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Examination of the magnetic hyperthermia and other magnetic properties of CoFe$_2$O$_4$@MgFe$_2$O$_4$ nanoparticles using external field Mössbauer spectroscopy

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CoFe$_2$O$_4$@MgFe$_2$O$_4$ core/shell nanoparticles were synthesized by high-temperature thermal decomposition with seed-mediated growth. The crystal structure and magnetic properties of the nanoparticles were investigated using X-ray diffractometry (XRD), vibrating sample magnetometry (VSM), and Mössbauer spectrometry. The magnetic hyperthermia properties were investigated using a MagneTherm device. Analysis of the XRD patterns showed that CoFe$_2$O$_4$@MgFe$_2$O$_4$ had a cubic spinel crystal structure with space group $Fd-3m$ and a lattice constant ($a_0$) of 8.3686 Å. The size and morphology of the CoFe$_2$O$_4$@MgFe$_2$O$_4$ nanoparticles were confirmed by HR-TEM. The VSM measurements showed that the saturation magnetization ($M_S$) of CoFe$_2$O$_4$@MgFe$_2$O$_4$ was 77.9 emu/g. The self-heating temperature of CoFe$_2$O$_4$@MgFe$_2$O$_4$ was 37.8 °C at 112 kHz and 250 Oe. The CoFe$_2$O$_4$@MgFe$_2$O$_4$ core/shell nanoparticles showed the largest saturation magnetization value, while their magnetic hyperthermia properties were between those of the CoFe$_2$O$_4$ and MgFe$_2$O$_4$ nanoparticles. In order to investigate the hyperfine interactions of CoFe$_2$O$_4$, MgFe$_2$O$_4$, and CoFe$_2$O$_4$@MgFe$_2$O$_4$, we performed Mössbauer spectrometry at various temperatures. In addition, Mössbauer spectrometry of CoFe$_2$O$_4$@MgFe$_2$O$_4$ was performed at 4.2 K with applied fields of 0–4.5 T, and the results were analyzed with sextets for the tetrahedral $A$-site and sextets for the octahedral $B$-site. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

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I. INTRODUCTION

Magnetic nanoparticles have been intensively investigated for use in bio-applications because of their unique properties, including their synthesis methods, structural characteristics, and remarkable magnetic properties. For example, CoFe$_2$O$_4$ nanoparticles have high saturation magnetization and are known to be hard ferrites. On the other hand, MgFe$_2$O$_4$ nanoparticles are close to being soft ferrites, although there have been few reports on MgFe$_2$O$_4$ nanoparticles to date. In order to reduce the large magnetic anisotropy of CoFe$_2$O$_4$ nanoparticles, we coated them with a shell of MgFe$_2$O$_4$ nanoparticles to form a core/shell structure. In this study, core/shell CoFe$_2$O$_4$@MgFe$_2$O$_4$ nanoparticles were prepared for use in magnetic hyperthermia, an experimental cancer treatment. The bio-applicability of nanoparticles to magnetic hyperthermia treatment was tested by examining the heating effects of the nanoparticles in an AC magnetic field. In addition, we show the relationship between the spin canting angle and the hyperthermia effect of CoFe$_2$O$_4$@MgFe$_2$O$_4$ nanoparticles by measuring the external magnetic field using Mössbauer spectroscopy.
II. EXPERIMENT PROCEDURE

A. Synthesis of CoFe$_2$O$_4$, MgFe$_2$O$_4$, and CoFe$_2$O$_4$@MgFe$_2$O$_4$

The CoFe$_2$O$_4$, MgFe$_2$O$_4$, and CoFe$_2$O$_4$@MgFe$_2$O$_4$ nanoparticles were prepared by high-temperature thermal decomposition, while CoFe$_2$O$_4$@MgFe$_2$O$_4$ core/shell nanoparticles were prepared by seed-mediated growth. Co(acac)$_2$ (1 mmol), Fe(acac)$_3$ (2 mmol), oleylamine (6 mmol), and oleic acid (6 mmol) were dissolved in 30 ml of benzyl ether. The solution was first heated at 200 °C for 30 min and heated up to 298 °C for 45 min. After the solution had cooled to room temperature, 40 ml of ethanol was added. The black precipitates were collected by centrifugation, washed several times with hexane and ethanol, and dried at 80 °C. A similar synthesis procedure was used to prepare the MgFe$_2$O$_4$ nanoparticles.

The CoFe$_2$O$_4$ core/MgFe$_2$O$_4$ shell nanoparticles were made using a solution of as-prepared nanoparticles in 4 ml of hexane, which was mixed with of Mg(acac)$_2$ (1 mmol), Fe(acac)$_3$ (2 mmol), oleylamine (6 mmol), and oleic acid (6 mmol) in 30 ml of benzyl ether. The solution was heated first at 200 °C for 30 min and heated up to 298 °C for a further 45 min. The collection and cleaning of the CoFe$_2$O$_4$@MgFe$_2$O$_4$ nanoparticles were performed as before.

