ONE-POT SYNTHESIS OF HYDROPHILIC AND HYDROPHOBIC FERROFLUID

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High-quality hydrophobic or hydrophilic ferrofluid based on magnetite (Fe₃O₄) nanoparticles can be synthesized by one-pot direct synthesis which involves thermolysis of Iron(III) acetylacetonate, Fe(acac)₃ in hydrophobic or hydrophilic stabilizing agent, respectively. The structure of the nanoparticles dispersed in the ferrofluid was studied using XRD, FTIR, XPS, and TGA analysis, while morphology and size of the nanoparticles were determined by TEM. The magnetic properties of the samples were measured using VSM and SQUID measurement. The results show that oleylamine (OM) and tri(ethylene glycol) (TREG) coated Fe₃O₄ nanoparticles which are well stabilized in hydrophobic and hydrophilic ferrofluid, respectively, are relatively monodisperse, single crystalline and superparamagnetic in nature with the blocking temperature at around 100K.

Keywords: Magnetite; superparamagnetic; ferrofluid; iron oxide; nanoparticles.

1. Introduction

Ferrofluid is a stable colloidal homogeneous suspension of ultrafine magnetic particles dispersed in an appropriate carrier liquid. The iron oxide nanoparticles particularly magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) have been most commonly used in ferrofluid synthesis due to their high saturation magnetization, high chemical stability, and non-toxicity property. The major concern of ferrofluid synthesis is the stability against sedimentation and agglomeration of the ultrafine particles which arises due to the gravitational force, van der Waals force, and magnetic attraction between the magnetic particles. Therefore, the iron oxide nanoparticles are usually stabilized either in a nonpolar organic solvent or in a polar solvent by an adsorbed layer of appropriate coating on their surface and the resulting stable suspension of hydrophobic or hydrophilic ferrofluid is obtained, respectively. The hydrophobic ferrofluids have long been used in technological applications such as rotary shaft sealing, oscillation damping, and position sensing, while the hydrophilic ferrofluids recently have been attracted a great attention in the bio-medical applications such as magnetic separation, drug delivery, cancer hyperthermia, and magnetic resonance imaging (MRI) enhancement. Ferrofluids have been synthesized using several synthesis methods such as chemical co-precipitation, microemulsion, and thermal decomposition method. However, the search for facile and flexible one-pot synthetic route which can be able to produce ferrofluids consisting of magnetic nanoparticles with the desired size, acceptable size distribution without particle aggregation is of extremely importance to realize the full potential of these materials in biomedicine. Here, we have been able to synthesize the ferrofluid using a one-pot facile synthetic route which includes the thermolysis of Fe(acac)₃ in an
appropriate stabilizing agent. Oleylamine and tri(ethylene glycol) have been used as the stabilizing agent for the preparation of hydrophobic and hydrophilic ferrofluid, respectively.

2. Experimental Section
Iron oxide nanoparticles are prepared following a modified thermal decomposition method. Typically, 2 mmol of Fe(acac)$_3$ is dissolved in a 20 ml of stabilizing agent (OM or TREG) and magnetically stirred under a flow of argon. The solution is dehydrated at 120°C for 1 h, and then quickly heated to 300°C (for OM) or 280°C (for TREG) and kept at this temperature for 2 h. The black solution is cooled to room temperature by removing the heat source. Then, 20 mL of ethanol (for OM) or 1:2 ethanol and ethyl acetate mixture (for TREG) is added into the solution and the precipitated particles are collected by centrifugation at 10,000 rpm followed by three times washing with ethanol or 1:2 ethanol and ethyl acetate mixture, respectively. The as-prepared OM coated hydrophobic and TREG coated hydrophilic nanoparticles are dispersed in hexane and water, respectively, and no phase separations are observed on exposure to a strong magnet which indicate the formation of stable hydrophobic and hydrophilic ferrofluid, respectively.

Particle size and morphology of as-synthesized nanoparticles are determined using transmission electron microscopy (TEM). The phase of the nanoparticles is identified by X-ray diffraction (XRD) while the stabilizing coating adsorbed to the particle surface is recognized by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectra (XPS). Magnetic properties of the nanoparticles are studied by the superconducting quantum interference device (SQUID) and vibrating sample magnetometer (VSM) measurement.

3. Results and Discussion
3.1. Structural characterization of the nanoparticles
3.1.1. XRD
Figures 1(a) and 1(b) show the XRD patterns of hydrophobic and hydrophilic nanoparticles, respectively. Position of the diffraction peaks matches well with the standard XRD data for bulk magnetite (JCPDS file no. 19-0629) which identifies the Fe$_3$O$_4$ phase of the nanoparticles. The average crystallite sizes are calculated using Scherrer’s equation$^{12}$ as 9.4±0.05 and 10.7±0.05 nm, respectively. The difference in crystallite size is due to the different growth rates of hydrophobic and hydrophilic nanoparticles in OM and TREG environment, respectively.

