J Mater Sci (2006) 41:7279–7282
DOI 10.1007/s10853-006-0952-4

Tuning of magnetite nanoparticles to hyperthermic thermoseed by controlled spray method

Dong-Hyun Kim · Kyoung-Nam Kim · Kwang-Mahn Kim · In-Bo Shim · Myung-Hyun Lee · Yong-Keun Lee

Received: 10 May 2005 / Accepted: 20 December 2005 / Published online: 24 October 2006

Abstract Magnetite nanoparticles with super-paramagnetic properties have great potential to achieve advances in fields such as hyperthermia, magnetic resonance imaging and magnetic drug targeting. In particular, magnetic particles less than 50 nm are easily incorporated into cells and generate heat under an alternating magnetic field by hysteresis loss. Various methods of preparing magnetic particles have attracted attention, such as spray pyrolysis, microwave irradiation of ferrous hydroxide, microemulsion technique and hydrothermial preparation technique. In this study, magnetite nanoparticles were synthesized with various molar ratio of Fe^{2+} and Fe^{3+} by coprecipitation using spray-guns and dropping syringe. Experiments at different molar concentrations of Fe ions were conducted, which shows the ideal molar concentration of Fe^{2+} to be 0.5 M for pure magnetite. Both in the spray and drop method, pure magnetite nanoparticles could be synthesized when the molar concentration of Fe^{2+} was 0.5 M. With increasing the molar ratio of Fe^{2+}, the particle size of the magnetite nanoparticles was increased. The smallest size could be reduced to approximately 7 nm by the spray method. The shape of the synthesized nanoparticles was nearly spherical. The calculated highest loss power by hysteresis losses was 597 W/g, generated with a molar concentration ratio of 0.5:1 (Fe^{2+}:Fe^{3+}).

D.-H. Kim · Y.-K. Lee (✉)
Research Center for Orofacial Hard Tissue Regeneration, Yonsei University College of Dentistry, Seoul 120-752, Korea
e-mail: leeyk@yumc.yonsei.ac.kr

K.-N. Kim · K.-M. Kim
Department and Research Institute of Dental Biomaterials and Bioengineering, Yonsei University College of Dentistry, Seoul 120-752, Korea

I.-B. Shim
Department of Electronic Physics, Kookmin University, Seoul 136-702, Korea

M.-H. Lee
Korea Institute of Ceramics, 233-5 Gasan-dong, Seoul 152-023, Korea

Introduction

Hyperthermia necrotizes tumors by heat application. The generation of thermal energy from the hysteresis losses of magnetite nanoparticles within an alternating magnetic field is expected to be a useful method for hyperthermic cancer treatment, since these nanoparticles can be targeted and confined to the cancer site [1]. Magnetite nanoparticles with super-paramagnetic properties have great potential to achieve advances in fields such as hyperthermia, magnetic resonance imaging and magnetic drug targeting. In particular, in vivo biomedical applications for hyperthermia using magnetite require the thermal energy from the hysteresis losses and a particle size of less than 50 nm [2]. These magnetic particles are easily incorporated into cells and generate heat under an alternating magnetic field by hysteresis loss [3]. Various methods of preparing magnetic particles have attracted attention, such as spray pyrolysis [4], microwave irradiation of ferrous hydroxide [5], microemulsion technique [6] and hydrothermial preparation technique [7]. Compared to above methods, controlled coprecipitation method have the advantages of the being relatively simple

Table 1 Properties of magnetite particles (A: spray method, B: drop method)

Fe^{2+}	Crystalline phases		Particle size, nm		Hc, kA/m		Ms, Am^2/kg		*Loss power (W/g)	
	A	B	A	B	A	B	A	B	A	B
0.05 M	Fe_3O_4 α-Fe_2O_3	Fe_3O_4 α-Fe_2O_3	7.6 (±3.8)	13.4 (±9.7)	5.8	2.2	17.8	6.6	25.0	38.1
0.1 M	Fe_3O_4 α-Fe_2O_3	Fe_3O_4 α-Fe_2O_3	8.5 (±4.2)	17.5 (±12.3)	5.0	0.4	18.6	25.0	28.2	42.3
0.5 M	Fe_3O_4	Fe_3O_4	10.8 (±4.9)	18.6 (±5.6)	6.6	3.3	68.8	58.8	597.0	224.0
1 M	Fe_3O_4	Fe_3O_4 α-Fe_2O_3	12.0 (±3.2)	21.8 (±7.3)	5.5	0.5	68.5	31.7	425.0	72. 6

