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Superparamagnetism of Magnetite Nanoparticles: Dependence on Surface Modification

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Superparamagnetic iron oxide nanoparticles (SPION) with an average particle diameter of 6 nm are prepared by controlled chemical coprecipitations. Colloidal suspensions of noninteracting SPION, where the surface has been modified with three different types of biocompatible substances, namely, starch, gold (Au), and methoxypoly(ethylene glycol) (MPEG) have been fabricated via three different techniques. Starch-coated SPION are prepared by coprecipitation in a polymeric matrix, Au-coated SPION are fabricated by the microemulsion method, and MPEG-coated SPION are prepared using the self-assembly approach. The magnetic nanoparticles form a core-shell structure, and the magnetic dipole-dipole interactions are screened by a layer of coating agents. The amounts of coating agents and SPION are indirectly calculated from the thermogravimetric analysis and superconducting quantum interference device measurements by assuming passive oxidation on the surface of the SPION, and the other conditions do not influence the measurements. The dependency of the spectral characteristics of Mössbauer spectroscopy as a function of an external magnetic field H_{ext} is measured to investigate the effect of dipole-dipole screening of the different coating layers on the SPION. Uncoated SPION show a stable magnetic moment under H_{ext} , and the superparamagnetic (SPM) fraction transforms to a ferrimagnetic state. Starch and Au-coated SPION retain the SPM fraction according to Mössbauer spectroscopy and magnetization measurements. MPEG-coated SPION show hyperfine magnetic structure without the quadrupole effect with increasing the value of the blocking temperature.

Introduction

The magnetic properties of superparamagnetic iron oxide nanoparticles (SPION) and ferrofluids prepared by dispersing the magnetic nanoparticles in a suitable liquid carrier were intensively studied as a result of their versatile applications in diverse areas including separation science and technology.^{1–3} Recently, the use of SPION is mainly focused on biomedical applications because they show rather low toxicity than other magnetic materials.^{4,5} It is known that the biocompatibility can be improved by the surface modification of SPION with various organic or inorganic substances such as dextran,^{6,7} DNA,⁸ YADH,⁹ poly(ethylene glycol) (PEG),^{10,11} silica,¹² poly(vinyl alco-

hol),¹³ heparin,¹⁴ phospholipids,¹⁵ and so forth. However, the immobilization process is usually quite complicated and requires special coupling agents.⁷ The development of new biocompatible systems is still considered a challenge for in vitro and in vivo applications.

The magnetic properties of the surface-modified SPION are mainly dominated by the coating materials and their interfacial interactions on the surface of SPION and can be drastically changed after the immobilization. In view of the technological consequence of producing the surface-modified SPION in the nanoregime, several techniques such as controlled chemical coprecipitation,^{3,16} sol-gel,¹⁷ microemulsion (μ E), and sonochemical¹⁸ techniques have been reported. However, the influences of coating substances on the magnetic properties of SPION and interparticle interactions have not been fully investigated.

In this study, SPION with a particle size of 6 nm are prepared by controlled chemical coprecipitations. The superconducting quantum interference device (SQUID) magnetometer and Mössbauer spectroscopy are used to investigate the magnetic properties after modifying the surface of SPION with different diamagnetic materials

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such as starch, gold, and methoxypoly(ethylene glycol) (MPEG). Specifically, Mössbauer spectroscopy is one of the widely applied techniques to investigate the properties of electronic and magnetic states of iron and the local surroundings¹⁹ and has been used to study the SPION with different particle sizes at different temperatures.^{18,20–22} The influence of the coating layers is also investigated by measuring the magnetic properties as a function of the temperature and an external magnetic field H_{ext} because it has been proved as a main factor to understand the physical properties of surface-modified SPION.

Experimental Section

Materials. All chemicals were of reagent grade and used without further purifications. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, >99%), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, >99%), octane (Aldrich, >99% HPLC grade), cyclohexane (Aldrich, 99+% HPLC grade), cetyltrimethylammonium bromide (CTAB, Fluka, 99%), and starch [25–30 kDa, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, >99%] were obtained from Aldrich. Hydrogen peroxide (H_2O_2 , >99%) and hydrochloric acid (HCl, 37%) were obtained from KEBO. Cationic starch [from potato, 25–30 kDa, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$] and MPEG 5000 [$\text{CH}_3-(\text{OCH}_2-\text{CH}_2)_n-\text{OH}$] were obtained from Sigma. The potato starch contained quaternary ammonium groups (2-hydroxy-3-trimethylammoniumpropyl starch), and its degree of substitution was 0.352. Milli-Q water was re-deionized (specific conductance < 0.1 S/cm) and deoxygenated by bubbling N_2 gas for 1 h prior to use.

