



# Mixture of silver and iron oxide nanoparticles produced by chemical methods

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**Abstract** A mixture of silver and iron oxide nanoparticles were synthesized by the reaction of  $\text{FeSO}_4$ ,  $\text{AgNO}_3$ , and  $\text{N}_2\text{H}_4$  in the presence of gelatin at room temperature. The silver/iron oxide nanoparticles were subsequently examined using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and Mössbauer spectroscopy. TEM observations revealed two distinct sizes of nanoparticles. The small nanoparticles with diameters of less than 10 nm were assigned to maghemite, and the large particles with diameters of approximately 20 nm were assigned to metallic silver. A Mössbauer spectrum of the maghemite nanoparticles at room temperature showed superparamagnetic behavior due to the small particle sizes. The Mössbauer spectrum measured at low temperature showed a magnetic sextet and a component of distributed hyperfine magnetic fields (DHMF). The DHMF component corresponded to the surface or defects of the maghemite nanoparticles. Silver enhanced the production of maghemite nanoparticles, and the size of the maghemite particles could be controlled by varying the amount of silver salt.

**Keywords** Silver/iron oxide nanoparticle · Chemical method · Gelatin

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## 1 Introduction

Magnetic nanoparticles are of significant interest because they have unique physical and chemical properties derived from size effects, including unusual crystal structures and magnetic behavior [1]. These nanoparticles have potential applications in a wide variety of areas, such as nanoelectronics and biomedicine-related fields involving drug delivery, hyperthermia, magnetic resonance imaging (MRI), and biosensing.

In addition, iron oxide composited with foreign metallic atoms is of interest because it is known to enhance the magnetic properties and stability [2]. In particular, silver/iron oxide nanoparticles have been extensively used due to their enhanced chemical reactivity, which results from the interactions between the two components [3, 4]. Although several studies have reported that silver/iron oxide nanoparticles are magnetite from X-ray diffraction (XRD) measurements, the samples could not be completely confirmed because magnetite and other iron oxides such as maghemite have very similar patterns. Therefore, it is necessary to conduct detailed Mössbauer spectroscopy measurements.

We have recently reported the preparation of magnetic nanoparticles, ferroxhyte  $\gamma$ -FeOOH, using a one-pot chemical method at room temperature [5], whereby magnetite particles were formed as precursors, and then rapidly oxidized in the air to produce ferroxhyte nanoparticles. More recently, we have reported the preparation of copper composited iron oxide nanoparticles at room temperature [6]. Mössbauer spectra of these nanoparticles indicate that  $\text{Cu}^{2+}$  cations are present in the spinel structure.

In the present study, we examined the preparation of a mixture of silver and iron oxide nanoparticles stabilized with gelatin under the ambient atmosphere at room temperature to determine the effects of silver on iron oxide nanoparticle formation. The structures and magnetic properties of these products were analyzed using powder XRD, transmission electron microscopy (TEM), and Mössbauer spectroscopy.

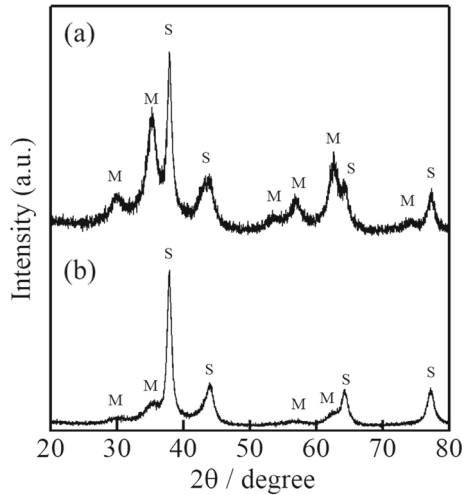
## 2 Experimental

Particles were prepared by a modified hydrazine reduction system under the ambient atmosphere at room temperature [5, 6]. Two silver/iron oxide nanoparticle samples, S1 and S2, were prepared with initial Ag/Fe molar ratios of 1/9 mmol and 2/8 mmol, respectively. In this synthesis, a mixture of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (iron(II) sulfate) and  $\text{AgNO}_3$  (silver(I) nitrate) (10 mmol of total metal salt), 10 mmol of  $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$  (sodium tartrate), and 400 mg of gelatin were dissolved in 50 mL of water. The pH of this solution was subsequently adjusted by the addition of 3 g of NaOH (sodium hydroxide). After 5 min, 15 mL of 10 M aqueous  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  solution was added slowly dropwise to the solution to dissolve the reagent completely under ultrasonication for 1.5 h. The precipitates obtained were collected by centrifugation, rinsed with water and ethanol, and 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/300 mA), and Mössbauer spectroscopy ( $^{57}\text{Co}/\text{Rh}$  source).

