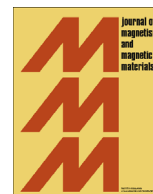




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Magnetic heating of silica-coated manganese ferrite nanoparticles

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ABSTRACT

Manganese ferrite nanoparticles were synthesized using the reverse micelle method; these particles were then coated with silica. The silica-coated nanoparticles were spherical in shape, with an average diameter of 14 nm. The inverse spinel crystalline structure was observed through X-ray diffraction patterns. The coating status of silica on the surface of the nanoparticles was confirmed with a Fourier transform infrared spectrometer. The superparamagnetic properties were revealed by the zero coercive force in the hysteresis curve. Controllable heating at a fixed temperature of 42 °C was achieved by changing either the concentration of nanoparticles in the aqueous solution or the intensity of the alternating magnetic field. We found that at a fixed field strength of 5.5 kA/m, the 2.6 mg/ml sample showed a saturation temperature of 42 °C for magnetic hyperthermia. On the other hand, at a fixed concentration of 3.6 mg/ml, a field intensity of 4.57 kA/m satisfied the required temperature of 42 °C.

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1. Introduction

Magnetic nanoparticles have been widely researched for possible application in medical uses such as contrast agents in magnetic resonance imaging [1–5], magnetic hyperthermia [6,7], and nano drug delivery system [8–13]. In particular, ferrite nanoparticles have attracted great attention because of their easy synthesis, high chemical stability, and high saturation magnetization. They have the chemical structure of MFe_2O_4 , where M represents the divalent metal ions of Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , etc. The ferrites have a cubic inverse spinel structure in which 32 O^{2-} ions constitute a face-centered cubic structure, eight Fe^{3+} ions are located at the center of eight tetrahedral sites, and eight M^{2+} and Fe^{3+} ions are located at the center of 16 octahedral sites. The magnetic moment of the Fe^{3+} ions on the octahedral sites is antiparallel to that of the Fe^{3+} ions on the tetrahedral sites. Thus, the magnetic moment of the ferrites is due to the magnetic moment of M^{2+} . The magnetic moment of M^{2+} comes from its unpaired 4d electrons, resulting in 5, 4, 3, and 2 μ_B for the Mn-, Fe-, Co-, and Ni-ferrites, respectively. These theoretical values of the magnetic moment are close to the experimental values of 4.6, 4.1, 3.7, and 2.3 μ_B , respectively [13].

Ferrite nanoparticles are toxic, thus surface modification is needed in order to apply them to the human body. This surface modification is also required for labeling various chemicals for drugs, targeting ligands, etc. on their surfaces. Various biocompatible

materials are used to achieve this surface modification, and include silica, polyethylene glycol (PEG), chitosan, dextran, carbon, gold, oleic acid, titania, etc. [1–3,14–18]. Titania and silica are nontoxic oxides of titanium and silicon, respectively. Titania coating is useful for photocatalytic activities and hydrolysis [18–20]. Silica coating plays a vital role in preventing magnetic nanoparticle agglomeration, and providing a suitable surface for drug loading [21] and chemical inertness in biological systems [22]. The Food and Drug Administration confirmed that silica coating is safe for use in human body [23].

Hyperthermia is a cancer treatment that exploits the fact that cancer tissues are killed if they are exposed to 42 °C for half an hour [24,25]. The blood vessels of cancer cells are not complete, so excess heat is not effectively released through blood flow. External hyperthermia uses an external heat source that is concentrated on the cancer cells. On the other hand, internal hyperthermia injects the heat source directly into the site of the cancer tissue. With the magnetic hyperthermia method, magnetic nanoparticles are injected into the cancer site. Then, these magnetic nanoparticles generate heat in the presence of an external magnetic field to raise the temperature of the cancer site to 42 °C. Intensive research on magnetic hyperthermia using magnetic nanoparticles, especially iron oxide nanoparticles, has been performed. Various basic studies and animal experiments for magnetic hyperthermia are currently under way. However, no clinical application has been reported yet.

In this study, manganese ferrite ($MnFe_2O_4$) nanoparticles were prepared for use in magnetic hyperthermia. The particles were coated with silica for biocompatibility. The superparamagnetic

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properties of magnetic nanoparticles are required in biomedical applications, since they exhibit their magnetic properties only in the presence of an external magnetic field. The particle size necessary for this superparamagnetic behavior is a few tens of nanometers in diameter. The applicability of nanoparticles to hyperthermia treatments can be tested by checking the heating effects of nanoparticles in an alternating magnetic field. The other requirement for hyperthermia applications is the ability to control the temperature of the nanoparticles to 42 °C. The malignant tissues are killed in an environment of 42 °C for half an hour, but temperatures higher than 46 °C burn the normal surrounding tissues. Thus, controlling the temperature to 42 °C is essential for hyperthermia treatments. In this paper, we report the heating effects of manganese ferrite nanoparticles in an alternating magnetic field. The concentration and field dependence of the heating effects will be presented.

2. Experimental method

We fabricated manganese ferrite nanoparticles by precipitating them in a water-in-oil nanoreactor. This reverse micelle method has been used for the synthesis of monodispersed and controlled-size nanoparticles [26]. In this method, co-precipitation of manganese ferrite nanoparticles occurs inside the nano-sized water droplets that are enclosed by a surfactant and distributed in the oil phase. Those encapsulated water droplets that are distributed in the oil phase act like mini-reactors, or so-called reverse micelles. The size of the mini-reactors depends on the molar ratio of water to surfactant. The application of the silica coating on the surface of the nanoparticles was performed simultaneously with the synthesis of the manganese ferrite nanoparticles.

