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Fabrication of spherical silica aerogel/magnetite nanocomposite particles

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1. Introduction

Because magnetite (Fe₃O₄) nanoparticles show superparamagnetism with high saturation magnetization, biocompatibility, and chemical stability, they have attracted much attention in biomedicine and bioengineering applications such as in drug delivery systems, magnetic resonance imaging contrast agents, and cancer therapies [1,2,3]. However, the anisotropic dipolar attraction of Fe₃O₄ nanoparticles often results in large aggregates and a loss of their superparamagentic characteristics [4]. Thus, Fe₃O₄ nanoparticles are dispersed within a nonmagnetic matrix in order to avoid agglomeration and/or to protect the magnetic nanoparticles against corrosion or oxidation [5]. In some cases, the nonmagnetic matrix can provide various surface sites for attaching a dedicated functional group for a specific reaction [6]. Silica (SiO₂) is the most suitable material for the matrix because of its nontoxicity, inertness to magnetic fields, and ease to form cross-linked network structures [7,8].

Several methods are used to fabricate silica-coated Fe_3O_4 nanoparticles. One is the sol-gel technique, in which silica is coated on colloidal Fe_3O_4 nanoparticles in an alkoxide/alcohol/ water mixture via hydrolysis and condensation [9,10]. Another one is based on the formation of Fe_3O_4 nanoparticles inside the pores of silica nanoparticles using iron salts such as iron chlorides or nitrates [11]. Emulsion polymerization was recently proposed, in which aqueous droplets containing magnetic nanoparticles

ABSTRACT

 Fe_3O_4/SiO_2 nanocomposite particles were synthesized from a hydrophobic Fe_3O_4 suspension, prepared by precipitating Fe (II) and Fe (III) chlorides and using a hydrophobic SiO_2 wet gel from a silicic acid solution derived from a sodium silicate (water glass) solution. Fe_3O_4 nanoparticles having a crystallite size of ~ 10 nm embedded in SiO_2 aerogel can be successfully fabricated by mixing the Fe_3O_4 suspension and silica wet gel in *n*-hexane. It was clearly observed that the Fe_3O_4 nanoparticles were well crystallized and homogeneously dispersed in the SiO_2 aerogel. The Fe_3O_4/SiO_2 nanocomposite particles exhibited superparamagentic behavior. The saturation magnetization was determined to 34.5, 18.2, and 8.3 emu/ g for 90 wt% Fe_3O_4 , 70 wt% Fe_3O_4 , and 50 wt% Fe_3O_4/SiO_2 nanocomposite particles, respectively. © 2013 Elsevier B.V. All rights reserved.

were dispersed in an organic solvent by using a surfactant; next, tetraethylorthosilicate (TEOS) is added to the microemulsion to form a silica coating around the magnetic nanoparticles [12].

In this study, nanocomposite of Fe_3O_4 nanoparticles embedded in a spherical silica (SiO₂) aerogel particle were synthesized via a novel synthesis route that comprises incorporation of hydrophobic Fe_3O_4 nanoparticles in a spherical silica wet gel, which is modified by hydrophobic surface methyl groups and subsequent drying at ambient pressure. It is considered that emulsion polymerization is the best way to synthesize mono-dispersed spherical silica aerogel particles. The silica aerogel particles can serves as a magnetite nano particle support for and also as surface sites for various functional groups. The morphology, microstructure, and magnetic properties of the nanocomposite were investigated in terms of the content of Fe_3O_4 nanoparticles.

2. Experimental procedure

The Fe₃O₄ nanoparticles were synthesized by coprecipitation of Fe²⁺ and Fe³⁺ by adding ammonia. Iron (III) chloride hexahydrate (FeCl₃ · 6H₂O) and iron (II) chloride tetrahydrate (FeCl₂ · 4H₂O) with a molar ratio of 1:2 were dissolved in water. The solution was stirred at 90 °C for 1 h before adding an aqueous ammonia solution (29%). Black Fe₃O₄ nanoparticles precipitated immediately after ammonia was added to the mixture. The solution was further stirred at 90 °C for 40 min. The obtained Fe₃O₄ nanoparticles were repeatedly washed with water and ethanol and then redispersed with oleic acid in *n*-hexane.







