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Synthesis and Characterization of SiO₂ Coated γ -Fe₂O₃ Nanocomposite Powder for Hyperthermic Application

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SiO₂ coated γ -Fe₂O₃ nanocomposite powder has been successfully synthesized by chemical vapor condensation process and its feasibility on hyperthermic application was investigated in this study. The power loss of SiO₂ coated γ -Fe₂O₃ nanocomposite powder which means the magnetic heating effect under alternative magnetic field was much higher than the single phase γ -Fe₂O₃ nano powder due to the very fine size under 20 nm and well dispersion in biologically compatible SiO₂ matrix. The superparamagnetism and hyperthermic property of SiO₂ coated γ -Fe₂O₃ nanocomposite powder were discussed in terms of microstructural development in this study.

KEY WORDS: Hyperthermia; Nano-Bio; Chemical vapor condensation; Silica coated iron oxide nanoparticle; Superparamagnetism

1. Introduction

Recently, with the great interest of fusion technology, biological applications of nanoparticles have been issued in medical and biochemical fields. Especially, for biological applications of magnetic nanoparticle, these magnetic particles are required to have superparamagnetism, mono-dispersivity as well as biological compatibility, in order to ensure the re-dispersion after removing the magnetic field in the human body.

Among the various bio applications with superparamagnetic nanoparticle, hyperthermia is one of the rising issues in biomedical field^[1]. Hyperthermia is the disease treatment with high temperature in human body. When body tissues are exposed to high temperature between 41 and 45°C, the temperature sensitive tumor cells are more damaged and killed than normal body cells.

Recently, the hyperthermia with the relaxational loss of superparamagnetic particles has been rarely

studied^[2,3]. The heating of magnetic materials, for example, iron oxides with low electrical conductivity, in an external alternating magnetic field is mainly due to either loss process during the reorientation of the magnetization (Néel relaxation) or frictional losses if the particle can rotate in an environment of sufficient low viscosity (Brownian relaxation). The relaxation times for both mechanisms, Néel relaxation and Brownian relaxation, decrease with decreasing of particle size. The effective relaxation process is dominated by the faster relaxation process. The developed power loss, P , given as the follow equation, which lead to heat of magnetic particle is inversely proportional to relaxation time, τ ^[4,5]

$$P = \frac{(mH\omega\tau)^2}{[2\tau kTV(1 + \omega^2\tau^2)]} \quad (1)$$

where m is magnetic moment, H and ω are applied magnetic field and frequency, respectively, and V is particle volume and absolute temperature, T .

In this study, SiO₂ coated γ -Fe₂O₃ nanoparticles were synthesized by chemical vapor condensation process that is suitable for fabricating com-

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pletely dispersed nanoparticle through evaporation-condensation of metal organic precursors^[6]. The heats generated from SiO₂ coated γ -Fe₂O₃ nanoparticles were measured in alternative magnetic fields and characterized as power loss, P . The magnetic heating effect of SiO₂ coated γ -Fe₂O₃ nanoparticle was discussed in term of microstructural aspect.

2. Experimental

The basic setup for chemical vapor condensation (CVC) process is similar to that described in literature elsewhere^[7]. Two metalorganic precursors, tetraethyl orthosilicate (TEOS, Sigma Co., 99.99%) and iron pentacarbonyl (Sigma Co., 99.99%) were fed into the vaporizer maintained at 210°C with constant flow rate of 0.37 ml/min by using a micropump. The vaporized precursors moved to reaction tube heated with 1000°C by helium carrier gas of 1 slm. And oxygen reactant gas was fed into the reaction tube with the flow rate of 2 slm. The pressure of reaction tube was maintained at 40 mbar. The vaporized precursors were decomposed and condensed to form a SiO₂ coated γ -Fe₂O₃ nanoparticle in the reaction tube. The synthesized nanoparticle was collected and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and VSM.

For the practical analysis of the power loss in hyperthermia process, firstly, the heat generated from SiO₂/ γ -Fe₂O₃ nanocomposite particle should be measured. In this practical process, another concept so called specific absorption rate (SAR) was introduced which means the value of power loss dividing by mole fraction of magnetic particle ($m_{\text{Fe}_2\text{O}_3}$) in unit volume as shown in the following equation,

$$\text{SAR} = \frac{P}{m_{\text{Fe}_2\text{O}_3}} = \frac{dQ/dt}{m_{\text{Fe}_2\text{O}_3}} = \frac{\sum c_{p_i} m_i dT/dt_{t=0}}{m_{\text{Fe}_2\text{O}_3}} (W/g_{\text{Fe}_2\text{O}_3}) \quad (2)$$

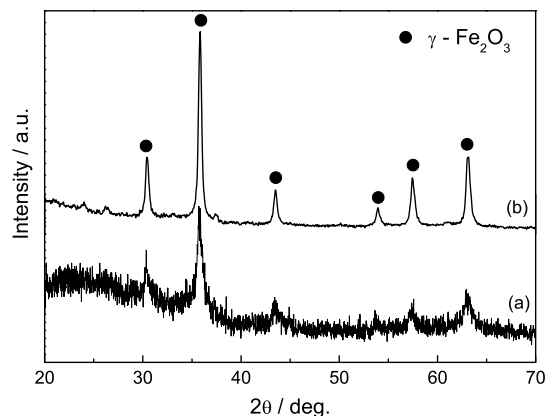


Fig. 1 X-ray diffraction patterns for (a) SiO₂/ γ -Fe₂O₃ nanocomposite particle and (b) γ -Fe₂O₃ nanoparticles

where Q and c_p are heat flow and heat capacity, respectively.