3.1.2. FTIR
Figures 2(a) and 2(b) are the FTIR spectra for the hydrophobic and hydrophilic nanoparticles, respectively. The peaks in Fig. 2(a) at about 2924; 2852, 1599; 1500 and 1411; 1047 cm$^{-1}$ are due to C–H stretching, N–H bending and C–N stretching vibration, respectively, attributed for chemically adsorbed OM coating to the hydrophobic particle surface.$^{13,14}$ On the other hand, the peaks in Fig. 2(b) at about 2930; 2870, 1632, 1455, 1350; 1251 and 1063 cm$^{-1}$ are due to C–H stretching, O–H stretching C–H bending, C–O bending, and O–H bending vibration.
respectively, attributed for chemically adsorbed TREG coating to the hydrophilic particle surface. The broad band between 3000 and 3600 cm$^{-1}$ i.e. 3400 cm$^{-1}$ represents the hydrogen bonded OH groups of water which is adsorbed by the nanoparticles. In addition, the strong absorption band at about 580 cm$^{-1}$ is due to Fe-O stretching vibration for the Fe$_3$O$_4$ nanoparticles.

3.1.3. XPS

Figures 3(a) and 3(b) show wide scan XPS spectra while Figs. 3(c) and 3(d) are the deconvoluted C(1s) spectra for the hydrophobic and hydrophilic nanoparticles, respectively. The peaks in Fig. 3(c) at 285.2 and 286.5 eV are due to C–C/C–H and C–N bond, respectively, attributed for the chemically adsorbed OM coating to the hydrophobic particle surface while the peaks in Fig. 3(d) at 285.5 and 288 eV are due to C–C/C–H and C–O–C bond, respectively, arises from the chemically adsorbed TREG coating to the hydrophilic particle surface. In addition, the Fe(3p$_{3/2}$), O(1s), Fe(2p$_{3/2}$), and Fe(2p$_{1/2}$) peaks in Figs. 3(a) and 3(b) at about 55, 530, 710, and 724 eV are due to Fe–O bond for the Fe$_3$O$_4$ nanoparticles.

3.2. Morphology and size of the particles

Figures 4(a) and 4(b) are the TEM images of the OM coated hydrophobic and TREG coated hydrophilic nanoparticles, respectively. The average
particle sizes are measured from the TEM images are about 10 and 11 nm, respectively which is very close to that of the calculated average crystallite size from XRD patterns. HRTEM images of a single hydrophobic and hydrophilic particle are shown in the inset of Figs. 4(a) and 4(b), respectively, indicating a well-ordered single crystal structure of both hydrophobic and hydrophilic nanoparticles.

3.3. Magnetic properties of the particles

Figures 5(a) and 5(b) show the room temperature M–H curves of OM coated hydrophobic and TREG coated hydrophilic nanoparticles, respectively. The $M_s$ of the hydrophobic and hydrophilic particles are 62 and 64 emu/g, respectively. Zero coercivity and zero remanence on the magnetization curves indicate that the particles are superparamagnetic in nature.\(^\text{17,18}\) Figure 6 shows the temperature dependence of magnetization under ZFC and FC for the hydrophobic nanoparticles and similar type of ZFC–FC curves are also observed for the hydrophilic nanoparticles. The feature of the ZFC–FC curves is indicating that the nanoparticles are of superparamagnetic.\(^\text{19}\) In the ZFC measurement, when the particles are cooled at zero field from room temperature, the magnetic moments of the particles are randomly oriented and the total magnetization tends to zero. When an external magnetic field is applied, more and more particles orient their magnetic moments parallel to the applied field with temperature increase. The ZFC curve reached the maximum at about 100 K, which corresponded to the blocking temperature ($T_B$) of the sample. At $T_B$ the thermal energy becomes comparable to the energy barrier gained in external magnetic field. Above $T_B$, the sample is superparamagnetic and below is ferromagnetic. In the case of FC procedure, magnetization monotonically increases as the temperature decreases. The divergence of FC and ZFC curves below $T_B$ is attributed to the existence of magnetic anisotropy barriers. Thus the resulting nanoparticles can be considered as magnetic single domains with a blocking temperature $T_B$ around 100 K.

4. Conclusions

High-quality superparamagnetic hydrophobic or hydrophilic ferrofluid can be fabricated by one-pot solvent-free thermolysis of Fe(acac)$_3$ in OM or TREG stabilizing agent, respectively. The nanoparticles dispersed in the ferrofluid are relatively monodisperse, single crystalline, and superparamagnetic at the room temperature.

References