Preparation of the Magnetic Colloid. SPION with an average particle size of 6 nm were prepared without any additional stabilizer according to the following procedure. Typically, 5 mL of a 0.1 M Fe^{2+} and 0.2 M Fe^{3+} iron solution was added dropwise into 50 mL of alkali solution (0.1 M NaOH) under vigorous mechanical stirring (223 xg) for 30 min at room temperature. The color of the suspension turned black immediately. The precipitated powders were collected and removed from the solution by applying a magnet. The supernatant solution was removed from the reaction mixture by decantation. Deoxygenated Milli-Q water was added to wash the powder, and the solution was decanted after centrifugation at 684 xg. The powder was washed four times followed by the addition of a 1×10^{-2} M HCl solution to neutralize the anionic charge on the surface of particles. The positively charged colloidal particles were then separated by centrifugation and peptized by adding deoxygenated Milli-Q water. On the basis of the X-ray diffraction (XRD) measurements, SPION with an average particle size of 6 nm were selected for the further coating process. Three different types of coated magnetic colloids were prepared according to the following procedures:

(a) *Au-Modified SPION.* Au-coated SPION were synthesized in the CTAB/octane/butanol/water μE system. The μE was prepared from octane, cyclohexane, CTAB, and an aqueous mixture (SM) of ferric chloride, ferrous chloride, and HAuCl_4 solutions. The concentration of the stock solutions was 1×10^{-1} M for FeCl_3 , 5×10^{-2} M for FeCl_2 , 0.8 M for NaBH_4 , and 1×10^{-1} M for HAuCl_4 using Milli-Q water (18 M Ω m), which was re-deionized and deoxygenated by bubbling N_2 gas for 1 h before use. Three parameters are necessary to define the composition of the four-component μE system: the molar ratio between water and surfactant [CTAB] (W_0) and that between cosurfactant (butanol) and surfactant (P_0), together with the molar concentration of the surfactant. The μE was prepared by weighing the appropriate amounts of surfactant, butanol, octane, and water in a volumetric flask. Several μE systems with different W_0 's

(>5) were obtained through dilution using water (or an aqueous salt solution) as a stock solution, prepared at $W_0 = 5$ and at a given P_0 . The water (or aqueous salt solution) used for the dilution was accurately measured by using microsyringes. An aliquot of 5 mL of the μE containing the mixture solution SM and 1×10^{-1} M CTAB, with $W_0 = 5$ and $P_0 = 10$, was poured into 5 mL of a μE containing 1 M NaOH and 1×10^{-1} M CTAB, with $W_0 = 5$ and $P_0 = 10$, while stirring in a closed system for 1 h. After the SPION were precipitated inside the micelle (with black color), 10 mL of the μE containing 0.8 M NaBH_4 , 1×10^{-1} M CTAB, with $W_0 = 10$ and $P_0 = 10$, was slowly added to the SPION containing a μE solution at 60 °C, to reduce Au on the surface of the SPION. The Au-coated SPION were isolated by applying a magnet, the supernatant solution was removed by decantation, and the powder was dried under a vacuum.

(b) *MPEG-Modified SPION.* The SPION suspension was prepared as described previously. After that, it was washed several times with analytical grade methanol (99.5%) with the help of a strong magnet. An aliquot of 5 mL with a concentration of 10 mg/mL SPION was dispersed in a toluene/methanol (1:1 v/v) mixture and heated at 95 °C under N_2 until 50 vol % of the solution was evaporated. After evaporation, methanol was added to an equal volume and the mixture was re-evaporated to one-half. This procedure was repeated three times, until the residual water was thoroughly removed. A solution of 3-aminopropyltrimethoxy silane (APTMS) was added to the suspension. APTMS acts as a coupling agent, where silanization takes place on the particle surfaces bearing hydroxyl groups in the organic solvent. This results in the formation of three-dimensional polysiloxane networks. The ferrofluid suspension was stirred and heated under an N_2 atmosphere at 110 °C for 12 h. The silanization taking place during the reflux of APTMS results in the formation of an APTMS coating with a thickness of two or three molecular layers tightly cross-linked with a large surface density of amines. The silanized SPION were subsequently sonicated for 2 min in a mixture of toluene/methanol (1:1 v/v). When the solution was cooled to 80 °C, an extra amount of MPEG 5000 was added to modify the surface of the SPION.

(c) *Starch-Modified SPION.* A total of 100 mg of starch was dissolved in 20 mL of distilled and deionized water at 80 °C under magnetic stirring. An aliquot of 5 mL of solution containing 0.1 M Fe^{2+} and 0.2 M Fe^{3+} was poured into a previously prepared starch solution under vigorous stirring. A total volume of 25 mL of the starch and iron ions mixture was then added dropwise into 250 mL of solution of 0.1 M NaOH under vigorous mechanical stirring (223 xg) at 60 °C for 2 h. Approximately 50 wt % of water was evaporated, and the remaining solution mixture was cooled to room temperature and allowed to stand for 12 h. The formed gel was washed with deionized water until the pH became less than 8.5. Excess salt and ions were removed by using dialysis at 37 °C for 2–3 days against 5 L of distilled water. A total of 5 mL of 0.46 M H_2O_2 solution was mixed with 20 mL (10 mg/mL) of starch-coated SPION to cleave the glycoside bond and reduce the molecular weight of the polymeric chain.