The temperature difference (dT) of SiO₂/ γ -Fe₂O₃ nanocomposite particle from outer part was measured and converted to P and SAR value^[5]. The SAR represent practical power loss including the effects of particle size, composition and dispersivity as well as theoretical relaxation loss.

3. Results and Discussion

Figure 1 shows XRD patterns of SiO₂/ γ -Fe₂O₃ nanocomposite particle synthesized by CVC process. The crystalline γ -Fe₂O₃ peak with amorphous SiO₂ was observed. The average crystal size calculated from full width half maximum (FWHM) of γ -Fe₂O₃ main peak was around 20 nm. In TEM observation of Fig. 2, the 10 to 30 nm sized γ -Fe₂O₃ particles were coated by 5 nm SiO₂ film and these particles forms weak agglomeration. And the composition of γ -Fe₂O₃ was around 10 wt pct in the SiO₂/ γ -Fe₂O₃ nanocomposite particle in TEM-EDS analysis.

The magnetic hysteresis loops for SiO₂/ γ -Fe₂O₃ nanocomposite particle are depicted in Fig. 3 with

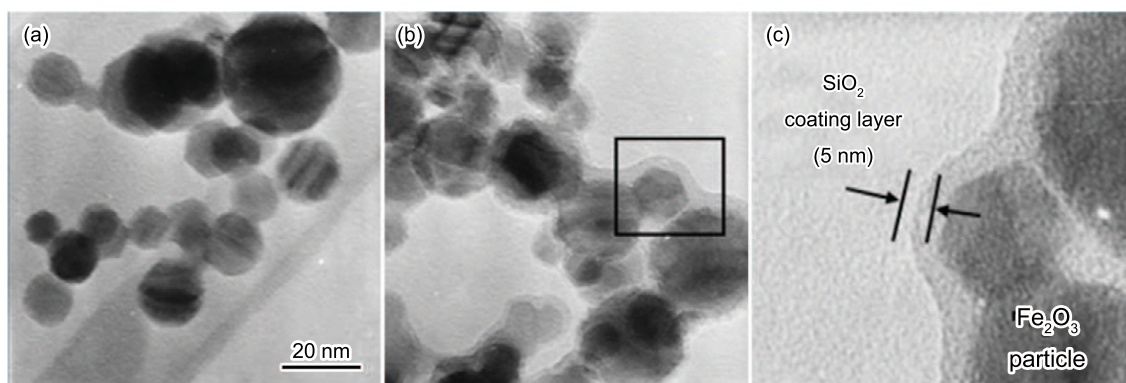


Fig. 2 TEM micrographs of (a) γ -Fe₂O₃, (b) SiO₂/ γ -Fe₂O₃ nanocomposite particle and (c) selected area in (b)

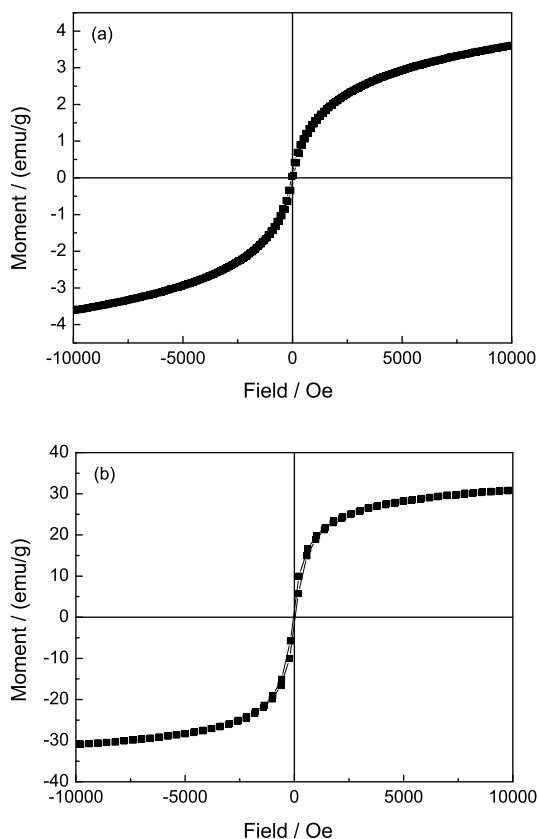


Fig. 3 Magnetic hysteresis loops for (a) $\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ nanocomposite particle and (b) $\gamma\text{-Fe}_2\text{O}_3$