B. Measurements

The crystal structure of the CoFe$_2$O$_4$@MgFe$_2$O$_4$ nanoparticles was investigated using X-ray diffraction (XRD) with a monochromatic Cu-Kα radiation source (λ = 1.5406 Å). The XRD patterns of the fabricated nanoparticles were analyzed with Fullprof software. High-resolution transmission electron microscopy (HR-TEM) was used to confirm the size and structure of the CoFe$_2$O$_4$@MgFe$_2$O$_4$ particles. The magnetic measurements were carried out using vibrating sample magnetometry (VSM). Hysteresis curves were recorded at 295 K under magnetic fields of up to ±1.5 T. Zero-field-cooled (ZFC) and field-cooled (FC) curves were performed at applied magnetic fields of 100 and 1000 Oe and at temperatures of 4.2–300 K. The magnetic hyperthermia properties of the nanoparticles were confirmed using a MagneTherm system at a frequency of 112 kHz and an alternating magnetic field strength of 250 Oe. Mössbauer spectra were obtained using the constant acceleration mode with a $^{57}$Co γ-ray source, at a temperature of 4.2 K and applied field strengths ranging from 0–4.5 T.

III. RESULTS AND DISCUSSION

The XRD patterns of CoFe$_2$O$_4$, MgFe$_2$O$_4$, and CoFe$_2$O$_4$@MgFe$_2$O$_4$ nanoparticles were analyzed using the Rietveld refinement method with Fullprof software, as shown in Fig. 1. It can be seen from the patterns that spinel phases were formed in all samples, with the single phases of all three crystal structures being determined to be cubic spinel with the space group Fd-3m. The lattice constants (a$_0$) of the samples were calculated to be 8.4017, 8.3848, and 8.3686 Å for CoFe$_2$O$_4$, MgFe$_2$O$_4$, and CoFe$_2$O$_4$@MgFe$_2$O$_4$, respectively. According to the HR-TEM images, the CoFe$_2$O$_4$@MgFe$_2$O$_4$ was approximately 17 nm (±3 nm) in size, and the core/shell structure of this material was also confirmed by HR-TEM.

The temperature-dependent magnetization of the core/shell ferrite was measured at temperatures ranging from 4.2–300 K under applied fields of 100 and 1000 Oe, as shown in Fig. 2. The zero-field-cooled CoFe$_2$O$_4$@MgFe$_2$O$_4$ showed a sharp decrease when a field of 1000 Oe was applied, whereas there was no significant change in the slope of the field-cooled nanoparticles, so this can be considered quite independent of the temperature. The magnetization of the CoFe$_2$O$_4$@MgFe$_2$O$_4$ increased steadily as the temperature decreased during zero-field-cooling, reaching a maximum at a critical temperature defined as the blocking temperature, $T_B$. We observed blocking temperatures of 300 and 275 K at 100 and 1000 Oe, respectively. Magnetic measurements of the CoFe$_2$O$_4$, MgFe$_2$O$_4$, and CoFe$_2$O$_4$@MgFe$_2$O$_4$ nanoparticles were performed using the VSM, and the magnetic hysteresis results obtained at room temperature are shown in Fig. 3. The saturation magnetizations were measured to be 68.4, 67.4, and 74.2 emu/g for the CoFe$_2$O$_4$, MgFe$_2$O$_4$, and CoFe$_2$O$_4$@MgFe$_2$O$_4$ nanoparticles, respectively.
FIG. 1. Rietveld refinements of XRD patterns of nanoparticles (left) and TEM images of CoFe$_2$O$_4$@MgFe$_2$O$_4$ (right).

FIG. 2. Zero-field-cooled and field-cooled magnetization curves of the CoFe$_2$O$_4$@MgFe$_2$O$_4$.
FIG. 3. Magnetic hysteresis loops of CoFe$_2$O$_4$@MgFe$_2$O$_4$, CoFe$_2$O$_4$, and MgFe$_2$O$_4$ measured at 295 K.

Plots of the self-heating temperatures of CoFe$_2$O$_4$, MgFe$_2$O$_4$, and CoFe$_2$O$_4$@MgFe$_2$O$_4$ nanoparticles as a function of time are shown in Fig. 4. The magnetic field was fixed at 250 Oe with a frequency of 112 kHz. The increase in the self-heating temperature of CoFe$_2$O$_4$ was observed to be considerable over the first 100 s. The maximum self-heating temperatures of the samples were 42.08, 34.45, and 37.87°C for CoFe$_2$O$_4$, MgFe$_2$O$_4$, and CoFe$_2$O$_4$@MgFe$_2$O$_4$, respectively. The decreased self-heating temperature of CoFe$_2$O$_4$@MgFe$_2$O$_4$ was due to the increase in the dipolar magnetic moment caused by the shell-deposited MgFe$_2$O$_4$, which affected the Néel relaxation time.