Characterizations. The crystal structure of the precipitated powders was measured by XRD with a Philips PW 1830 diffractometer, using a monochromatized X-ray beam with nickel-filtered $\text{Cu K}\alpha$ radiation. A JEOL-2000EX transmission electron microscope (TEM) was used to investigate the particle size, morphology, and size distribution of SPION. The particle size and size distribution were calculated from TEM images for all prepared samples using an image analysis program and by measuring the diameters of at least 500 particles. The surface morphology of Au-coated SPION (see Supporting Information) was examined by atomic force microscopy (AFM). An AFM Nanoscope IIIa system was used in the tapping mode by employing a silicon tip with a resonance frequency in the range of 286–313 kHz.

Thermogravimetric analysis (TGA) was carried out for powder samples (~10 mg) with a heating rate of 10 °C/min using a Perkin-Elmer TGA 7 thermogravimetric analyzer in a synthetic air atmosphere up to 700 °C.

Mössbauer spectra were recorded with a conventional transmission Mössbauer spectrometer operating in the constant acceleration mode ($T = 300$ K). A ~100 mCi of a ^{57}Co (Rh) source

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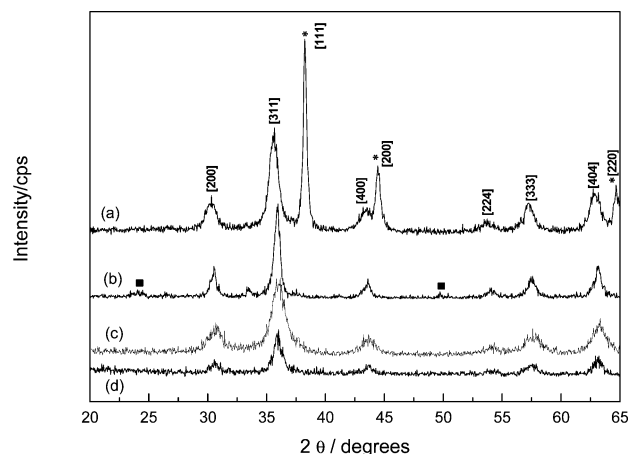


Figure 1. X-ray powder diffraction patterns of (c) uncoated and (a) Au-, (d) starch-, and (b) MPEG-coated SPION: (*) Au peaks, (■) MPEG peaks

was used, and the spectrometer was calibrated using α -iron at room temperature.

The magnetization of the samples was measured with a 7 T Quantum Design SQUID magnetometer in the temperature range of 5–300 K. For zero-field cooled (ZFC) experiments, the sample was cooled and a constant field was applied during the warm scan. Additionally, magnetic susceptibility was measured by the Faraday method in the temperature range of 77–400 K.

Results and Discussion

XRD patterns of (c) uncoated and (a) Au-, (d) starch-, and (b) MPEG-coated SPION are shown in Figure 1. The diffractograms of all the samples show peaks corresponding to the spinel structure. The uncoated SPION prepared by a controlled chemical coprecipitation process can be expected as magnetite with a pure phase on the basis of the results from thermodynamic modeling.²³ In the case of Au-coated SPION, the characteristic peaks of Au are also observed. The peaks assigned to metallic Au show a high degree of crystallinity. The line broadening is observed for the starch-coated SPION, which is similar to the uncoated SPION because of the crystal size. The low peak intensity for sample (d) is due to the presence of the layer of an amorphous starch on the surface of the SPION. The MPEG-coated SPION show a better crystallinity with the presence of a small amount of MPEG as a second phase compared to the starch-coated SPION.

Figure 2 shows TEM images of (a) uncoated and (b) Au-, (c) starch-, and (d) MPEG-coated SPION taken from the colloidal suspension. The particles size distribution is calculated on the basis of a log-normal function with image analysis software. The particles show roughly a spherical or ellipsoidal shape with some irregularities. The particles sizes calculated from the TEM images are shown in Table 1. The size distribution is log-normal with a standard deviation of $\sigma \sim 0.2$.

