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Synthesis and surface modification of hydrophobic magnetite to processible magnetite@silica-propylamine

Kyoungja Woo*, Jangwon Hong, Jae-Pyoung Ahn

Korea Institute of Science and Technology, Nanomaterials Research Center, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

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Abstract

Hydrophobic magnetite nanoparticles with a narrow size distribution were prepared by thermal decomposition of $\text{Fe}(\text{CO})_5$ in octyl ether solution of oleic acid and by consecutive aeration. The nanoparticles were converted into magnetite core/silica shell (magnetite@silica) structured particles with hydrophilic and processible aminopropyl groups on their surfaces.

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Keywords: Magnetite; Nanoparticles; Surface modification; Silica shell; Functionalization; Propylamine groups; Synthesis

Iron oxide nanoparticles have been of great interest in a field of clinical uses [1–4]. Clinical application requires that iron oxide nanoparticles should be discrete and superparamagnetic with sizes smaller than 20 nm and have a narrow size distribution for uniform physical and chemical properties. Magnetite and maghemite nanoparticles are commonly studied magnetic iron oxides for clinical applications. The advantage of using iron oxide nanoparticles relies on their chemical stability, in contrast to commonly used nanoparticles of pure Fe metal.

Iron oxide nanoparticles prepared by classical methods [5–7] have been quite limited to meet the requirement for clinical applications since they are frequently aggregated and have a wide size distribution. Recently, thermal decomposition of the iron precursor in hot organic solution containing surfactants has been developed for the synthesis of discrete and monodisperse iron oxide nanoparticles satisfying the requirement. It has been demonstrated that direct decomposition of $\text{Fe}(\text{Cup})_3$ single precursor [8], or decomposition of $\text{Fe}(\text{CO})_5$ followed by oxidation [9], can lead to maghemite nanoparticles with a narrow size distribution. Also has been shown that high temperature reaction of iron (III) acetylacetonate in phenyl ether in the presence of alcohol and surfactant can be used to make magnetite

*Corresponding author. Tel.: +82 2 958 5265;
fax: +82 2 958 5529.

E-mail address: kjwoo@kist.re.kr (K. Woo).

nanoparticles with a narrow size distribution [10]. Discreteness and narrow size distribution are the advantages of nanoparticles produced by thermal decomposition of organometallic precursors in organic solution of surfactants. However, without surface modification, these magnetic nanoparticles are hydrophobic and not amenable to applications in medical uses.

Meanwhile, most of the proteins and biocompatible molecules are hydrophilic and have carboxyl ($-\text{COOH}$) or amine ($-\text{NH}_2$) functional groups, which can be utilized to make amide bonds with their counter parts [11,12]. Therefore, surface modification of hydrophobic nanoparticles is of great importance to provide hydrophilic and processible functional groups, $-\text{NH}_2$ or $-\text{COOH}$. In this study, we report synthesis and surface modification of hydrophobic magnetite nanoparticles to hydrophilic and processible state with $-\text{NH}_2$ end groups on their surfaces.

According to our easy reaction, all the reagents and solvents were used as purchased without further purification. Magnetite nanoparticles were synthesized under a nitrogen flow as follows: 2.00 mL (15.2 mmol) of $\text{Fe}(\text{CO})_5$ (Aldrich, 80–90%) was injected into a mixture containing 100 mL of octyl ether (Aldrich, 99%) and 14.4 mL (45.6 mmol) of oleic acid (Aldrich, 90%) at 100 °C. The resulting mixture was slowly heated and refluxed for 2 h. This solution was cooled to 80 °C, aerated for 14 h and then, refluxed for 2 h again. A portion (25 mL) of this solution was conserved for surface modification. The remaining solution was treated with excess ethanol and separated by centrifugation. Drying the solid in the air yielded 1.42 g of magnetite nanoparticles.

For a conversion to magnetite@silica-propylamine, 20 mL of the conserved solution was diluted with 20 mL of toluene and treated with 0.10 mL of NH_4OH /ethanol (1/1 by volume). Then, 3.04 mL (13.6 mmol) of tetraethyl orthosilicate (Aldrich, 99+ %) was added for 1 day and the solution was heated to 150 °C for 1 h. After cooling, 0.10 mL (0.60 mmol) of 3-aminopropyltrimethoxysilane (Aldrich, 97%) was added slowly and the solution was heated to 150 °C for 1 h. After cooling, this solution was treated with excess ethanol and the solid was separated by centrifugation. Drying the

solid in the air yielded 0.143 g of silica-coated magnetite particles with propylamine functional groups on their surfaces.

The overall surface modification procedure is shown in Fig. 1. The $-\text{NH}_2$ functional group of the third structure is expected to give diverse applicability via amide bonding with biological molecules or biocompatible polymers.

