

Synthesis of water dispersible magnetite nanoparticles in the presence of hydrophilic polymers

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Abstract Water dispersible magnetite nanoparticles (Fe_3O_4) were synthesized by thermal decomposition of iron (III) acetylacetonate ($\text{Fe}(\text{acac})_3$) in the presence of carboxylic acid-terminated poly(ethylene glycol) (mPEG acid), poly(vinyl alcohol) and NH_2 -containing polyether. Crystal structure was investigated using X-ray diffractometry (XRD) and it showed that the as-synthesized particles had high crystallinity with distinct lattices. Particle size of the nanoparticles was investigated using XRD (15.32 nm), transmission electron microscopy (18.8 nm) and photo correlation spectroscopy (32 nm) techniques. Vibrating sample magnetometry indicated that magnetite nanoparticles exhibited superparamagnetic behavior at room temperature. Influence of each functional group on magnetic properties of the particles was also examined. These magnetite nanoparticles remained dispersible in aqueous dispersions with only 5% particles aggregating after 1 month of preparing.

Keywords Magnetite · Nanoparticle · Thermal decomposition ·
Water dispersible · Hydrophilic

Introduction

Magnetic iron oxide nanoparticles especially magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) have been of scientific and technological interest in last few decades.

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They have been markedly used in numerous biomedical applications such as magnetic resonance imaging (MRI) diagnostic contrast enhancement [1, 2], magnetic cell separation [3], hyperthermia [4] and drug delivery [5]. These applications require the particles having good response to an applied magnetic field and possessing uniform chemical and physical properties [6]. Moreover, these nanoparticles need to be coated with hydrophilic polymeric stabilizers to render them water dispersible, non-toxic and biocompatible [7].

The conventional coprecipitation procedure of Fe(II) and Fe(III) salts in a basic aqueous solutions of NaOH or NH_4OH has been extensively used for making magnetite nanoparticles for mass production [8–11]. However, it needs fine adjustment of pH of the solutions for magnetite nanoparticle formation and stabilization, and a wide range of particle size distribution was obtained [12]. An alternative method of synthesizing magnetite nanoparticles with tunable size and narrow size distribution is thermal decomposition of iron (III) acetylacetonate ($\text{Fe}(\text{acac})_3$) [13–16]. The reactions were carried out in organic solvents, such as octyl ether [17], phenol ether and benzyl ether [18] in the presence of organic compounds containing reactive functional groups, such as polyvinylpyrrolidone (PVP) [17], oleic acid, oleyl amine and 1,2-hexadecane diol [18]. Carboxylic acid and amine functional groups have been reported that they provided chemisorption onto the particle surfaces [14, 19, 20]. Nanoparticles presented in these reports were dispersible in a variety of organic solvents but not in water, and this limited their uses in biomedical applications. Sun et al. [18] succeeded in synthesizing water dispersible magnetite nanoparticles by introducing a bipolar surfactant into the resultant products prepared from thermal decomposition of $\text{Fe}(\text{acac})_3$ in organic solvents.

Recently, precedents have reported the syntheses of water dispersible magnetite nanoparticles through one-pot decompositions in organic compounds containing reactive functional groups, such as benzyl alcohol [14], tetraethylene glycol, triethylene glycol [19] and 2-pyrrolidone [20]. These organic compounds functioned as both reaction solvents and steric stabilizers because they have high boiling point, high polarity and coordinating capacity with the particle surfaces.

In the present article, we report a facile one-step reaction to obtain water dispersible magnetite nanoparticles by thermal decomposition of $\text{Fe}(\text{acac})_3$ in the presence of water soluble carboxylic acid-terminated poly(ethylene glycol) (mPEG acid), poly(vinyl alcohol) (PVA) and NH_2 -containing polyether (Jefamine M-2070). According to the previously reported papers [21, 22], carboxylic acid and amine functional groups were thought to coordinate onto the particle surfaces. Magnetic behavior at room temperature of the as-synthesized particles was also determined via vibrating sample magnetometry (VSM). Crystal structure of the as-synthesized magnetite was studied via X-ray diffractometry (XRD). Particle size of the nanoparticles was investigated using XRD, transmission electron microscopy (TEM) and photo correlation spectroscopy (PCS) techniques.