## 3 Results and discussion

Figure 1 shows XRD patterns of the two samples. The XRD patterns of both samples had the characteristic peaks of metallic silver (JCPDS Card No. 00-04-0783) and maghemite (JCPDS Card No. 00-025-1402). As the XRD patterns of maghemite and magnetite (JCPDS

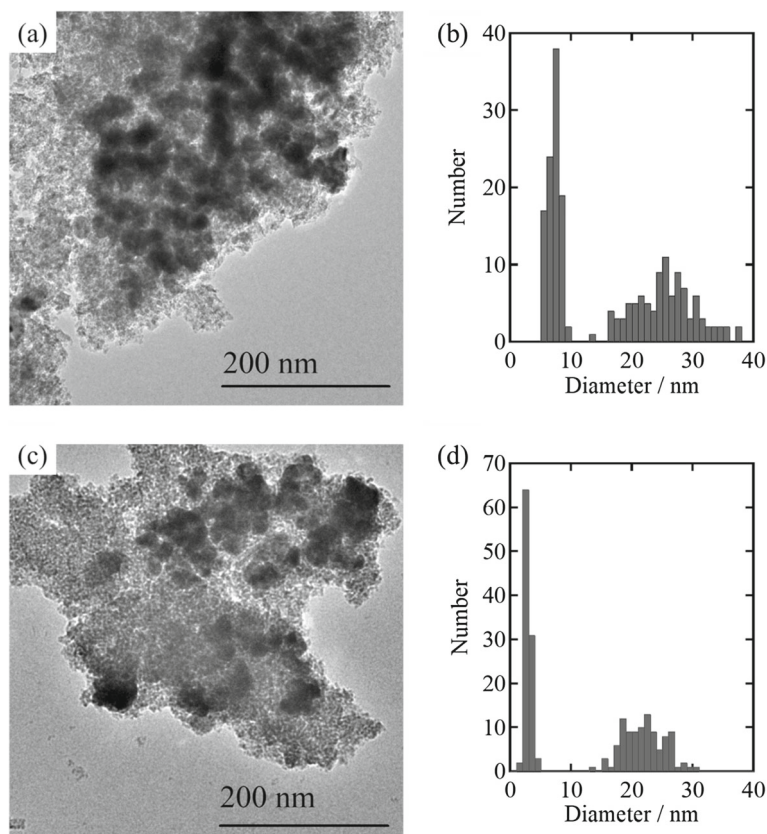
**Fig. 1** X-ray diffraction patterns of as-prepared samples (a) S1, and (b) S2 prepared with Ag/Fe molar ratios of 1/9 and 2/8, respectively. The labels S and M correspond to metallic silver (JCPDS Card No. 00-004-0783) and maghemite (JCPDS Card No. 00-025-1402)/magnetite (JCPDS Card No. 00-019-0629), respectively



Card No. 00-019-0629) are very similar to each other, they are difficult to distinguish from XRD patterns alone. Therefore, Mössbauer spectroscopy was employed, which, as shown later, indicated that the product was maghemite. Silver ferrite (JCPDS Card No. 00-021-1080 or 00-021-1081) was not observed in the XRD patterns. Silver metal and maghemite nanoparticles were obtained separately, and no  $\text{AgFeO}_2$  was produced by this synthetic method. While the peaks of maghemite were broad, which indicates small crystallite size, the peaks of metallic silver were sharp because the metallic silver consisted of large crystallites. The average sizes of metallic silver were estimated using the Scherrer equation to be 10 and 11 nm in S1 and S2, respectively. In addition, the peaks of maghemite in S2 were broader than those in S1. The average sizes of the maghemite nanoparticles were estimated to be 5 and 2 nm in S1 and S2, respectively. This result indicates that the maghemite crystallite size was reduced by the larger amount of silver salt, and that an intermediate species prior to oxidation in the air plays an important role in the formation of maghemite nanoparticles.

Figure 2 shows typical TEM images and distributions of particle diameter for both samples. Two distinct nanoparticle sizes were observed. The small nanoparticles with diameters of less than 10 nm were assigned to maghemite in consideration of the XRD results, and the large particles with diameters of approximately 20 nm were assigned to metallic silver. The metallic silver and maghemite nanoparticles existed separately due to their distinctly different sizes. The size of the maghemite nanoparticles in S2 (Fig. 2c and d) was smaller than that in S1 (Fig. 2a and b), and the size distributions were relatively narrow in the particles of S2, which is in agreement with the XRD results.