* Calculated loss power per mass Fe_3O_4 for a field amplitude of 63.7 kA/m

and providing good control over particles properties. Synthesis technique of ceramics can produce fine, high purity, stoichiometric particles. Furthermore, if process conditions such as solute concentration, reaction temperature, reaction time and the type of solvent are carefully controlled, ceramic particles of the desired shape and size can be produced [8]. The magnetic properties and size of the magnetite nanoparticles also depend highly upon the synthetic procedure [9]. Therefore, synthetic methods for magnetite are important in making these effective hyperthermic thermoseeds. In this study, by varying the molar concentration of Fe^{2+} and Fe^{3+} either at spray or drop coprecipitation methods, the synthesis of magnetite was conducted for suitable hyperthermic thermoseed.

Materials and Method

Magnetite nanoparticles were prepared under various reaction conditions by coprecipitation of Fe^{2+} and Fe^{3+} in the presence of NaOH. Concentrations of the precursor solution and the coprecipitation method are two factors that control the properties of magnetite in this process. Forty millimeters of a mixed solution of Fe^{2+} and Fe^{3+} ions in a 1:2 molar ratio was prepared from $FeCl_3{\cdot}6H_2O$ (Sigma, USA) and $FeCl_2{\cdot}4H_2O$ (Sigma, USA) in a 0.5 M HCl solution. To verify the effect of Fe^{2+} molar concentration, samples were prepared by the addition of an aqueous mixture of $FeCl_2{\cdot}4H_2O$ (0.05–1 M) and $FeCl_3{\cdot}6H_2O$ (0.1–2 M) to a 1 M NaOH solution. When an aqueous mixture of $FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ was added to the 1 M NaOH solution, spray-guns (Gunpiece, Fuso Seiki Co. Ltd., Japan) and 5 ml syringe (21 G, Medi-Hut Int'l (Mfg). Co. Ltd., Korea) were employed in a coprecipitation system. The spray-coprecipitation system consists of four parts: spray-gun, homogenizer (~3500 rpm), reactor and N_2 carrier gas. Droplet size was measured in the syringes as well as in variously sized nozzles of the spray-gun by optical microscope (CK2 Olympus, Japan). Under an N_2 pressure of 25 psi, an aqueous mixture of Fe^{2+} and Fe^{3+} was sprayed into the NaOH solution and the stirring rate was simultaneously increased to 3000 rpm using the high-speed homogenizer. After the reaction, the beaker containing the suspension was placed on a permanent magnet. Black powders quickly settled on the bottom of the beaker. The supernatant was discarded and fresh water and ethyl alcohol were added to the beaker. This procedure was repeated several times until most of the ions in the suspension were removed. Dry powders were obtained by drying at 50 °C in a vacuum. The dropping method using 5 ml syringes was similar to the conventional coprecipitation method [10]. The structure of the precipitated powders was obtained by X-ray diffractometer (XRD; D/MAX Rint 2000, Rigaku, Japan) with Ni-filtered Cu-$k\alpha$ rays and was identified according to JCPDS. A vibrating sample magnetometer (VSM; 7300, Lakeshore, USA) was used to measure magnetic properties. Average size was estimated using Scherrer's formula and a transmission electron microscope (TEM; JEM 4010, JEOL, Japan).

Results

As shown in Table 1, the hematite phase appeared in 0.05 and 0.1 M samples of Fe^{2+}. Magnetite peaks resulting from the spray method were remarkable compared with the drop method. When the molar concentration of Fe^{2+} was 0.5 M in the spray and drop methods, pure magnetite particles could be synthesized. In the synthesis of iron oxide, the oxidation state of the Fe ions determined the crystalline phases. The oxidation condition in the reactor was controlled by the molar concentration of Fe^{2+}. Therefore, the pure magnetite was synthesized by oxidation when the concentration of Fe^{2+} was 0.5 M in this study.