Experimental

Materials

Unless stated otherwise, all reagents and solvents were used without further purification. Poly(ethylene glycol) monomethyl ether (mPEG) with \overline{M}_n 750 g/mol (Acros) was dried in vacuo at 60 °C under phosphorus pentoxide for 48 h. Succinic anhydride, 97% (Aldrich) and dibutyltin oxide 98% (Aldrich) were kept in a desiccator. Iron (III) acetylacetonate ($\text{Fe}(\text{acac})_3$), 99+% (Acros) was used as received. Jeffamine M-2070, an EO/PO oligomer ($M_n \sim 2,000$ g/mol) with a methoxy group on one end and an amine group on another end ($\text{CH}_3\text{O-EO/PO-NH}_2$) was obtained from Huntsman Chemical Co. and dried at 60 °C under reduced pressure before used. Tetraethylene glycol dimethyl ether, 99% (Acros) was kept in activated 4 Å molecular sieves. Poly(vinyl alcohol) (PVA), 99-100% hydrolyzed with M_n 100,000 g/mol (Fluka), were dried at 60 °C under phosphorus pentoxide.

Synthesis

Synthesis of carboxylic acid-terminated poly(ethylene glycol) monomethyl ether (mPEG acid)

Dried mPEG (0.013 mole of hydroxyl group), succinic anhydride (2.6 g, 0.026 mole) and dibutyltin oxide (0.0020 g) were charged into a 100-ml two-neck round-bottom flask. Twofold excess of succinic anhydride was used to ensure that hydroxyl terminals of mPEG were completely reacted. The reaction mixture was maintained at 180 °C under N_2 for 24 h. During the reaction, it was observed that the excess of succinic anhydride sublimed inside the reaction vessel. After the reaction was complete, mPEG acid was dissolved in cold CH_2Cl_2 and the unreacted succinic anhydride was easily removed by filtration. After evaporating, mPEG acid was dried at 60 °C under reduced pressure overnight.

Preparation of water dispersible magnetite nanoparticles via the decomposition method

The reaction apparatus consisting of a 250-ml three-neck round-bottom flask equipped with a mechanical stirrer having a tight adapter, condenser and nitrogen purge was flame dried. mPEG acid (0.0028 mole) was then dissolved into tetraethylene glycol dimethyl ether (20 mL) in the presence of Jeffamine M-2070 (0.0020 mole) and PVA (0.014 mole of OH). One gram of $\text{Fe}(\text{acac})_3$ (0.0028 mole) was subsequently introduced into the solution and then the reaction temperature was heated at 200 °C for 30 min to yield a black solution, indicating the formation of magnetite nanoparticles. The iron precursor was decomposed at 275 °C for 6 h with consistently nitrogen purging. Upon cooling, the dispersion was centrifuged at 5,000 rpm to remove large aggregate. The dispersion was then ultracentrifuged at 30,000 rpm to precipitate nanoparticles and the supernatant was discarded. Hexane was again added to extract the reaction solvent. Solvent extraction and

ultracentrifugation were repeated for several cycles to remove uncoordinated species and the reaction solvent from the dispersion.

Characterization

Characterization of polymers

^1H NMR was performed on a 400 MHz Bruker NMR spectrometer using CDCl_3 as a solvent. FTIR was performed on a Perkin–Elmer Model 1600 Series FTIR Spectrophotometer. The neat samples were directly cast onto potassium chloride plates.