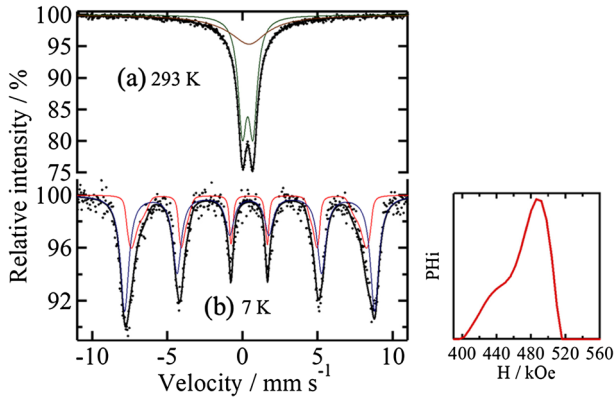
It is difficult to distinguish maghemite and magnetite solely from XRD patterns. Therefore, further characterization was performed using Mössbauer spectroscopy. Mössbauer spectra of the S1 sample were acquired at 293 K and 7 K (Fig. 3), and the parameters are summarized in Table 1. The spectrum acquired at 293 K was fitted into a combination of a doublet and a relaxation component, which indicates the superparamagnetic behavior of the small nanoparticles. Room-temperature (RT) Mössbauer spectra of maghemite nanoparticles with various sizes (10–60 nm) have been reported in the literature [7]; some magnetic sextets apart from the superparamagnetic components were observed, even for 10 to 20 nm maghemite nanoparticles. The Mössbauer spectra of the present maghemite nanoparticles did not reveal magnetic sextets at 293 K, which indicates that the particles were smaller than



**Fig. 2** TEM images and particles size distributions of samples (a,b) S1 and (c,d) S2

10 nm, and was in agreement with the size observed using TEM and that estimated from the XRD peak widths. The Mössbauer spectrum measured at 7 K was fitted into a combination of a sextet and a component with distributed hyperfine magnetic fields (DHMF); the specimen no longer exhibited superparamagnetism at low temperature. The relaxation time was estimated to be  $\tau = 0.3$  ns, assuming that it had the same hyperfine magnetic field ( $H = 516$  kOe) measured at low temperature. The Mössbauer parameters were comparable to those of maghemite nanoparticles with diameters of 6.8 nm reported in the literature (20 K, A:  $\delta = 0.40$  mm/s,  $\Delta E_Q = -0.021$  mm/s,  $H = 504$  kOe, B:  $\delta = 0.41$  mm/s,  $\Delta E_Q = 0.02$  mm/s,  $H = 524$  kOe and sextet:  $\delta = 0.36$  mm/s,  $\Delta E_Q = 0.004$  mm/s,  $H = 477$  kOe) [8]. Magnetite was not observed in the Mössbauer spectra. The DHMF component corresponded to surface atoms or defects of the maghemite particles [9].

Mössbauer spectra for sample S2 were also acquired at 293 K and 3 K (Fig. 4 to Table 2). The spectrum at 293 K had a doublet, and no relaxation component was observed; the size of the maghemite nanoparticles of this sample was smaller; therefore, the average relaxation time became shorter and all of the species showed a doublet. This tendency was in agreement with the sizes estimated by TEM observation and the XRD peak widths. In the spectrum measured at 3 K, the component of the surface showing DHMF increased, which indicates that the nanoparticles of S2 were smaller in size. Yoshida et al. referred to the



**Fig. 3** Mössbauer spectra of S1 obtained at (a) 293 K and (b) 7 K

**Table 1** Mössbauer parameters obtained at 293 K and 7 K for silver/iron oxide nanoparticles prepared with a Ag/Fe molar ratio of 1/9 (S1)

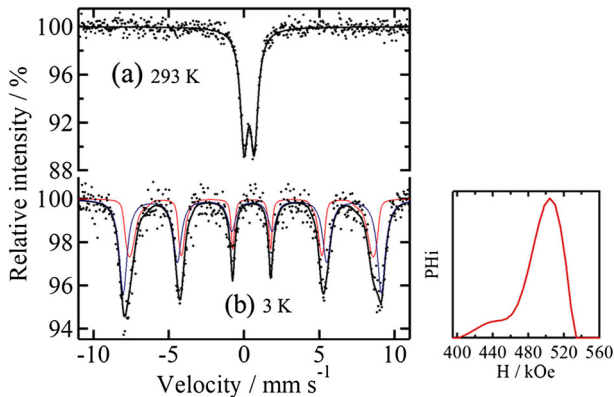
Component		$\delta/\text{mms}^{-1}$	$\Delta E_Q/\text{mms}^{-1}$	$H/\text{kOe}$	$\Gamma/\text{mms}^{-1}$	Yields/%
293 K	(i)	0.28(4)	-0.37(35)	516 <sup>a</sup>	0.99(45)	38.7
	(ii)	0.33(0)	0.71(1)		0.68(2)	61.3
7 K	(iii)	0.45(1)	0.02(1)	516(0)	0.68(2)	67.2
	(iv)	0.43(1)	-0.02(2)	486 <sup>b</sup>		32.8