Hysteresis loops of synthesized particles were shown in Fig. 1. In the case of the spray method, increasing the molar concentration of Fe^{2+} from 0.05 M to 0.5 M

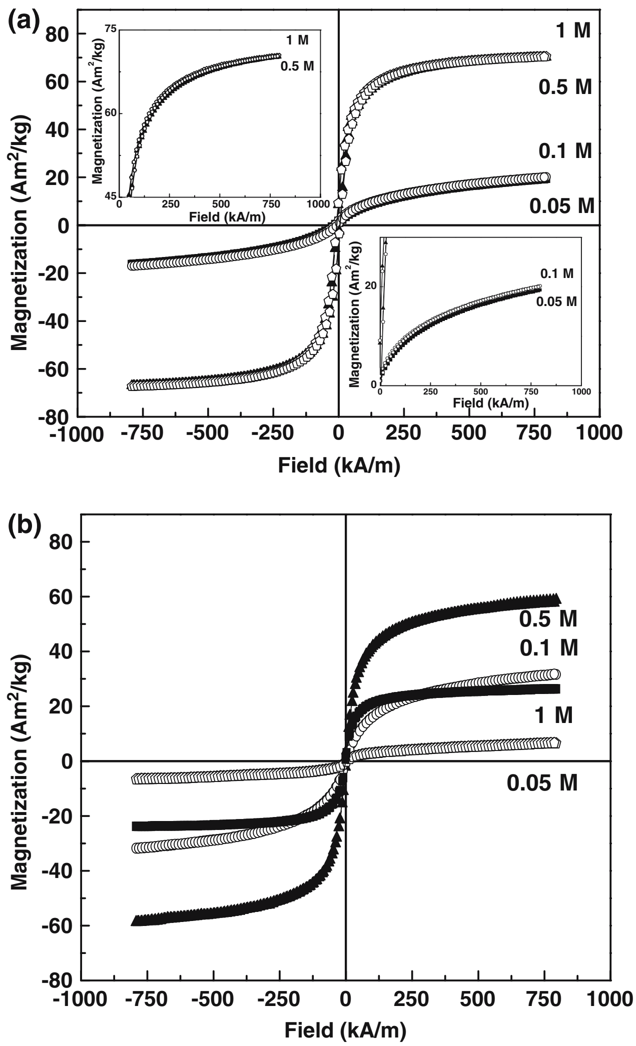

Fig. 1 Hysteresis loops of different molar concentration of Fe^{2+} by (**a**) spray method and (**b**) drop method

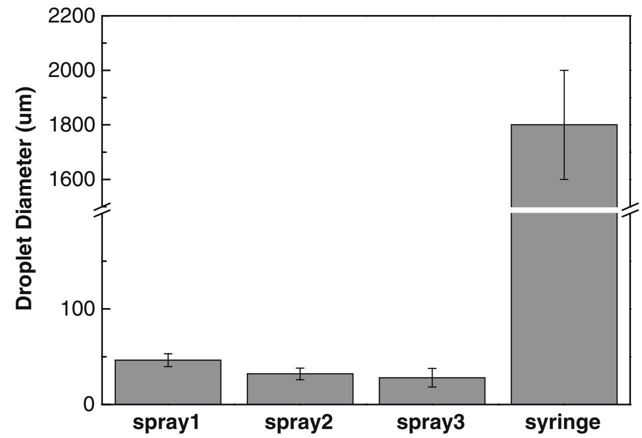

Fig. 2 Droplet size in different condition. spray1: nozzle area 2.865 mm^2; the pressure of N_2 carrier gas: 25 psi, spray2: 1.348 mm^2; 25 psi, spray3: 0.282 mm^2; 25 psi, syringe: 1.539 mm^2; dropping condition: in air

increased the magnetization saturation (Ms) to 68.84 Am^2/kg. The Ms was decreased by the emerged hematite phase at 0.05 and 0.1 M Fe^{2+}. When only the magnetite phase was formed by coprecipitation, the Ms was much higher than when mixed with the hematite phase. As the hyperthermic thermoseed, the exthothermic ability of synthesized magnetite was calculated from measured hysteresis losses [11]. We calculated that the highest loss of power from magnetite synthesized by the spray method (molar concentration of Fe^{2+} = 0.5) was 597 W/g.