Characterization of magnetite nanoparticles

Magnetite concentrations in dispersions were investigated by treating the samples with hot concentrated nitric acid followed by concentrated perchloric acid to obtain complete dissolution. Iron concentrations were analyzed by flame atomic absorption spectrometer (AAS) and calculated from sample responses relative to those of standards and blanks. Crystalline structure and crystalline size were determined with XRD. XRD patterns of the particles were collected on a Philips X'pert X-ray diffractometer under CuK_α radiation ($\lambda = 1.540598 \text{ \AA}$) operated at 30 kV and 2θ ranging from 0 to 90° . Particle size and its size distribution were observed using TEM. A drop of dispersions was dried on carbon-coated copper grids and the images were taken using a Philips Tecnai 12 operated at 120 kV equipped with Gatan model 782 CCD camera. Hydrodynamic diameter of the particles was measured by PCS using NanoZS4700 nanoseries Malvern instrument. The sample dispersions were filtered through $0.22 \mu\text{m}$ nylon syringe filters and sonicated for 10 min before the measurement at 25°C . Magnetic properties of the polymer–magnetite complexes were measured in the solid state at 300 K using a Standard 7403 Series, Lakeshore vibrating sample magnetometer (VSM). The magnetic moment of each sample was investigated over a range of applied magnetic fields from $-10,000$ to $+10,000$ G using 30 min sweep time.

Results and discussion

The primary objective of this work was to develop a simple method for synthesizing water dispersible magnetite nanoparticles. The advance of this work over the previously reported papers was that we have prepared the particles in hydrophilic polymers, whereas the precedent reported the preparation of particles in small molecules such as benzyl alcohol [14], triethylene glycol [19] and 2-pyrrolidone [20]. However, the mere presence of hydroxyl groups of these small molecules does not evidence a thin layer of polymeric surfactants on the particles surface, so that long-term stability of the particles is concerned. To acquire particles with long-term stability, suitable polymeric surfactants having specific functional groups are necessary to coordinate with the particle surface and long chain polymers sterically

prevent them from aggregation. It is well established that carboxylic acid [21] and amine groups [23, 24] can effectively bind to iron oxide surfaces. We have thus herein reported an alternative and facile synthetic approach of water dispersible magnetite nanoparticles in hydrophilic polymers having these functional groups. The as-synthesized particles are anticipated to remain dispersible in aqueous medium extensively. In the current work, tetraethylene glycol dimethyl ether was selected as the reaction solvent due to its high boiling point (275 °C), so that it can thermally decompose $\text{Fe}(\text{acac})_3$. In addition, this solvent completely dissolves all components and lacks of oxidizable functional groups for the iron precursor.

mPEG acid was prepared via the reaction of mPEG with succinic anhydride. ^1H NMR spectra exhibited the formation of ester linkages (peak a and e, Fig. 1a) due to coupling reaction of hydroxyl groups of mPEG and succinic anhydride without remaining of unreacted succinic anhydride (3.00 ppm, Fig. 1a). An FTIR spectrum of mPEG acid was in good agreement with ^1H NMR as indicated by the presence of carbonyl functional groups of ester bonds at $1,738\text{ cm}^{-1}$ (Fig. 1b). In addition, the signal corresponding to the OH stretching in carboxylic acid terminals of mPEG acid ($3,510\text{ cm}^{-1}$) exhibited significantly less intensity than that of hydroxyl-terminated mPEG ($3,420\text{ cm}^{-1}$) (Fig. 1b). This is probably due to inherently labile protons of carboxylic acid functional groups allowing, to some extent, the formation of carboxylate-terminated mPEG. It should also be mentioned that the signals corresponding to the carbonyl group of succinic anhydride ($1,865\text{ cm}^{-1}$ due to an asymmetric C=O stretching mode and $1,782\text{ cm}^{-1}$ due to a symmetric C=O stretching mode) [25] did not appear, indicating that there was no unreacted succinic anhydride remaining after purification.