Figure 3 shows the TGA thermograms for uncoated and surface-modified SPION. The absolute weight loss of the (a) uncoated SPION is 4% for the whole temperature range because of the removal of adsorbed physical and chemical water. The thermogram of starch-coated SPION shown in Figure 3b has a weight loss that is small until ~ 180 °C, moderate between 180 and 230 °C, and significant above 230 °C. The major transition due to the weight loss occurs between 150 and 450 °C. The two main peaks imply that at least one decomposition reaction is taking place

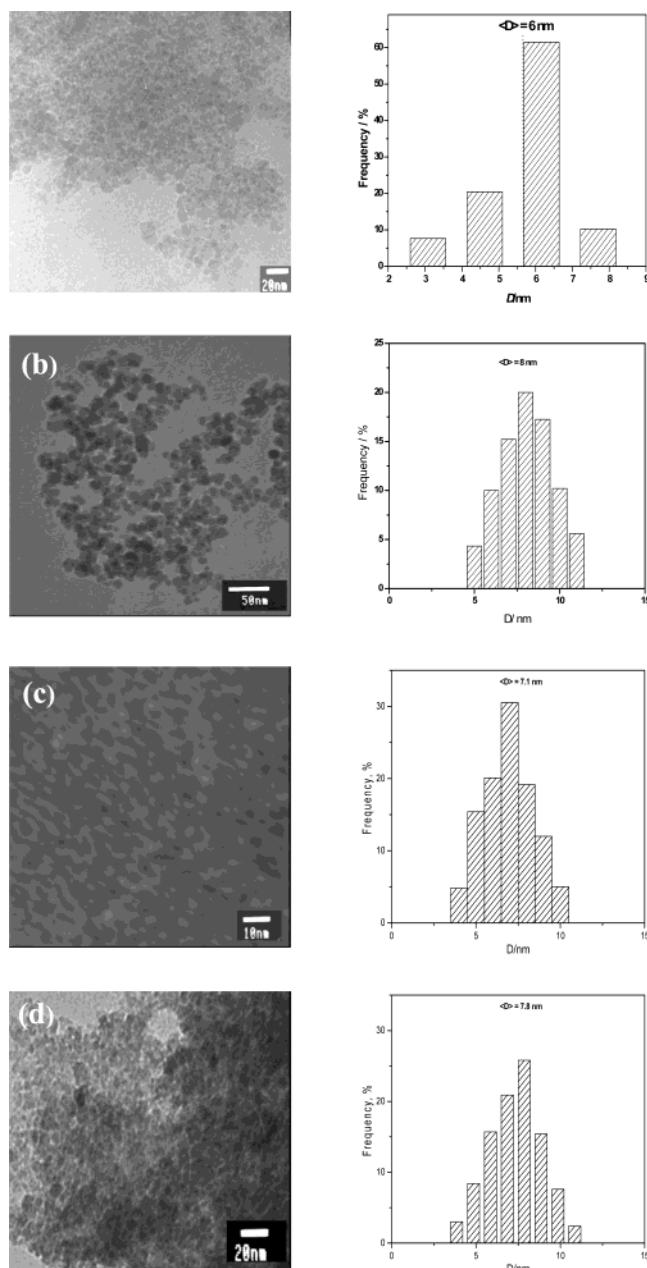


Figure 2. TEM images (left) and the corresponding particle size histograms (right) of (a) uncoated and (b) Au-, (c) starch-, and (d) MPEG-coated SPION.

Table 1. Average Particle Sizes (D) for Uncoated and Au-, Starch-, and MPEG-Coated SPION Calculated from TEM and Magnetization Data

sample	D_{TEM} (Å)	D_{MAG} (Å)
SPION	6.0	5.4
Au-coated SPION	8.0	7.8
starch-coated SPION	7.1	5.2
MPEG-coated SPION	7.8	6.4

in this temperature range. The weight loss of the MPEG-coated SPION is quite small below 100 °C, moderate up to 180 °C, but significant at temperatures higher than 180 °C (Figure 3c). PEG with low M_w (550 and 5000) can be degraded at ~ 280 °C.²⁴ According to the TGA data, the main weight loss is observed at about 300 °C. The amount of MPEG coated on the surface of the SPION can be calculated on the basis of the TGA data and was found to be 39.6 ± 5 wt %.

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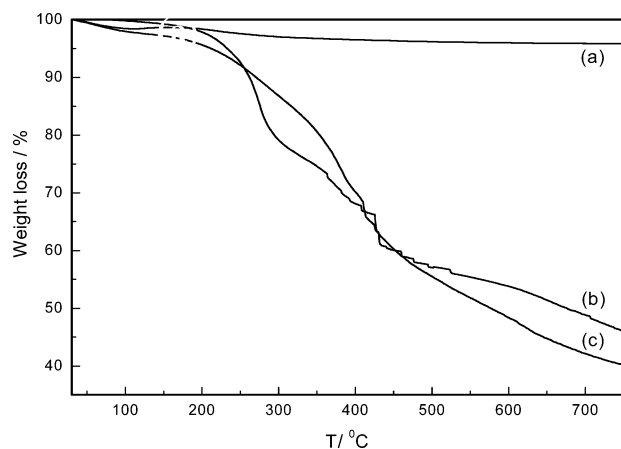


Figure 3. TGA thermograms of (a) uncoated and (b) starch- and (c) MPEG-coated SPION.