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A sodium silicate solution (water glass) was used as a precursor to prepare silicic acid because it is cheap and easy to handle compared to alkoxide-based precursors such as tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS). The water glass solution (Young Il Chemical, South Korea) was diluted with distilled water to make an 8 wt% silicate solution. The solution was then passed through a column filled with an ion-exchange resin (Amberite, IR-120H, H. Rohm & Haas Co., PA, USA). The sodium concentration in the silicic acid solution was estimated to be in the range between 40 and 90 ppm.

Silicic acid droplets were produced by mixing the obtained silicic acid solution and a surfactant (span 80) with *n*-hexane using a homogenizer (T25 D, IKA, Germany). The stirring speeds were 3200, 4000, 6000, 9000, and 14,000 rpm. Subsequently, a base catalyst (NH_4OH) was used to adjust the pH of the silicic acid to 6.0. The silicic acid droplets were gelated at room temperature.

The obtained spherical hydrogels were surface-modified in a 10% (trimethylchlorosilane (TMCS), Si(CH₃)₃Cl, 98% ACROS)/*n*-hexane solution for 10 h at room temperature. The surface-modification process was repeated seven times. Finally, the surface-modified wet gels were washed with *n*-hexane to remove residual agents and reaction products such as hydrochloric acid (HCl). Finally, the spherical wet gels were mixed with *n*-hexane containing Fe₃O₄ nanoparticles for 4 h and then dried at 80 °C in an electric oven at ambient pressure.

X-ray diffraction (XRD) patterns were taken using a diffractometer (DMAX-2500, Rigaku, Japan) with Ni-filtered Cu-K α radiation to perform a crystallographic study on the Fe₃O₄ and Fe₃O₄/ SiO₂ composite nanoparticles. The crystallite size of the synthesized particles was estimated using the Scherrer equation [13]:

$$D = 0.9\lambda/\beta \cos \theta \tag{1}$$

Here λ , θ , and β are the X-ray wavelength (0.15418 nm for Cu-K α), Bragg diffraction angle, and full width at half maximum (FWHM) of the diffraction peak, respectively. The morphology and microstructure of the Fe₃O₄ and Fe₃O₄/SiO₂ composite nanoparticles were examined by scanning (SEM, S-4300 Hitachi, Japan) and transmission (TEM, JEM2100F, JEOL, Japan) electron microscopy. A vibrating sample magnetometer (VSM, Physical Property Measurement System (PPMS), Quantum Design, USA) was used at room temperature to measure the magnetization of the Fe₃O₄ and Fe₃O₄/SiO₂ composite nanoparticles.

90Fe₃O₄/SiO₂ Fe O 70Fe₃O₄/SiO₂ (311)50Fe,O,/SiO, Fe₂O (422) (511) (440) Intensity (arb. units) (400) (533)(c) (b) 30 40 10 20 50 60 70 80 20 (degrees)

Fig. 1. XRD patterns of Fe₃O₄ (a), 50 wt% Fe₃O₄/SiO₂ (b), 70 wt% Fe₃O₄/SiO₂ (c), and 90 wt% Fe₃O₄/SiO₂ (d) nanocomposite particles.