<sup>a</sup> Relaxation time  $\tau = 0.3$  ns

<sup>b</sup> Hyperfine magnetic field at the mode of the distribution

Mössbauer parameters of maghemite with good crystallinity (4 K,  $H = 520$  and  $531$  kOe) [10]. The component with the larger hyperfine magnetic field in the present work had a similar value to that of large grained maghemite solid. It is generally considered that smaller particles exhibit smaller  $H$  values; therefore, it was unexpected that S2 (Fig. 4b) would have a larger  $H$  value than S1. Considering the difference in the diameters of the particles in S1 (5 nm) and S2 (2 nm), S2 particles were 2.5 times larger in terms of surface area per volume than S1; however, the areal intensities of DHMF in the Mössbauer spectra were almost the same for both samples. The difference in the Mössbauer spectra of the two samples was thus attributed to a difference of crystallinity. Although the size of maghemite nanoparticles in S2 is smaller, the crystallinity of the nanoparticles was largely without defects, which resulted in larger  $H$  values and a lower areal intensity of DHMF.

We have previously reported a similar synthetic procedure in the absence of silver [5], whereby magnetite nanoparticles were formed as precursors, and all of them were rapidly oxidized to feroxyhyte nanoparticles in the atmosphere. We have also reported a similar synthetic study using copper instead of silver [6]; copper ferrite was obtained because  $\text{Fe}^{2+}$  in the magnetite was substituted by  $\text{Cu}^{2+}$ , which prevented further oxidation of the nanoparticles. In the present case, metallic silver inhibits rapid oxidation of the precursor magnetite produced in solution, and the mild oxidation of magnetite in the atmosphere produces maghemite nanoparticles. Zhai et al. demonstrated that the Ag nanoparticles of  $\text{Ag-Fe}_3\text{O}_4$  hybrids are very stable due to the protection of magnetite nanoparticles, which may reduce



**Fig. 4** Mössbauer spectra of S2 obtained at (a) 293 K and (b) 3 K

**Table 2** Mössbauer parameters obtained at 293 K and 3 K for silver/iron oxide nanoparticles prepared with a Ag/Fe molar ratio of 2/8 (S2)

Component		$\delta/\text{mms}^{-1}$	$\Delta E_Q/\text{mms}^{-1}$	$H/\text{kOe}$	$\Gamma/\text{mms}^{-1}$	Yields/%
293 K	(i)	0.33(1)	0.67(1)		0.61(1)	
3 K	(ii)	0.52(1)	0.02(2)	531(1)	0.63(3)	61.3
	(iii)	0.49(1)	-0.01(2)	504 <sup>a</sup>		38.7

<sup>a</sup> Hyperfine magnetic field at the mode of the distribution

the oxidation of Ag cores and prevent aggregation by acting as a physical barrier [11]. In the present case, it is expected that the Ag-Fe<sub>2</sub>O<sub>3</sub> hybrid was obtained as a precursor, which prevented rapid oxidation. Therefore, magnetite was then oxidized into maghemite nanoparticles under mild conditions, so that the production of ferroxhyte was prevented. The Ag nanoparticles stabilized the maghemite nanoparticles, and the size and crystallinity of the maghemite nanoparticles could be controlled according to the amount of Ag nanoparticles.

## 4 Conclusions

Silver/maghemite nanoparticles were synthesized via a room temperature chemical reaction of FeSO<sub>4</sub> and AgNO<sub>3</sub> in the presence of gelatin. The sizes of the silver and maghemite nanoparticles were different; the small nanoparticles with diameters of less than 10 nm were assigned to maghemite and the large particles with diameters of approximately 20 nm were assigned to metallic silver (which were attached onto the maghemite nanoparticles). Mössbauer spectrum of the maghemite nanoparticles at room temperature exhibited superparamagnetic behavior due to the small particle sizes. The Mössbauer spectrum measured at low temperature showed a sextet and a DHMF component because the superparamagnetism of the specimen was no longer present at this low temperature. Smaller maghemite nanoparticles with improved crystallinity were obtained by synthesis from a starting mixture with a larger Ag/Fe ratio; Ag atoms in the Ag-Fe<sub>2</sub>O<sub>3</sub> precursor in solution induced mild oxidation to produce the maghemite nanoparticles.

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