The Mössbauer spectrum of uncoated SPION at 300 K represents a broad line, shown in Figure 4a, in the absence of an external magnetic field (H_{ext}). The spectrum consists of a doublet with an isomer shift of $\delta = 0.38 \text{ mm s}^{-1}$, a line width of $\Gamma = 0.992 \text{ mm s}^{-1}$, and a quadrupole splitting of $\Delta E_Q = 0.755 \text{ mm s}^{-1}$ and a sextet with a magnetic hyperfine field of $B_{\text{hf}} = 474 \text{ kOe}$, an isomer shift of $\delta = 0.321 \text{ mm s}^{-1}$, a line width of $\Gamma = 1.355 \text{ mm s}^{-1}$, and a quadrupole splitting of $\Delta E_Q = -0.071 \text{ mm s}^{-1}$. The area of the components for the uncoated SPION without H_{ext} is in the ratio of doublet/sextet (34.2:65.8%). The quadrupole component (doublet) is assigned to the superparamagnetic (SPM) fraction. The Mössbauer spectrum of uncoated SPION corresponds to the particles sizes between 3 and 10 nm, accordingly, which is in agreement with data reported in refs 18 and 21. In the case of an ultrafine state, two iron sublattices do not resolve at 300 K and about one-third of the sample remains in the SPM state. The SPM component disappears when H_{ext} (0.17 T) is applied as a result of the induced magnetization of the sample (data not shown). In the presence of H_{ext} , the Mössbauer spectrum of uncoated SPION is approximated by one sextet with a very large line width of $\Gamma = 5.466 \text{ mm s}^{-1}$, a magnetic hyperfine field of $B_{\text{hf}} = 328 \text{ kOe}$, an isomer shift of $\delta = 0.332 \text{ mm s}^{-1}$, and a quadrupole splitting of $\Delta E_Q = -0.056 \text{ mm s}^{-1}$. The line broadening of the sextet is due to the particle size distribution of SPION and the various types of crystallographic surroundings of iron atoms. This is in agreement with a spinel structure, where Fe^{2+} and Fe^{3+} ions are located in different crystallographic positions (octa- and tetrahedral). Mössbauer spectra of magnetite reveal two sextets with an isomer shift of $\delta = 0.27 \text{ mm s}^{-1}$ (Fe^{3+} ions in tetrahedral A sites) and $\delta = 0.65 \text{ mm s}^{-1}$ (Fe^{2+} and Fe^{3+} ions in octahedral B sites).²⁵ The ion state of iron atoms Fe^{2+} and Fe^{3+} cannot be distinguished at room temperature as a result of the fast electron-hopping process.²⁶ The random distribution of iron cations in octahedral B sites results in an average valence state of $\text{Fe}^{2.5+}$. The value of the isomer shift decreases probably because of the presence of the non-stoichiometric magnetite phase.²⁷ Moreover, it is also known that the maghemite phase can coexist with magnetite during the synthesis of magnetite by controlled chemical coprecipitation.

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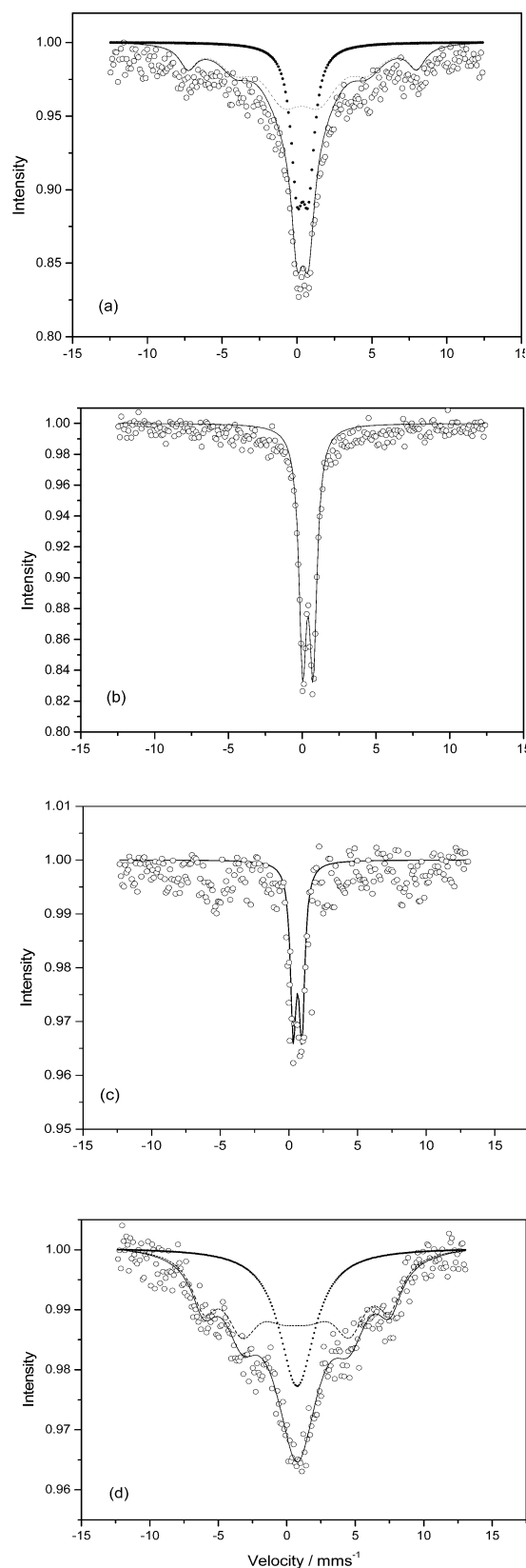


Figure 4. Mössbauer spectra of (a) uncoated and (b) starch-, (c) Au-, and (d) MPEG-coated SPION in the absence an external magnetic field.

