

# One-pot production of copper ferrite nanoparticles using a chemical method

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Abstract Copper ferrite nanoparticles were synthesized via the oxidation of precipitates obtained from the reaction of FeCl<sub>2</sub>, CuSO<sub>4</sub> and N<sub>2</sub>H<sub>4</sub> in the presence of gelatin. These copper ferrite particles were subsequently examined using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and Mössbauer spectroscopy. The average size of the copper ferrite nanoparticles was less than 5 nm, and they exhibited superparamagnetic behavior as a result of their small size. The low temperature Mössbauer spectrum exhibited three sets of sextets, two corresponding to the tetrahedral and octahedral sites of the copper spinel structure and one with small hyperfine magnetic field corresponding to the surface or defects of the nanoparticles. When the ratio of copper salt was increased, the tetrahedral site became preferable for copper, and metallic copper and copper ferrite were both present in a single nanoparticle.

Keywords Copper ferrite nanoparticle · One-pot production · Chemical method · Gelatin

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#### **1** Introduction

Spinel ferrites with the general formula MFe<sub>2</sub>O<sub>4</sub> (M = Cu, Mn, Mg, Zn, Ni, Co, etc.) have remarkable magnetic, catalytic, optical, and electrical properties [1]. In particular, copper ferrite (CuFe<sub>2</sub>O<sub>4</sub>) is an important material for understanding the behavior of all spinel ferrites. The structure of copper ferrite is a cubic close-packed arrangement of oxygen ions with Cu<sup>2+</sup> and Fe<sup>3+</sup> ions in two different sites, vis. tetrahedral (A-site) and octahedral (B-site) oxygen coordination [2]. The structure is neither the spinel nor the inverse spinel structure, but is a disordered structure containing both types of ions in both types of sites [3].

Nanosized copper ferrites have potential for applications in a wide variety of fields, including catalysis [4], cell labeling [5], gas sensing [6], and electrochemistry [7]. Smaller particles are expected to act more efficiently in such applications due to their higher specific surface areas, so it is desirable to obtain very small nanoparticles. Although various methods have been reported for the synthesis of copper ferrite nanoparticles, these methods suffer from disadvantages such as the requirement for a high temperature annealing processes. Research has also shown that polypeptides, in particular a native polypeptide gelatin, can serve as efficient stabilizing reagents for various nanoparticles [8].

In the present study, we examined the preparation of small copper ferrite nanoparticles (<5 nm diameter) stabilized with gelatin under an ambient atmosphere at room temperature. The structures and magnetic properties of these products were analyzed using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and Mössbauer spectroscopy.

#### 2 Experimental

Copper ferrite nanoparticles were prepared with initial Cu/Fe molar ratios of 3/7 mmol and 7/3 mmol. FeCl<sub>2</sub> and CuSO<sub>4</sub> were reduced with hydrazine in the presence of sodium tartrate and gelatin [8]. FeCl<sub>2</sub>·2H<sub>2</sub>O, CuSO<sub>4</sub>·5H<sub>2</sub>O, sodium tartrate (10 mmol), and 400 mg of gelatin were dissolved in 50 mL of pure water. The pH was then adjusted by adding NaOH. The solution was left to stand for 10 min in order to dissolve the reagents completely, after which 15 mL of a 10 M aqueous N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O solution was added slowly dropwise while ultrasonicating the mixture. The obtained precipitates were collected by centrifugation and rinsed with water. The precipitate was then dried in a vacuum desiccator. The product samples were characterized using TEM (JEOL, JEM-2100, operated at 200 kV), XRD (Rigaku, RINT2500, operated at 50 kV/100 mA), and Mössbauer spectroscopy (<sup>57</sup>Co/Rh source).

#### 3 Results and discussion

Two samples were synthesized from initial Cu/Fe ratios of 3/7 and 7/3. Based on the typical TEM images and particle size (diameter) distributions shown in Fig. 1 for both samples, spherical nanoparticles with diameters of less than 5 nm were predominantly obtained, and the size distributions were relatively narrow. The particle sizes of both samples were almost unchanged with the change in the Cu/Fe ratio.