3. Results and discussion

Fig. 1 shows typical XRD patterns of Fe₃O₄ and Fe₃O₄/SiO₂ composite nanoparticles. The obtained particle was found to be Fe₃O₄ with cubic inverse spinel structure (XRD pattern (a)). The peaks correspond to the (111), (220), (311), (400), (422), (511), (440), and (533) reflection of the Fe_3O_4 crystal structure. The presence of the broad diffraction peak at $2\theta = 23^{\circ}$ in the Fe₃O4/ SiO₂ nanocomposite particles indicates that SiO₂ has a typical amorphous structure that has been established in various silica aerogels [14]. For the nanocomposite samples, the intensity of the peaks corresponding to Fe_3O_4 increased with increasing Fe_3O_4 content. The crystallite sizes of Fe₃O₄ and nanocomposite samples were estimated using the Scherrer equation and the results are listed in Table 1. The crystallite size of Fe_3O_4 and 90 wt% Fe_3O_4 / SiO₂ nanocomposite sample were 9.7 and 10.0 nm, respectively. This result suggests that the Fe₃O₄ nanoparticles are well dispersed within the pore structure of SiO₂ aerogel particles. On the other hand, the crystallite size gradually decreased as the Fe₃O₄ content was decreased.

Fig. 2 shows SEM images and energy dispersive X-ray spectroscopy (EDS) analysis result for the SiO₂ aerogel and Fe₃O₄/SiO₂ nanocomposite particles. The size of the spherical SiO₂ aerogel particle was estimated to be ~150 μ m. The SEM images (Fig. 2 (a)) show the typical mesoporous microstructure that can be observed in a silica aerogel. The pore diameter of the silica aerogel determined by Brunauer–Emmett–Teller (BET) isotherm was ~14 nm [15], which is larger than the crystallite size of the Fe₃O₄ nanoparticles, as specified in Table 1. The EDS analysis confirmed that the particles inside the pores consist of Fe₃O₄, while the matrix particles were composed of SiO₂. Figs. 1 and 2 clearly indicate that the Fe₃O₄ nanoparticles are homogeneously dispersed in the pore structure of the SiO₂ aerogel particles.

Fig. 3(a)–(d) shows TEM images of Fe_3O_4 and Fe_3O_4/SiO_2 nanocomposite particles at low magnification. In Fig. 3(b)-(d), the dark areas correspond to Fe₃O₄ particles while the gray matrix originates from the SiO₂ aerogel. It can be observed that Fe₃O₄ nanoparticles are quasispherical with an average diameter of 10 nm. In the case of Fe₃O₄/SiO₂ nanocomposite samples, the Fe₃O₄ nanoparticles were homogeneously dispersed in the silica aerogel structure. In addition, it seems that the Fe₃O₄ nanoparticles were embedded in the mesopores of the SiO_2 aerogel as Fig. 3(b) and (c) shows. The highly magnified TEM image (Fig. 3(e)) and the selected area electron diffraction (SAED) pattern (Fig. 3(f)), aligned with the electron beam parallel to the $\langle 110 \rangle$ axis, reveal that the Fe₃O₄ nanoparticle in the SiO₂ aerogel has a single crystalline structure. As can be seen in Fig. 3 (e), the distance between two adjacent planes was measured to be 0.484 and 0.295 nm, corresponding to the (111) and (220) planes of the cubic Fe₃O₄ structure, respectively. In addition, it was determined that spots 1, 2, 3, 4, and 5 in Fig. 3(f) corresponds to (220), (311), (400), (511), and (440) plane, respectively, and the obtained result is good agreement with previous XRD measurements (Fig. 1).

Fig. 4 shows the room-temperature magnetization curves of the Fe_3O_4 and Fe_3O_4/SiO_2 nanocomposite particles. Similar to pure

Table 1						
The cryst	allite s	ize of	Fe_3O_4	and	Fe ₃ O ₄ /SiO ₂	nanocomposite
particles.						

Sample	Crystallite size (nm)
Hydrophilic Fe ₃ O ₄	11.2
Hydrophobic Fe ₃ O ₄	9.7
90Fe ₃ O ₄ /SiO ₂	10
70Fe ₃ O ₄ /SiO ₂	9.7
50Fe ₃ O ₄ /SiO ₂	9.3

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