Fig. 2 shows the TEM/HRTEM images of magnetite nanoparticles before and after silica coating. Before coating, magnetite nanoparticles were discrete and showed a relatively narrow size distribution (Fig. 2(A) and (C)). The average particle size over 100 particles was 28 nm (standard deviation = 2.4 nm). This size is larger than the requirement for clinical applications and this sized magnetite nanoparticles are expected to be ferrimagnetic at room temperature [13]. According to our easy synthesis and Mössbauer data, the particles with sizes of 19 nm or larger were magnetite and those of 11 nm or smaller were maghemite [14]. However, the surface properties of these particles are expected to be chemically similar and so the surface modification reactions will work out similarly. In this report, we have focused on the surface properties of the nanoparticles rather than the superparamagnetism by size effect. After silica coating, the magnetite cores were still discrete with the same sizes (Fig. 2(B) and (D)). The shape of the silica shell fringe in HRTEM image (D) suggests that silica nanoparticles are formed by separate seeding and then adhere onto the surface of magnetite core. However, it seems like that the magnetite@silica nanoparticles are connected together by interparticle gelation during silica coating. This phenomenon has been reported in silica coating process of semiconductor nanoparticles [12], too and needs further investigation.

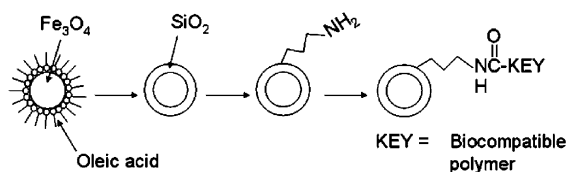


Fig. 1. Overall surface modification procedure.

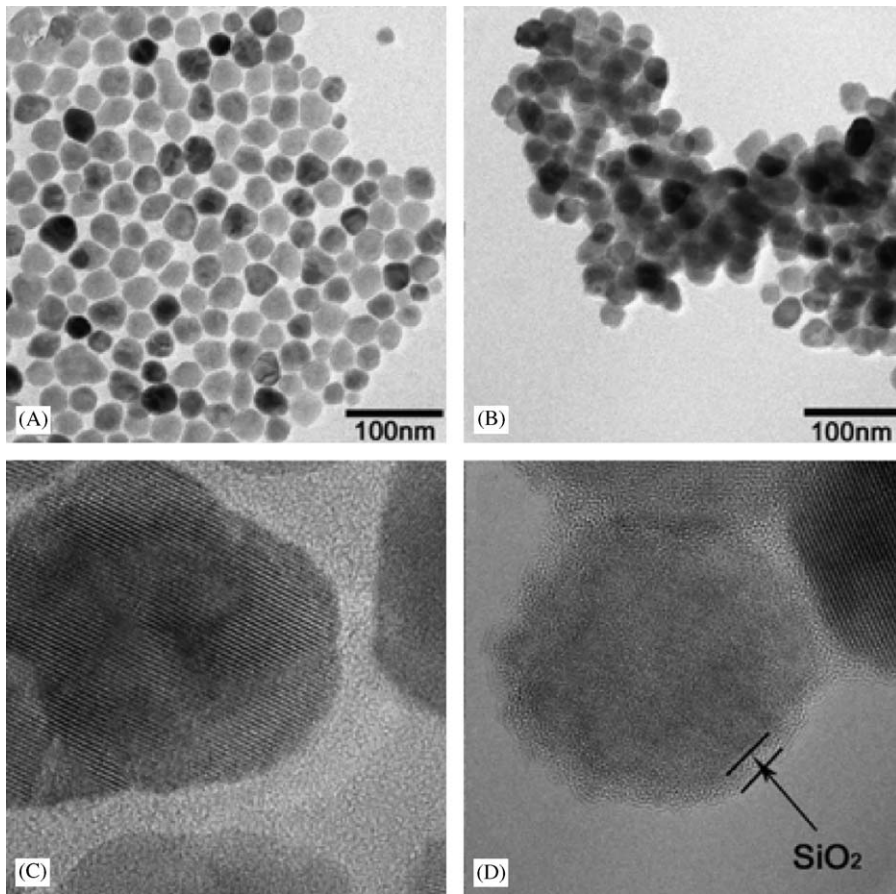


Fig. 2. Relative TEM/HRTEM images of nanoparticles: (A)/(C) magnetite, (B)/(D) magnetite@silica.

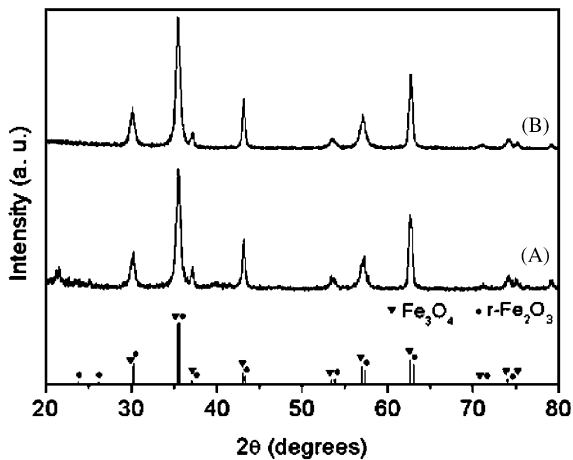


Fig. 3. XRD patterns of nanoparticles: (A) magnetite, (B) magnetite@silica-propylamine.