Figure 2 shows XRD patterns of both prepared samples, in which peaks of metallic copper (JCPDS Card No. 4-0836) and copper ferrite (JCPDS Card No. 34-0425) were observed. The copper ferrite peaks were broad, which indicates that the crystallite size of the samples was small. In addition, the copper ferrite peaks were broader and the intensities of the metallic copper peaks were higher for the sample prepared with a Cu/Fe molar ratio of 7/3.This



Fig. 1 TEM images and particle size distributions of copper ferrite nanoparticles prepared with Cu/Fe molar ratios of **a**, **c** 3/7 and **b**, **d** 7/3





**Fig. 3** Mössbauer spectra of copper ferrite nanoparticles (Cu/Fe molar ratio = 3/7) measured at 293 and 19 K



result indicated that the reduction of the copper ferrite crystallite size was dependent on the amount of copper salt. Despite the difference in crystallite size for both samples elucidated from the XRD patterns, our TEM observations indicated that the particle sizes of the two samples were almost the same.

However, the XRD patterns of the samples could not be completely confirmed, because copper ferrite and other iron oxides such as magnetite have very similar patterns. Therefore, further characterization was performed using Mössbauer spectroscopy to distinguish the samples. Mössbauer spectra of the sample prepared with a Cu/Fe molar ratio of 3/7 were acquired at 293 and 19 K (Fig. 3), and the parameters obtained are summarized in Table 1. The spectrum acquired at 293 K exhibited a doublet, which was attributed to the superparamagnetic behavior of the small nanoparticles. The Mössbauer spectrum of the same sample at 19 K exhibited three sets of sextets, because the superparamagnetism of the specimen was no longer present at this low temperature. Two of the sets correspond to the tetrahedral (i) and octahedral (ii) sites of the copper spinel structure [2], and the other sextet with a small hyperfine magnetic field and broad linewidth (iii) may be attributed to Fe<sup>3+</sup> ions at the interface of nanostructured copper ferrite and/or to Fe<sup>3+</sup> ions surrounded by more vacancies (and/or Cu<sup>2+</sup> ions) [9]. The Mössbauer spectrum of magnetite generally shows two clear hyperfine magnetic splittings due to the mixed valence state of the magnetite structure, which corresponds to the tetrahedral ( $Fe^{3+}$ ) and octahedral sites ( $Fe^{2+}$  and  $Fe^{3+}$ ). However, the hyperfine magnetic splittings in the copper ferrite sample are smaller than that for magnetite, which indicates that Cu<sup>2+</sup> cations are present in the spinel structure. While the isomer shift for octahedral  $Fe^{3+}$  is larger than that for tetrahedral  $Fe^{3+}$  in magnetite, it has been reported that the difference of isomer shifts for Fe<sup>3+</sup> in the two sites was small in nanosized copper ferrite at low temperature [2, 10].

ent	$\delta/\mathrm{mms}^{-1}$	$\Delta E_{\rm Q}/{\rm mms}^{-1}$	<i>H</i> /kOe	$\Gamma/{\rm mms^{-1}}$	Yields/%
CuFe <sub>2</sub> O <sub>4</sub>	0.35 (2)	0.53 (3)		0.47 (5)	
CuFe <sub>2</sub> O <sub>4</sub> (i)	0.46(1)	0.01 (1)	491 (1)	0.58 (5)	30.3
CuFe <sub>2</sub> O <sub>4</sub> (ii)	0.49(1)	0.04 (1)	517 (1)	0.65 (3)	35.4
CuFe <sub>2</sub> O <sub>4</sub> (iii)	0.47 (2)	-0.04 (3)	459 (3)	1.11 (5)	34.3
	cuFe <sub>2</sub> O <sub>4</sub> CuFe <sub>2</sub> O <sub>4</sub> (i) CuFe <sub>2</sub> O <sub>4</sub> (ii) CuFe <sub>2</sub> O <sub>4</sub> (iii)	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\frac{\delta/\text{mms}^{-1}}{\text{CuFe}_2\text{O}_4} \qquad \frac{\delta/\text{mms}^{-1}}{0.35 (2)} \qquad \frac{\Delta E_Q/\text{mms}^{-1}}{0.01 (1)}$ $\frac{\text{CuFe}_2\text{O}_4 (i)}{\text{CuFe}_2\text{O}_4 (ii)} \qquad \frac{0.46 (1)}{0.49 (1)} \qquad \frac{0.04 (1)}{0.04 (1)}$ $\frac{\text{CuFe}_2\text{O}_4 (iii)}{0.47 (2)} \qquad -0.04 (3)$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 1 Mössbauer parameters of copper ferrite nanoparticles prepared with a Cu/Fe molar ratio of 3/7 obtained at 293 and 19 K

Mössbauer spectra were also acquired at 293 and 19 K for the sample prepared with a Cu/Fe molar ratio of 7/3 (Fig. 4 and Table 2). The spectrum at 293 K also exhibited a doublet due to the superparamagnetic behavior of the small nanoparticles. The spectrum measured at 19 K was fitted into two sets of sextets. The spectral component having a larger hyperfine magnetic field (iv) corresponds to tetrahedral or/and octahedral sites, in which two sites were indistinguishable. The component of the surface or defects with the smaller hyperfine magnetic field (v) increased, which indicates that metallic copper and copper ferrite are both present in a single nanoparticle. These results are consistent with the peak broadening of the XRD patterns for the copper ferrite samples.