The Mössbauer spectrum of the starch-coated SPION at 300 K is shown in Figure 4b in the absence of H_{ext} . The spectrum consists of one doublet with an isomer shift of $\delta = 0.387 \text{ mm s}^{-1}$, a line width of $\Gamma = 0.617 \text{ mm s}^{-1}$, and a quadrupole splitting of $\Delta E_Q = 0.712 \text{ mm s}^{-1}$. The

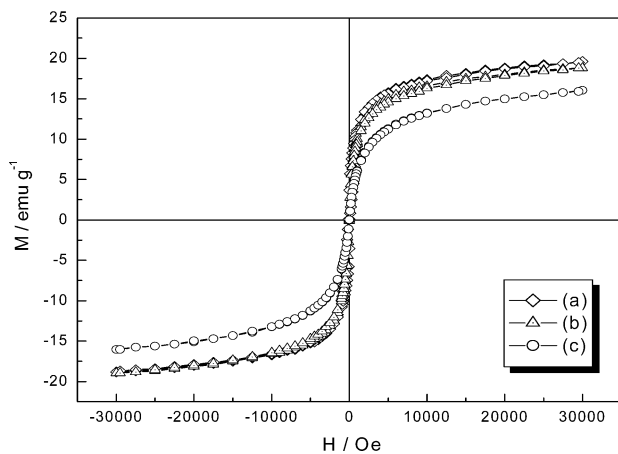


Figure 5. SQUID magnetization of Au-coated SPION: (a) 5, (b) 100, and (c) 300 K.

temperature-dependent Mössbauer spectra for dextran-coated iron oxide particles reported by Kilcoyne and Gorisek²⁸ represent the doublet until 120 K with an isomer shift of 0.39 mm s^{-1} and a quadrupole splitting of $\Delta E_Q = 0.72 \text{ mm s}^{-1}$, which is in good agreement with the data on starch-coated SPION in the current study. Mössbauer spectrum of Au-coated SPION without H_{ext} has only one doublet (Figure 4c) with an isomer shift of $\delta = 0.632 \text{ mm s}^{-1}$, a line width of $\Gamma = 0.52 \text{ mm s}^{-1}$, and a quadrupole splitting of $\Delta E_Q = 0.616 \text{ mm s}^{-1}$. The value of the isomer shift of the Au-coated SPION is greater than that for starch-coated SPION because of the transfer of electron density from Au to the surface of the SPION. A comparison of the Mössbauer spectra of uncoated and coated SPION shows that the doublet associated with the SPM state is retained only for starch- and Au-coated SPION.

The Mössbauer spectrum of MPEG-coated SPION at 300 K is displayed in Figure 4d, which consists of a singlet with an isomer shift of $\delta = 0.765 \text{ mm s}^{-1}$ and a line width of $\Gamma = 3.142 \text{ mm s}^{-1}$ and a sextet with a magnetic hyperfine field of $B_{\text{hf}} = 425 \text{ kOe}$, a line width of $\Gamma = 2.172 \text{ mm s}^{-1}$, an isomer shift of $\delta = 0.691 \text{ mm s}^{-1}$, and a quadrupole splitting of $\Delta E_Q = -0.067 \text{ mm s}^{-1}$ in the absence of H_{ext} . The areas of the components of MPEG-coated SPION without H_{ext} are in the ratio of singlet/sextet of 31.7:68.3%, whereas the Mössbauer spectrum in the presence of H_{ext} (data not shown) has double sextets, where one sextet has 52.5% of area of the component with a line width of $\Gamma = 1.216 \text{ mm s}^{-1}$, a magnetic hyperfine field of $B_{\text{hf}} = 451 \text{ kOe}$, an isomer shift of $\delta = 0.714 \text{ mm s}^{-1}$, and a quadrupole splitting of $\Delta E_Q = 0.004 \text{ mm s}^{-1}$ and the other sextet has 47.5% of the area of the component with a line width of $\Gamma = 1.043 \text{ mm s}^{-1}$, a magnetic hyperfine field of $B_{\text{hf}} = 369 \text{ kOe}$, an isomer shift of $\delta = 0.533 \text{ mm s}^{-1}$, and a quadrupole splitting of $\Delta E_Q = -0.273 \text{ mm s}^{-1}$. According to these data, the MPEG layer cannot completely protect the SPION against the formation of small aggregates, and as a consequence, the magnetic interactions mask the SPM fraction, resulting in a sharp increase of the line width in the spectra. According to the parameters from Mössbauer spectroscopy, the SPM fraction decreases for a long period in the presence of MPEG compared to Au- or starch-coated SPION.