To prepare magnetite nanoparticles, $\text{Fe}(\text{acac})_3$ was introduced into the polymer solution and it was then heated to thermally decompose the iron precursor. An FTIR spectrum of the as-synthesized magnetite was illustrated to compare with those of the iron precursor and all reactive components (Fig. 2). A signal at approximately $3,000\text{ cm}^{-1}$ corresponding to C–H stretching of aliphatic compounds indicated the presence of organic compounds in the polymer–magnetite complexes (Fig. 2e). It should be noted that non-coordinated species have been removed from the dispersions before FTIR analyses. From Fig. 2e, a strong signal at 590 cm^{-1} corresponds to Fe–O linkages of magnetite particles. It was also observed that a

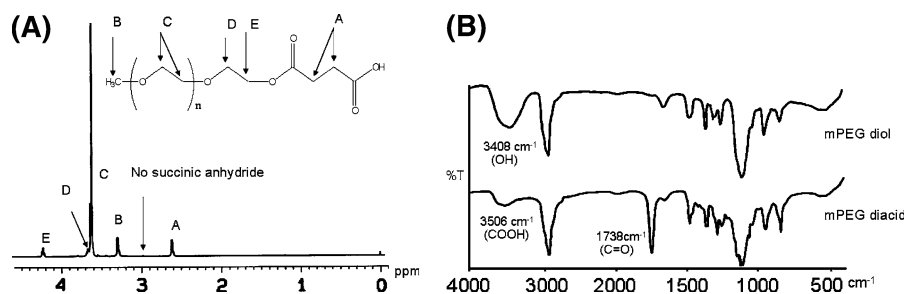


Fig. 1 a ^1H NMR spectrum of mPEG acid and b FTIR spectra of hydroxyl-terminated mPEG and mPEG acid

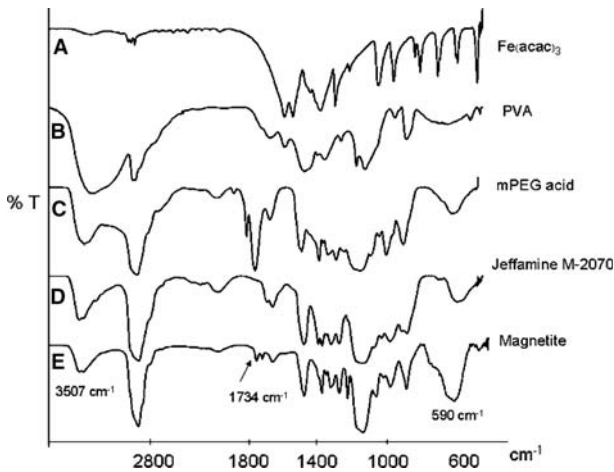


Fig. 2 FTIR spectra of **a** $\text{Fe}(\text{acac})_3$, **b** PVA, **c** mPEG acid, **d** Jeffamine M-2070 and **e** the polymer–magnetite complexes