The obtained samples were not magnetite, as confirmed by the absence of  $Fe^{2+}$  components in the Mössbauer spectra of the samples.  $CuFe_2O_4$  has the greatest amount of Cu uptake with respect to the valences of Cu and Fe (Cu is only Cu<sup>2+</sup>, while Fe is mixed with  $Fe^{3+}$  and  $Fe^{2+}$ ). When the Cu/Fe ratio is 3/7, the presence of copper metal in the precipitate was evident from the XRD pattern, even though there was less Cu than Fe. However, there was no evidence of Fe metal from the XRD and Mössbauer measurements. These results indicate that Fe in the starting materials formed ferrite and the Cu uptake was less than that in the starting materials.

Goya et al. measured Mössbauer spectra of bulk and nanoparticles of copper ferrite [2]. The spectrum of the particles in the present work measured at 19 K and that of bulk copper ferrite measured at room temperature [2] were similar; the Mössbauer spectrum of bulk copper ferrite is composed of two partially resolved magnetic sextets due to  $Fe^{3+}$  in tetrahedral (A) and octahedral (B) sites. In addition, the ratio of the areal intensities from the present results was in agreement with that reported in the literature [2]. Furthermore, the Mössbauer parameters measured at 4.2 K for copper ferrite nanoparticles prepared by ball-milling [2] are in good agreement with those of the Cu/Fe = 3/7 sample in the present work. Assuming that the sample has an inverse spinel structure, the areal intensities of the Mössbauer spectrum indicated that almost all of the Cu<sup>2+</sup> ions occupied B sites, while the  $Fe^{2+}$  ions of magnetite occupied B sites. We believe that  $Fe^{2+}$  is exchanged for Cu<sup>2+</sup> at the B sites of magnetite.

Mössbauer spectra of the sample prepared with a Cu/Fe molar ratio of 7/3 indicated an increase of the surface or defects, although the signal-to-noise ratio of the Mössbauer spectra was not sufficient due to the interference of Cu atoms. It was reported that when the particle size became smaller, the areal intensity of A sites decreased, which indicated that A sites are more affected by ionic disorder than B sites [2]. This is in agreement with the smaller crystallite size of copper ferrite when the sample was prepared with a Cu/Fe molar ratio of 7/3; metallic copper and copper ferrite coexist in a single nanoparticle of the sample, even though the particle size determined from TEM observations was almost unchanged for the different Cu/Fe ratios.





Table 2 Mössbauer parameters of copper ferrite nanoparticles prepared with a Cu/Fe molar ratio of 7/3 obtained at 293 and 19 K  $\,$ 

Compone	ent	$\delta/\mathrm{mms}^{-1}$	$\Delta E_{\rm Q}/{\rm mms}^{-1}$	<i>H</i> /kOe	$\Gamma/{\rm mms^{-1}}$	Yields/%
293 K	CuFe <sub>2</sub> O <sub>4</sub>	0.36 (2)	0.53 (3)		0.57 (5)	
19 K	CuFe <sub>2</sub> O <sub>4</sub> (iv)	0.49 (2)	0.02 (4)	484 (2)	0.57 (10)	38.5
	CuFe <sub>2</sub> O <sub>4</sub> (v)	0.46 (1)	-0.05 (0)	449 (5)	1.09 (14)	61.5

### 4 Conclusions

Copper ferrite nanoparticles were successfully synthesized by the room temperature chemical reaction of FeCl<sub>2</sub> and CuSO<sub>4</sub> in the presence of gelatin. The resulting nanoparticles were spherical and less than 5 nm in diameter. Mössbauer spectra of the copper ferrite nanoparticles showed superparamagnetic behavior due to the small particle sizes. The Mössbauer spectrum measured at low temperature exhibited three sets of sextets because the superparamagnetism of the specimen was no longer present at this low temperature; two sets of sextets correspond to the tetrahedral and octahedral sites of copper spinel structure and the other sextet with small hyperfine magnetic field corresponds to the surface or defects of the nanoparticles. Furthermore, the Mössbauer spectrum of the sample prepared with an increased ratio of copper salt indicated that the tetrahedral sites are preferable for copper, and that metallic copper and the copper ferrite coexist in a single nanoparticle.

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