As shown in Fig. 2, the droplet size of the syringe was greater than the droplet size of the spray-gun. The droplet size increased with the increasing nozzle size of the spray-gun. When the droplet size of the iron solution was decreased by adjusting the spray-gun, the average size was decreased from 13 ~ 22 nm to 8 ~ 12 nm in the syringe and spray 3. Figure 3 shows TEM images of coprecipitated particles from the spray and drop methods, respectively. The shape of the spray-coprecipitated particles was approximately spherical. A typical electron diffraction pattern obtained from the magnetite samples is shown in Fig. 3. The continuous concentric rings were presented in the particles synthesized via the spray method. The positioning of the rings corresponds to the crystalline structure of magnetite. The mean diameter of the spray-coprecipitated particles increased from 7.6 to 12 nm with an increase of the molar concentration of Fe^{2+} from 0.05 to 1 M. In the dropping method, particles size was increased to 21.8 nm with the increased the molar concentration of Fe^{2+}.

Discussion

According to chemical principles, Fe^{3+}/Fe^{2+} should be two after reduction (based on the theoretical ratio for stoichiometric Fe_3O_4). However, in practice, such as the concentrations of $FeCl_2$, $FeCl_3$ and NaOH may not be in the ideal ratio [12]. Experiments at different molar concentrations of Fe ions were conducted and the results are summarized in Table 1, which shows the ideal molar concentration of Fe^{2+} to be 0.5 M for pure magnetite. We synthesized controlled magnetite nanoparticles by the spray method. With this method, the particles size could be reduced to approximately 7 nm. The calculated highest loss power by hysteresis losses was 597 W/g, generated with a molar concentration ratio of 0.5:1 (Fe^{2+}:Fe^{3+}). Magnetite particles for effective hyperthermic thermoseeds were synthesized by a controlled spray-coprecipitation method.

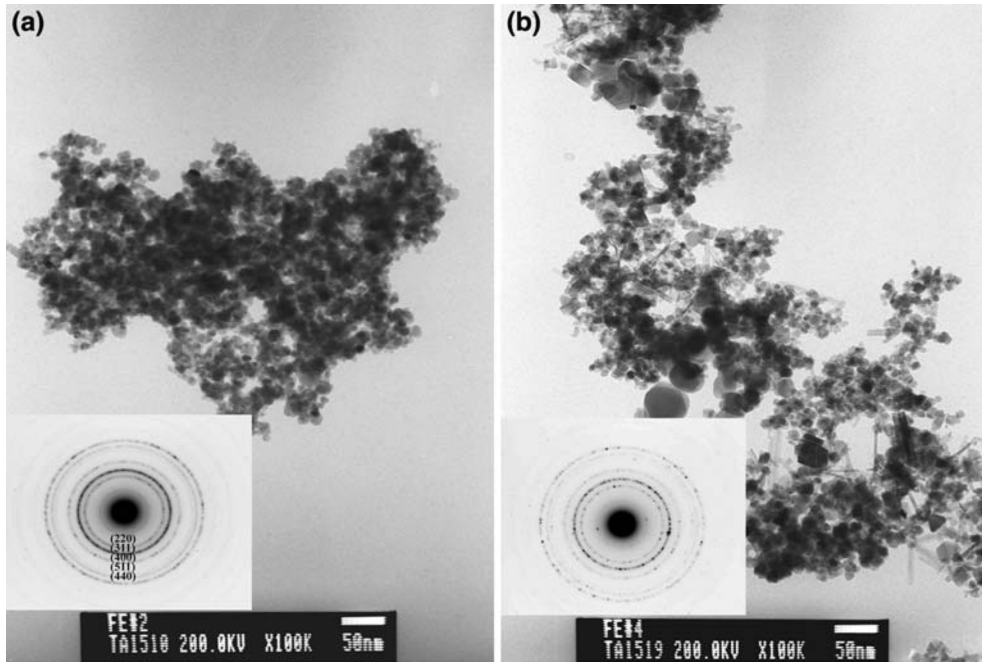

Fig. 3 TEM images and ED patterns of magnetite prepared by (**a**) spray method and (**b**) drop method (Fe^{2+} = 0.5 M)

Acknowledgement This work was supported by grant No. R13-2003-13 from the Medical Science and Engineering Research Program of the Korea Science & Engineering Foundation.

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