcined in air at temperatures of 300, 400 and 500 °C for 1 h were measured by XRD as seen in figures 4 and 5, respectively. Figure 4(a) shows the XRD pattern for the CuFe₂O₄ sample, which indicates a distorted cubic structure assigned to the cubic CuFe₂O₄ spinel (JCPDS NO: 25–0283). The impurity phases of monoclinic CuO (JCPDS NO: 65–2309) is found in the CuFe₂O₄ samples calcined at 300 °C. The refinement plot represented by the 300 °C sample can be seen in figure 4(b), shows the wt% of CuFe₂O₄ is 84.5% and CuO is 15.5%. As the calcine temperature of sample at 400 °C, the impurity phases of rhombohedral α-Fe₂O₃ (JCPDS NO: 33–0664) and monoclinic CuO were also found in the CuFe₂O₄ samples. The remaining CuO phase and α-Fe₂O₃ phase were obtained with the higher temperature of 500 °C. The results showed that α-Fe₂O₃ and CuO could be formed via the decomposition of CuFe₂O₄ as the annealing temperature increased. The formation of ZnFe₂O₄ (JCPDS NO: 65–3111) is shown in figure 5(a). Less α-Fe₂O₃ (JCPDS NO: 39–1346) was observed in ZnFe₂O₄ sample after calcined at 300 °C–500 °C. The refinement plot represented by the 300 °C sample can be seen in figure 5(b), shows the wt% of ZnFe₂O₄ is 84% and Fe₂O₃ is 16%. Moreover, CuO and ZnO also appeared...
in the CuFe$_2$O$_4$ and the ZnFe$_2$O$_4$ as the impurities phases, respectively. From XRD peak broadening, the crystallite size of the products were calculated to be 20 nm and 16 nm, respectively, based on Scherrer’s law. The lattice parameters were also determined using the diffraction angles corresponding to specific crystal planes of the spinel-type structures.

The morphologies of the CuFe$_2$O$_4$ samples were observed by SEM. Figure 6 shows the microstructure which is affected by the calcination temperature. The SEM images shown in figures 6(a)–(f) correspond to the CuFe$_2$O$_4$ products obtained at 300, 400 and 500 °C, respectively. The CuFe$_2$O$_4$ powder calcined at 300 °C consist of rod-like grains with an average diameter of 1.0 ∼ 4.0 μm and a length of 6.0 ∼ 8.0 μm. The microstructure of CuFe$_2$O$_4$ samples calcined at 400 and 500 °C were identical. Figure 7 shows the microstructure of ZnFe$_2$O$_4$ samples. The SEM images in figures 7(a)–(f) correspond to the ZnFe$_2$O$_4$ samples obtained at 300, 400 and 500 °C, respectively. The ZnFe$_2$O$_4$ sample calcined at 300 °C is formed by cubic-like grains with an average size of 1.0 ∼ 5.0 μm. However, nonuniform grain sizes were also prepared in the samples obtained at 400 and 500 °C. Some agglomerations with fine particles were observed in the sample obtained at 300 °C. Moreover, the grain size was largely influenced by the calcination temperature.

3.4. TEM studies of MFe$_2$O$_4$

The morphologies and the structures of the CuFe$_2$O$_4$ and ZnFe$_2$O$_4$ samples calcined at 300 °C were further observed by TEM, shown in figures 8 and 9. The SAED shows the disk pattern with the radius corresponding to a few hundred nanometers. The SAED and micro-XRD of the crystal prove the symmetry of the crystal lattice, which can be used to calculate the interplanar distances by Bragg’s law. All the powders were polycrystalline formed by lots of tiny single crystals based on the XRD results of figure 4(a). The diffraction patterns of those samples were formed with the superposition of diffraction spots from each crystal. A series of concentric rings
were formed due to the randomly oriented crystals. Moreover, the family of planes with the same interplanar spacings was reflected by each ring. The TEM images of the CuFe$_2$O$_4$ are shown in figures 8(a)–(d), with a rod-like structure composed of small particles with an average size of 20 nm. High-resolution structure characterization was done by HRTEM. Figure 8(e) shows the single nanoparticle marked with a rectangular box in figure 8(d). An enlarged image shows that the outer of a nanoparticle is crystallized. The 0.296 nm interval of the lattice fringe observed in the image agrees well with the spacing of the (220) planes of the cubic CuFe$_2$O$_4$ structure. The agglomeration of fine particles of the CuFe$_2$O$_4$ samples may result by different values of particle size which were established by XRD and TEM techniques. The corresponding SAED patterns of the CuFe$_2$O$_4$ samples in figure 8(f) reveal the polycrystalline spinel structure. The results confirmed that both samples had the cubic structure of the CuFe$_2$O$_4$, consistent with the powder XRD patterns in figure 5(a).