Fig. 3 shows the XRD patterns of magnetite and magnetite@silica-propylamine nanoparticles. Both XRD patterns are close to magnetite rather than maghemite, comparing with the standard JCPDS data [15]. No additional peak, after surface modification, suggests that the silica shell is amorphous. The small peak below 25° in Fig. 3(A) is likely to be caused by oleic acid layer on the particle surface since it has disappeared after surface modification.

Fig. 4 shows the FT-IR spectra of magnetite nanoparticles before and after surface modification. Spectrum (A) implicates the existence of magnetite covered with oleate, which shows C–H stretching bands just below 3000 cm^{-1} , iron carboxylate bands around 1450 cm^{-1} , and F–O band at 577 cm^{-1} [12,16,17]. Spectrum (B) showed

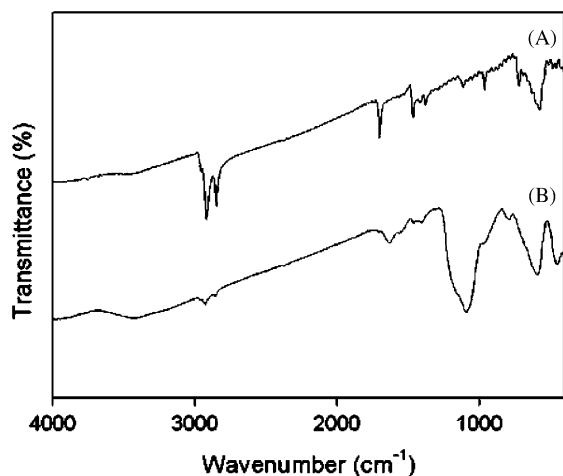


Fig. 4. FT-IR spectra of nanoparticles: (A) magnetite, (B) magnetite@silica-propylamine.

a new strong band around 1093 cm^{-1} originating from Si–O bond of silica [12]. A weak and broad band around 3400 cm^{-1} is caused by hydrogen bonded N–H and O–H stretching modes. The C–H stretching bands just below 3000 cm^{-1} have reduced greatly after the $\text{C}_3\text{H}_7\text{-NH}_2$ moiety replaced the $\text{C}_{18}\text{H}_{35}$ moiety by surface modification. The absorption bands around 1450 cm^{-1} by iron carboxylate [17] have mostly disappeared after surface modification.

Fig. 5 shows the magnetization curves of nanoparticles. The coercivity and remanence values are similar before and after surface modification. However, the magnetization values of magnetic nanoparticles have increased after surface modification. This is contrasted with the results of a classical synthesis and surface modification, in which uncoated nanoparticles show slightly higher magnetization than their (3-aminopropyl)triethoxysilane-coated magnetite nanoparticles [13]. It suggests that the weight fraction of oleic acid in magnetite nanoparticles is higher than that of silica-propylamine in magnetite@silica-propylamine nanoparticles. Besides, the surface layer of magnetite in magnetite@silica-propylamine seems to be magnetically more active than that of magnetite covered with oleic acid due to the continuity of Fe–O–Si bonds.

It has been shown that hydrophobic magnetite nanoparticles with a narrow size distribution were

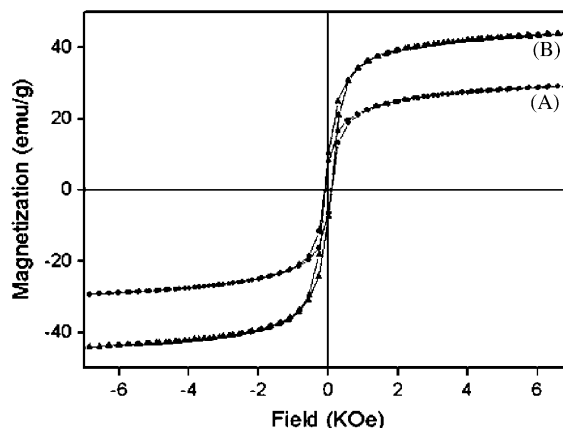


Fig. 5. Magnetization curves of nanoparticles: (A) magnetite, (B) magnetite@silica-propylamine.

prepared by thermal decomposition of $\text{Fe}(\text{CO})_5$ and by consecutive aeration. They were converted to hydrophilic and processible silica-coated magnetite nanoparticles with aminopropyl groups on their surfaces. The silica-coated magnetite nanoparticles showed higher magnetization values than the uncoated ones, due to weight reduction of diamagnetic materials and the continuity of Fe–O–Si bonds. The amine end group is expected to give diverse applicability via amide bonding with biocompatible molecules.

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