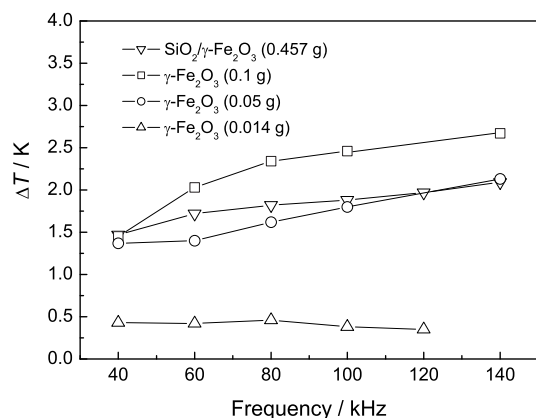


Fig. 4 Generated heat (ΔT) from magnetic nanoparticles as a function of alternative frequency under 6 mT of applied field

comparing to the single phase $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle synthesized by same condition in CVC process. The $\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ nanocomposite particle has 10 times lower values of saturation magnetization and retentivity than those of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle. This is mainly due to the composition of 10% iron oxide in the composite particles, quite well proving with above TEM-EDS result. The low coercivity and retentivity of $\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ nanocomposite particle shows the nearly superparamagnetism and it means that $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle are homogeneously dispersed in

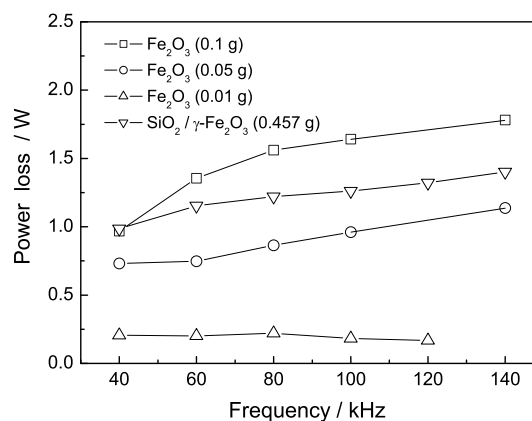


Fig. 5 Power loss for magnetic nanoparticles as a function of alternative frequency under 6 mT of applied field

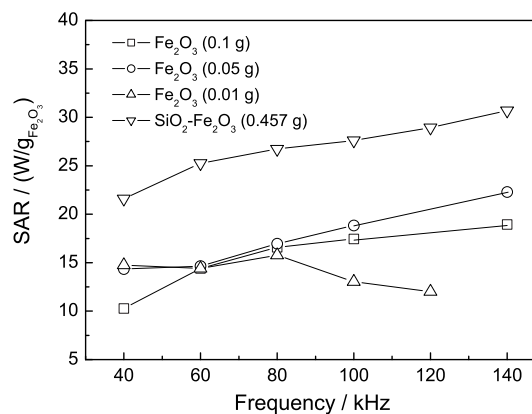


Fig. 6 Specific adsorption rate for magnetic nanoparticles as a function of alternative frequency under 6 mT of applied field

the SiO_2 matrix.

Figure 4 shows the temperature differences (ΔT) with varying applied frequencies. In this study the amplitude of magnetic field is fixed at 6 mT and the frequencies varied from 40 to 140 kHz. The temperature differences, ΔT , increased with increasing of frequencies and the amount of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle. The measured ΔT of $\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ nanocomposite particle is similar to that of 0.05 g $\gamma\text{-Fe}_2\text{O}_3$ sample. But with considering that the concentration of $\gamma\text{-Fe}_2\text{O}_3$ in $\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ nanocomposite was 10 wt pct in previous result, it is quite acceptable. Because the real amount of $\gamma\text{-Fe}_2\text{O}_3$ in $\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ nanocomposite was calculated to be around 0.045 g.

From the measured ΔT , the power loss, P and SAR values were calculated and depicted in Figs. 5 and 6, respectively. The power loss and SAR increased with increasing of the applied frequency and the amount of $\gamma\text{-Fe}_2\text{O}_3$. These dependences of P and SAR on the applied frequency mean that the magnetic properties of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles are in the superparamagnetic regime according to the equation^[1].

With comparing to the result of ΔT , the power

loss (P) and SAR values of $\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ nanocomposite particle are much higher than those of 0.05 g $\gamma\text{-Fe}_2\text{O}_3$ sample. This is mainly due to the higher superparamagnetic relaxation heat of $\gamma\text{-Fe}_2\text{O}_3$ phase in the lower thermal conductivity of SiO_2 matrix. If total amounts of $\gamma\text{-Fe}_2\text{O}_3$ are same for both samples, the fully dispersed $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle in SiO_2 matrix doesn't interact with each other, and then has closer behavior to superparamagnetic. So the magnetic heating effect of $\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ nanocomposite particle having superparamagnetic relaxation behavior is much higher than the single phase $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle.

4. Conclusion

Biological compatible $\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ nanocomposite particles have been successively synthesized by CVC process. The $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles of 20 nm in size were well coated by amorphous SiO_2 shell, and have superparamagnetic property. In the result of magnetic heating experiment, the $\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ nanocomposite particles have much higher magnetic heating effect which represents higher power loss and SAR value than single phase $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle. This is resulted from well dispersion of fine $\gamma\text{-Fe}_2\text{O}_3$

nanoparticle in SiO_2 matrix and closer behavior of superparamagnetism.

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