The saturation magnetization (M_s), coercivity, and remanence magnetization are derived from the SQUID measurements for the Au-coated (Figure 5), uncoated, starch-coated, and MPEG-coated SPION (data not shown).

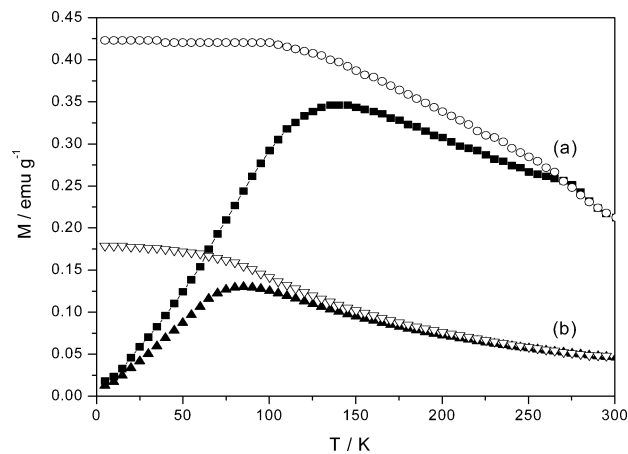


Figure 6. ZFC at 10 Oe and FC measurements of (a) MPEG- and (b) Au-coated SPION.

All samples show typical SPM behaviors. Figure 5 shows typical magnetization loops for Au-coated SPION at different temperatures, where no reduced remanence and coercivity were observed. M_s is not reached even at 30 kOe and is derived from the extrapolation of M versus $1/H$. The M_s at 5 K is 21 emu/g and is decreased to 18 emu/g as the temperature is raised to 300 K. However, the M_s value is not directly correlated with a bulk magnetite (92 emu/g) because the amount of Au in the sample is not considered in the calculation. As reported earlier,¹⁶ uncoated SPION show an M_s of 42.1 emu/g at 300 K. Therefore, the content of the Au-coated SPION can be calculated by assuming that the other variables do not influence the magnetization, resulting in the composition of 58 wt % of Au and 42 wt % of magnetite. The small hysteresis loop appears in the temperature range of 5–80 K. The value of magnetization will decrease by increasing the thickness of the coating layer on the surface of the SPION as a result of the presence of the diamagnetic component.

The magnetic core size for all the samples is calculated by assuming a log-normal size distribution according to ref 29. At 300 K, the size of the magnetic core is estimated for uncoated and Au-, starch-, and MPEG-coated SPION with a standard deviation $\sigma_m \sim 0.4$ (Table 1). The value of the magnetic core size of coated SPION is smaller than that obtained from the TEM data because of the presence of a nonmagnetic or magnetically dead layer on the surface of the SPION.³⁰

The ZFC and field cooled (FC) magnetization of Au- and MPEG-coated SPION are shown in Figure 6. The maximum on the ZFC curve is attributed to T_b and can be calculated by considering the intrinsic magnetization of the crystal:¹⁴

$$T_b = \frac{\beta}{k_b} \frac{KV_m}{\ln(\tau_m/\tau_0)} \quad (1)$$

where β is a constant depending on the crystal size distribution ($\beta = 9.2$), K is the anisotropy constant of the crystal ($K = 5 \times 10^4 \text{ J m}^{-3}$), V_m is the median crystal volume, k_b is the Boltzmann constant, τ_m is the measurement time, and τ_0 is a characteristic relaxation time³¹ of crystal of 10^{-11} s . T_b for Au-coated SPION is found to be

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~ 80 K and for MPEG-coated SPION is ~ 130 K. The calculation of T_b from eq 1 gives lower values: $T_b \sim 50$ and ~ 100 K for the Au- and MPEG-coated samples, respectively. The increase of T_b in the case of MPEG-coated SPION indicates the increase of dipole–dipole interactions and, thus, the loss of the SPM fraction. This is in agreement with the hyperfine magnetic structure of Mössbauer spectra obtained in the present study. The value of T_b for Au-coated SPION is higher than the Au-coated iron sample ($T_b = 42$ K),³² which confirms that stronger magnetic interactions do exist in the former case. Any rapid change of the FC magnetization for both cases is not observed. In an earlier publication,³³ T_b was reported as 100 K for starch-coated and 150 K for the uncoated SPION. According to the present data, the highest interparticle interactions are observed in the case of uncoated SPION. The reduction of T_b may indicate a decrease of magnetic interactions, as a result of the existence of a homogeneous Au coating layer.