We obtained the Mössbauer spectra of CoFe$_2$O$_4$, MgFe$_2$O$_4$, and CoFe$_2$O$_4$@MgFe$_2$O$_4$ at room temperature in order to obtain insights into the chemical compositions and structures of the nanoparticles, and the results are shown in Fig. 5(a). The Mössbauer spectra were analyzed two sextets for tetrahedral and octahedral. The Mössbauer spectra of CoFe$_2$O$_4$ and CoFe$_2$O$_4$@MgFe$_2$O$_4$ were analyzed with a tetrahedral A-site sextet (blue line) and an octahedral B-site sextet (red line), as two hyperfine sextet patterns were obtained in these spectra. The MgFe$_2$O$_4$ spectrum was analyzed with a tetrahedral A-site sextet (red line), an octahedral B-site sextet (blue line), one quadruplet (green line), and one amorphous (cyan line). CoFe$_2$O$_4$@MgFe$_2$O$_4$ had the largest value of $H_{hf}$, with 445 kOe being obtained for the A-site and 477 kOe for the B-site. Mössbauer spectra were also measured at 4.2 K with an external field of 0–4.5T, as shown in Fig. 5(b). When the external field was 0 T, two overlapping sextets were observed. As the external field was increased, the absorption...
FIG. 5. (a) Mössbauer spectra of \(\text{CoFe}_2\text{O}_4@\text{MgFe}_2\text{O}_4\), \(\text{CoFe}_2\text{O}_4\), and \(\text{MgFe}_2\text{O}_4\) nanoparticles at RT and (b) \(\text{CoFe}_2\text{O}_4@\text{MgFe}_2\text{O}_4\) nanoparticles at various external fields at 4.2 K.

Lines of the two sextets could be distinguished. Because the magnetic spin direction is parallel to the gamma rays due to the external magnetic field, the average canting angle \(\theta\) can be calculated using equation (1):

\[
(\theta) = \sin^{-1} \left[ \frac{\frac{3}{2}(A_{2,5}/A_{1,6})}{1 + \frac{3}{2}(A_{2,5}/A_{1,6})} \right]^{1/2} \tag{1}
\]

where \(A_{2,5}\) represents the area ratio of the 2nd or 5th absorption line and \(A_{1,6}\) represents the area ratio of the 1st or 6th absorption lines. Thus, a decrease of the second/fifth absorption line indicates a decrease in the canting angle. The canting angle gradually decreased from 56.96° to 17.04° as the external magnetic field was increased from 0 to 4.5 T. The dependence of the canting angle on the magnetic field indicates that the sample had soft-magnetic properties. Furthermore, these characteristics can be confirmed through the hyperthermia behavior of the material.

IV. CONCLUSION

We have investigated \(\text{CoFe}_2\text{O}_4@\text{MgFe}_2\text{O}_4\) nanoparticles using XRD, TEM, VSM, and Mössbauer spectrometry, while its applicability to magnetic hyperthermia was also examined. According to XRD analysis with Rietveld refinement, the nanoparticles had a single phase and a cubic spinel structure with the space group \(Fd-3m\). In the temperature-dependent magnetization curves, blocking temperature transitions were observed at 300 and 275 K at magnetic fields of 100 and 1000 Oe, respectively. The self-heating magnetic hyperthermia properties of \(\text{CoFe}_2\text{O}_4@\text{MgFe}_2\text{O}_4\) were determined to be intermediate in value, with those of \(\text{MgFe}_2\text{O}_4\) and \(\text{CoFe}_2\text{O}_4\) being lower and higher, respectively. The Mössbauer spectra at were observed room temperature, and it was found that \(\text{CoFe}_2\text{O}_4@\text{MgFe}_2\text{O}_4\) had the highest \(H_{hf}\). Mössbauer spectra were also measured at applied magnetic fields of 0–4.5 T at 4.2 K to allow the canting angle to be observed. It was confirmed that the canting angle decreased as the magnetic field increased. The decrease in canting angle indicates that the magnetic spin maintained weak directionality, which can be considered to show soft-magnetic properties, as confirmed by the magnetic hyperthermia experiments. The core/shell nanoparticle structure investigated in this study has high saturation magnetization and moderate thermal properties. Therefore, these nanoparticles are of sufficient value for studying magnetic hyperthermia.
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