The TEM images of ZnFe$_2$O$_4$ samples calcined at 300 °C are shown in figure 9. Fine pellet with the size of 16 nm were observed. HRTEM images shown in figure 9(e) were done from a single nanoparticle which confirmed that the particle is crystallized. The 0.295 nm interval of the lattice fringe was observed in the image which agreed well with the spacing of the (220) planes of the cubic ZnFe$_2$O$_4$ structure. The SAED patterns of the ZnFe$_2$O$_4$ sample in figure 9(f) show the spotty ring patterns, revealing the polycrystalline spinel structure.
3.5. Magnetic measurements

The magnetic properties of prepared MFe₂O₄ samples calcined at 300 °C for 1 h were investigated by the VSM technique under an applied field of ±30 kOe at room temperature (25 °C). Figure 10(a) (a’) was the partial enlarged view of (a) and b (b’) was the partial enlarged view of (b) show the specific magnetization field dependence of CuFe₂O₄ and ZnFe₂O₄ products with ferrimagnetic behavior. However, most spinel ferrites are cubic, but there were some exceptions like CuFe₂O₄ and ZnFe₂O₄ which could have two types: tetragonal and cubic unit cell, determined by the conditions of heat treatment. Moreover, at room temperature, the tetragonal phase with an inverse spinel is stable. Both the tetrahedral and the octahedral sites with the Fe³⁺ ions are almost the equal amounts. However, for the Cu²⁺ ions, they only occupy the octahedral sites, which leads to the tetragonal distortion because of the cooperative Jahn-Teller effect [18]. This CuFe₂O₄ sample had the Ms of 10.10 emu g⁻¹ with the coercivity of 92.18 Oe, Meanwhile, the ZnFe₂O₄ sample had the Ms of 8.27 emu g⁻¹ with the coercivity of 25.42 Oe at room temperature. Sun [19] and Stewart [20] had reported the super-paramagnetic characteristic of a similar sample with a particle size of about 10 nm. The higher Ms value of the ceramic bulk sample with respect to the powder products is because of the lower surface-to-volume ratio. Moreover, the distribution of Cu²⁺ between the octahedral and tetrahedral sites can also influence the magnetization.
3.6. Growth mechanism for MFe$_2$O$_4$ nanocrystalline powders

In this paper, direct thermal decomposition reaction of FeC$_2$O$_4$·2H$_2$O with ZnC$_2$O$_4$·2H$_2$O and CuC$_2$O$_4$·2H$_2$O in an oven, was used to prepare the CuFe$_2$O$_4$ and ZnFe$_2$O$_4$, respectively. The chemical reaction for syntheses of CuFe$_2$O$_4$ and ZnFe$_2$O$_4$ can be expressed as follows:

$$
\text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \downarrow
$$

(1)

$$
\text{Cu}^{2+} + \text{C}_2\text{O}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CuC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \downarrow
$$

(2)

Figure 8. TEM images of (a) CuFe$_2$O$_4$ calcined at 300 °C for 1 h. (a)–(c) TEM; (d)∼(e) HRTEM; (f) SAED.
This reaction, according to the TEM and SEM images, indicates that the growth process of rod-like CuFe$_2$O$_4$ and the cubic-like ZnFe$_2$O$_4$ structure may be determined by the second step. In the first step, the C$_2$O$_4^{2-}$ was added to the solution containing Fe$^{2+}$, Cu$^{2+}$, and Zn$^{2+}$ to form FeC$_2$O$_4$·2H$_2$O, CuC$_2$O$_4$·2H$_2$O, and ZnC$_2$O$_4$·2H$_2$O precipitation (equations (1)–(3)). After that, the CuFe$_2$O$_4$ and ZnFe$_2$O$_4$ could be prepared by the
decomposition of $\text{FeC}_2\text{O}_4\cdot2\text{H}_2\text{O}$, $\text{CuC}_2\text{O}_4\cdot2\text{H}_2\text{O}$ and $\text{ZnC}_2\text{O}_4\cdot2\text{H}_2\text{O}$ in a solid reaction process (equations (4), (5)).

The model of synthetic process for rod-like $\text{CuFe}_2\text{O}_4$ is proposed in figure 11. In the beginning, the whole solution nucleated uniformly at room temperature. As the reaction progress, an increasing number nuclei were formed (figure 11(a)) with some of them aggregated together to get the primary rod-like structures (figure 11(b)). Finally, many rod-like structures were formed (figure 11(c)). The growth of the cubic-like $\text{ZnFe}_2\text{O}_4$ is shown in figure 12. At the early stage of reaction, homogeneous nucleation occurred in the solution at room temperature. As the progressing of reaction, more nuclei were also formed (figure 12(a)). With some of the aggregated, the primary cubic-like structures were formed (figure 12(b)). At last, many cubic-like crystals were obtained (figure 12(c)). The mechanism process is confirmed by the TEM images, as seen in figures 8 and 9. Those rods consisted of a large amount of small crystallites with the size of 16 and 20 nm.
This research indicates that to achieve the monodispersity of colloid, it is necessary to have a separated, rapid nucleation process, followed by the formation of crystal nucleus slowly with a narrow distribution in particle size \[21\]. According to the LaMer model \[22\] (figure 13), to obtain uniform monodisperse solid particles from the liquid phase, the degree of the supersaturation of the solute must be controlled. The secondary nucleation or the emergence of nucleation phenomenon during the grain growth process must be restricted as much as possible. With the precipitation growth process based on the 'outbreak of nucleation, slow growth' principle, the total number of particles was determined at the nucleation stage while the particle size is determined by the slow growth process. At the stage I in figure 13, the solute concentration \(C\) was accumulated but without crystal nucleus formation. When \(C\) reaches the minimum supersaturated concentration \(C_{\text{min}}\), needed for nucleation, the process enters the stage II (nucleation). After that, \(C\) is sharply decreased due to the fast consumption by the nucleation process. When \(C\) is less than the \(C_{\text{min}}\), the nucleation process is finished and the process enters the growth stage III until the concentration \(C\) is too low.