The stability of the colloidal suspension of magnetic nanoparticles is an important parameter for biomedical applications. Therefore, the changes in magnetization are measured as a function of time. The magnetization value for uncoated SPION is ~ 2.8 emu/g with a field of 1.4 kOe at 300 K and increases linearly by increasing H_{ext} . The magnetization of the same sample is measured again after 1 month (to assess the long-term stability) and is found to be nonlinear and equal to 8.0 emu/g with magnetic field of 1.4 kOe (data not shown) at 300 K. Similar changes in the value of magnetization and the character of the curves are observed for starch- (Figure 7a) and MPEG- (data not shown) coated SPION. For starch-coated SPION, for example, a magnetization value of 1.7 emu/g with a field of 1.4 kOe at 300 K is obtained and after 1 month this value is increased to 3.5 emu/g at 300 K with the same field. Such magnetic behavior points to the growth of the particles, their interaction, and an initiation of the ferrimagnetic state. The unusual magnetic behaviors of the starch-coated SPION are in the transfer of the state from SPM to the ferrimagnetic at the temperature range of 160–200 K, where the magnetization becomes nonlinear when the field increases, as shown in Figure 7. The SPION coated with Au are of special interest (Figure 7b) because they remain to be SPM, for example, their magnetic behavior does not change with time. This indicates that SPION coated with Au are stable as a result of the protective homogeneous Au coating layer on the surface of the SPION.

Conclusions

In this study, uncoated SPION with an average diameter of 6 nm are prepared and modified with biocompatible substances such as starch, gold, and MPEG. Mössbauer spectroscopy data for uncoated SPION indicates that 30% of the particles have SPM properties, which disappear when H_{ext} is applied. The transformation has been observed to the ferrimagnetic state for starch-coated SPION in the range of 160–200 K after 1 month, which can be explained by the increase of dipole–dipole interactions between the magnetic particles in a polymer matrix. However, the SPM fraction is retained for the starch-coated SPION in the absence of H_{ext} . The Mössbauer spectroscopy data for MPEG-coated SPION do not show a stable SPM fraction, and a hyperfine magnetic structure appeared in the presence and absence of H_{ext} .

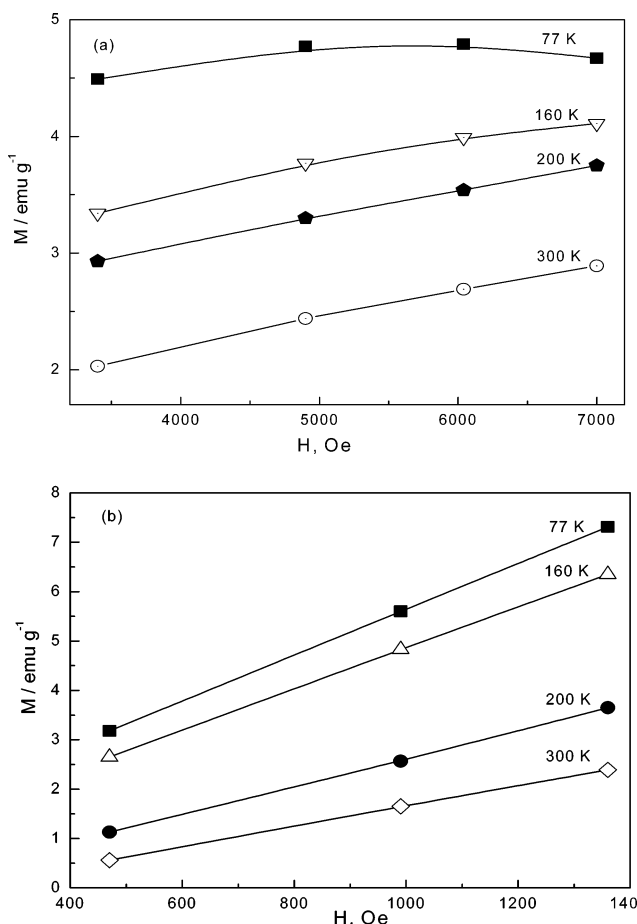


Figure 7. Specific magnetizations versus applied magnetic field measured after 1 month: (a) starch- and (b) Au-coated SPION.

The value of T_b for the Au-coated SPION is ~ 80 K, whereas the value of T_b for the MPEG-coated SPION is ~ 130 K. The value of T_b for the MPEG-coated SPION increases compared to that of the Au-coated SPION as a result of the high density of interactions between the SPION embedded in the polymer matrix.

The optimal properties of the SPION such as the particle size, the coating layer, the strength of the magnetic field, and their movement and distribution in the biological fluid can be determined by monitoring the long-term stability of SPION. According to the magnetic and Mössbauer spectroscopy data, Au is the best coating layer, which retains the SPM fraction for a longer period. A low toxicity of the Au-coated SPION sample has to be noted here also, which is a critical parameter for biomedical applications.

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Supporting Information Available: AFM image analysis of Au-coated SPION arrayed on a silicon substrate and the cross-section analyses of the X and Y axes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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