In brief, the water-in-oil system was obtained by mixing two different solutions by mechanical stirring at 500 rpm. The two solutions were a transparent solution of 3.5 g sodium dodecylbenzenesulfonate (NaDBS) dissolved into 30 ml xylene (isomers plus ethyl benzene, 98.5%), and a 1.8 ml aqueous solution containing stoichiometric amounts of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and iron (III) nitrate nanohydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 98%). The transparent solution became a milky whitish color upon the addition of the aqueous solution. The resultant water-in-oil system was continuously stirred for about 16 h, followed by an additional 1 h of stirring under nitrogen protection. After stirring, the system was heated to 90 °C at the rate of 2 °C/min, and 1 ml hydrazine (34 wt-% water solution) was added. The addition of the hydrazine caused a change in color (from dark brown to black). The resultant system was kept at 90 °C for 3 h, and then cooled down to 40 °C in about 1.5 h. During this process, manganese ferrite nanoparticles were formed inside the mini-reactors of the reverse micelle (water-in-oil) system.

The coating of the ferrite nanoparticles with silica was performed by adding 4 ml of tetraethyl orthosilicate (TEOS) into the manganese ferrite nanoparticle solution at 40 °C and stirring for about 6 h at 500 rpm. The silica shells were formed on the surface of the manganese ferrite nanoparticles by the hydrolysis of the TEOS inside the encapsulated water droplet by the micelles. The silica-coated manganese ferrite nanoparticles were separated from the oil phase using acetone and subsequent centrifugations at 13,000 rpm. The particles were dried at ambient temperature for 8 h to obtain a powder sample. The powder samples were dispersed in water for characterization.

An aqueous solution of the manganese ferrite nanoparticles was prepared to observe the heating effect of the magnetic nanoparticles in an alternating magnetic field. A 20 mg powder sample of the silica-coated manganese ferrite nanoparticles was dispersed in 50 ml of deionized water with ultrasonication for

20 min. The resultant dispersion was observed to be highly stable for months. This dispersion of the manganese ferrite nanoparticles was very dilute. A concentrated sample was obtained by keeping the diluted sample in the vacuum oven at 40 °C for about 5 days. The amounts of manganese and iron in the aqueous solution were measured by using an inductively coupled plasma (ICP) technique. Five more samples were prepared by diluting the sample to 75%, 62.5%, 50%, 37.5%, and 25% for measuring the concentration dependence of the magnetic heating effect.

The morphology and particle size distribution of the manganese ferrite nanoparticles were analyzed using a transmission electron microscope (TEM; H-7600, Hitachi Ltd.). The crystal structure of the bare and silica-coated manganese ferrite nanoparticles was investigated using X-ray diffraction (XRD; X'pert PRO, PANalytical). The chemical composition and concentration of the nanoparticles in the aqueous solution were measured using ICP spectrometry (Thermo Jarrell Ash IRISAP). The bonding of silica to the surface of the nanoparticles was confirmed using Fourier transform infrared spectroscopy (FTIR; Nicolet 380, Thermo Scientific USA). The magnetic measurements were carried out using a vibrating sample magnetometer (VSM; MPMS, Quantum Design). The magnetic heating effects of the nanoparticles dispersed in water were measured using an induction heating system (OSH-120-B, Osung High Tech) under an alternating magnetic field at 260 kHz. The temperature of the solution was measured with a CALEX infrared thermometer (PyroUSB CF, Calex Electronics Limited).

3. Results and discussions

Fig. 1-a shows a TEM image of the silica-coated manganese ferrite nanoparticles. The particle size distribution is given in Fig. 1-b, which shows the histogram of the diameter of 100 nanoparticles obtained from the TEM image. The average diameter of the coated nanoparticles is 14 nm, with a margin of 0.1 nm.

The XRD patterns of the bare and silica-coated manganese ferrite nanoparticles are shown in Fig. 2. The peaks at 30.19°, 35.50°, 43.22°, 53.6°, 57.09°, and 62.6° correspond to the crystal planes of (220), (311), (400), (422), (511), and (440), respectively, matching those observed in inverse spinel ferrite [27,28]. The extra peak at around 22° to 26° for the coated particles arises from amorphous SiO_2 adsorbed on the surface of the nanoparticles [29]. The lattice constant “a” was calculated to be 8.3 Å, using the (440) peak. The differences in peak angles between the bare and the silica-coated nanoparticles are negligible.

The bonding of the silica to the surface of the manganese ferrite nanoparticles was checked by FTIR in the range of 400 to 4000 cm^{-1} , as shown in Fig. 3. The absorption band at 3430 cm^{-1} in the figure corresponds to the stretching mode of the O–H group, while the band at 1627 cm^{-1} represents the vibration mode of the O–H group present at the surface of the samples [30,31]. In addition, the absorption band at 1100 cm^{-1} on the spectra is the characteristic peak of the anti-symmetric stretching vibrational mode of the Si–O–Si siloxane bridges. The absorption at 957 cm^{-1} is due to the contribution from the Si–O–H stretching vibration [32], while the band at 802 cm^{-1} is due to the SiO_4 ring vibration [33]. The faint band at 625 cm^{-1} corresponds to the Fe–O stretching in the Fe–O–Si bonding [34]. In summary, the FTIR spectra confirm the bonding of the silica to the surface of the manganese ferrite nanoparticles.

Fig. 4 shows the hysteresis curve of the silica-coated manganese ferrite nanoparticles at room temperature. In the inset of this figure, zero remanence and coercivity are apparent, indicating that the nanoparticles exhibit superparamagnetic properties at room temperature.

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