4. Conclusion

In summary, the rod-like CuFe\(_2\)O\(_4\) and cubic-like ZnFe\(_2\)O\(_4\) were prepared by a simple thermal decomposition method. It is indicated that the preparation of the precursors is the key to obtaining rod-like and cubic-like microstructure. The samples are expected to be used in nanodevices with potential applications in large number of other nano material fields. Based on this, the microstructure and performance of rod-like CuFe\(_2\)O\(_4\) and cubic-like ZnFe\(_2\)O\(_4\) are investigating in more detail.
Acknowledgments

This work was financially supported by Natural Science Foundation of Shaanxi Provincial Department of Education(20JK0502).

Data availability statement

No new data were created or analysed in this study.

ORCID iDs

Q G Jia @ https://orcid.org/0000-0001-6672-1001

References

[1] Vadiyar M M, Bandgar S B, Kolekar S S, Chang J Y, Ling C Y, Ye Z B and Ghule A V 2019 ACS Appl. Energy Mater. 2 6693
[2] Zhang W, Quan B, Lee C D, Park S K, Li X H, Choe E J, Diao G W and Piao Y Z 2015 ACS Appl. Mater. Interfaces 7 2404
[3] Zhao W, Liang C, Wang B B and Xing S T 2017 ACS Appl. Mater. Interfaces 9 41927
[4] Li J N, Li X Y, Yin Z F, Wang X Y, Ma H F and Wang L Z 2019 ACS Appl. Mater. Interfaces 11 29004
[5] Zhou X, Li X W, Sun H B, Sun P, Liang X S, Liu F M, Hu X L and Lu G Y 2015 ACS Appl. Mater. Interfaces 7 15414
[6] Baldo T A, Lima L F, Mendes L F, Araujo W R, Paixão T R L C and Coltro W K T 2021 ACS Applied Electronic Materials 3 68
[7] Zhao N N, Yan L M, Zhao X Y, Chen X Y, Li A H, Zheng D, Zhou X, Dai X G and Xu F J 2019 Chem. Rev. 119 1666
[8] Shevale V B, Dhodamani A G, Delekar S D and Omega A C S 2020 5 1098
[9] Zhu X S, Cao C X, Su C S B, Xia A L, Zhang H Y, Li H L, Liu Z Y and Jin C G 2021 Ceram. Int. 47 15173
[10] Li L, Bi H, Gao S H, He F, Gao P, Dai Y, Zhang X, Yang D, Zhang M and Yang P 2017 Sci. Rep. 7 43116
[11] Zhu M, Zhang X, Zhou Y, Zhao C, Huang J and Li S 2015 RSC Adv 5 39270
[12] Guo X, Zhu H J, Si M S, Jiang C J, Xue D S, Zhang Z H and Li Q 2014 The Journal of Physical Chemistry C 118 30145
[13] Ai J P, Hu L L, Zhou Z H, Cheng L H, Liu W J, Su K Y, Zhang R B, Chen Z Q and Li W K 2020 Ceram. Int. 46 11786
[14] Huang Z B, Zhu Y, Wang S T and Yin G F 2006 Crystal Growth & Design 6 1931
[15] Zhu M Y, Meng D H, Wang C J and Diao G W 2013 ACS Appl. Mater. Interfaces 5 6030
[16] Sarkar K, Mondal R, Dey S, Kumar S and Physica B 2020 Condensed Matter 583 41205
[17] Askari M B, Salarizadeh P, Seifi M, Zadeh M H R and Bartolomeo A D 2021 J. Alloys Compd. 860 158497
[18] Laokul P, Amornkitbamrung V, Saraphin S and Maensiri S 2011 Curr. Appl. Phys. 11 101
[19] Sun Y Y, Wang W Z, Zhang L, Sun S M and Gao E P 2013 Mater. Lett. 98 124
[20] Stewart S J et al 2007 Requejo, Physica B 389 155
[21] Murray C B, Kagan C R and Bawendi M G 2000 Annu. Rev. Mater. Sci. 30 545
[22] Sugimoto T 2001 Monodispersed Particles. (Amsterdam: Elsevier Science B.V)