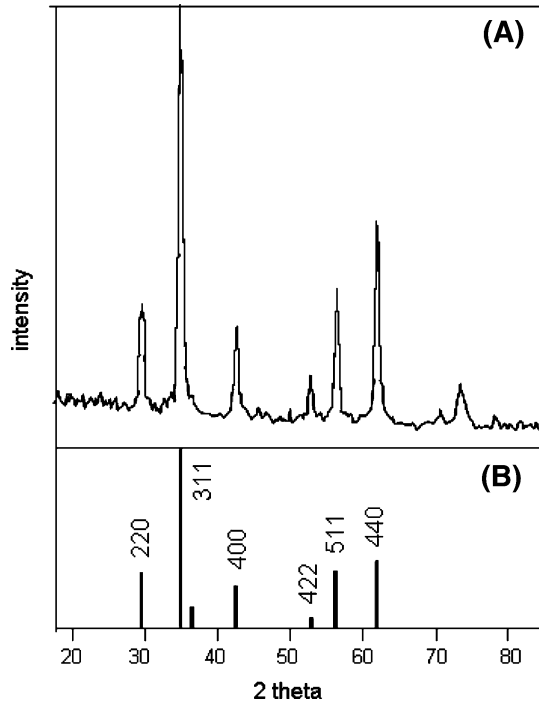
carbonyl stretching signal ($1,734\text{ cm}^{-1}$) of polymer–coated magnetite was weak, indicating that only small amounts of mPEG acid remained in the complex. In addition to mPEG acid, Jeffamine M-2070 also presented in the polymer–magnetite complexes as indicated by the existence of the signal at $3,507\text{ cm}^{-1}$ corresponding to N–H stretching of amine groups. The FTIR pattern in the range of $1,500\text{--}700\text{ cm}^{-1}$ of the as-synthesized magnetite was similar to that of Jeffamine M-2070 (Fig. 2e, d, respectively). This result was in good agreement with the previous reports discussing about stabilization of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles with alkylamine surfactants due to NH_2 groups coordinating with Fe on the surface of the particles [23, 24]. According to AAS analyses, there was 42% of Fe_3O_4 in the polymer–magnetite complexes. To study the stability of the particles in water, the dispersions were centrifuged once a week to precipitate unstable particles or large aggregate that may arise and %magnetite in the supernatant was analyzed via AAS technique. As compared to the initial concentration, these particles were stable in water with less than 5% particles aggregating after 1 month of synthesizing. The particles from aqueous dispersions were then used for XRD, TEM, PCS and VSM analyses.

The powder X-ray diffraction patterns of the as-synthesized nanoparticles are shown in Fig. 3. The position and relative intensities of all diffraction signals match well with the characteristic peaks of magnetite crystal having isometric-hexaoctahedral crystal system ($2\theta = 30.2, 35.6, 43.3, 53.7, 57.2$ and 62.7°) obtained from standard Fe_3O_4 powder diffraction data (ICSD No. 01-075-0449). The particle size can be estimated from the average crystallite size from the Debye–Scherrer equation [26, 27],

$$D = 0.9\lambda / \beta \cos\theta$$

where D is the average crystallite size (\AA), λ is the wavelength of X-rays ($\text{CuK}\alpha$: $\lambda = 1.540598\text{ \AA}$), θ is the Bragg diffraction angle and β is the full width at half maximum (FWHM) (in radians). According to the FWHM of the diffraction peak at

Fig. 3 XRD patterns of **a** the polymer–magnetite complexes and **b** an XRD pattern from standard Fe_3O_4 powder diffraction data (ICSD No. 01-075-0449)



$2\theta = 35.6^\circ$ of the (311) plane, the crystallite size of magnetite nanoparticles was approximately 15.3 nm in diameter. The particle size was large when compared to the particles prepared *via* thermal decomposition of $\text{Fe}(\text{acac})_3$ in other systems [14].

TEM images and particle size distribution of magnetite nanoparticles were illustrated in Fig. 4a–c. Particle size was determined by measuring diameter of 100 particles in different regions of a given TEM grid. The particle size was ranging between 10 and 30 nm in diameter with the average of approximately 18.8 ± 3.8 nm. This average size was slightly larger than the value calculated from the Debye–Scherrer equation obtained from XRD result (15.32 nm). It should be noted that the reported size is the value excluding the thickness of the polymeric shell. Figure 4b illustrates the enlargement of a TEM image showing nanoscale agglomeration of multiple nanoparticles. It is hypothesized that this nanoscale aggregation might take place during the decomposition reaction due to the existence of polymer aggregation in the reaction vessel. This occurrence might be the results of the possible formation of hydrogen bonding between functional groups existing in the polymers (COOH , NH_2 and OH). This aggregation stopped at this length scale probably because the presence of thin polymeric shells surrounding the particles prevented them from further approaching to each other. The visibility of shells along the periphery of each particle is indicative of the presence of a thin polymeric layer on the particle surface (Fig. 5). It shows the lattice fringes of the 20 nm magnetite nanoparticles. These lattice fringes correspond to a group of atomic

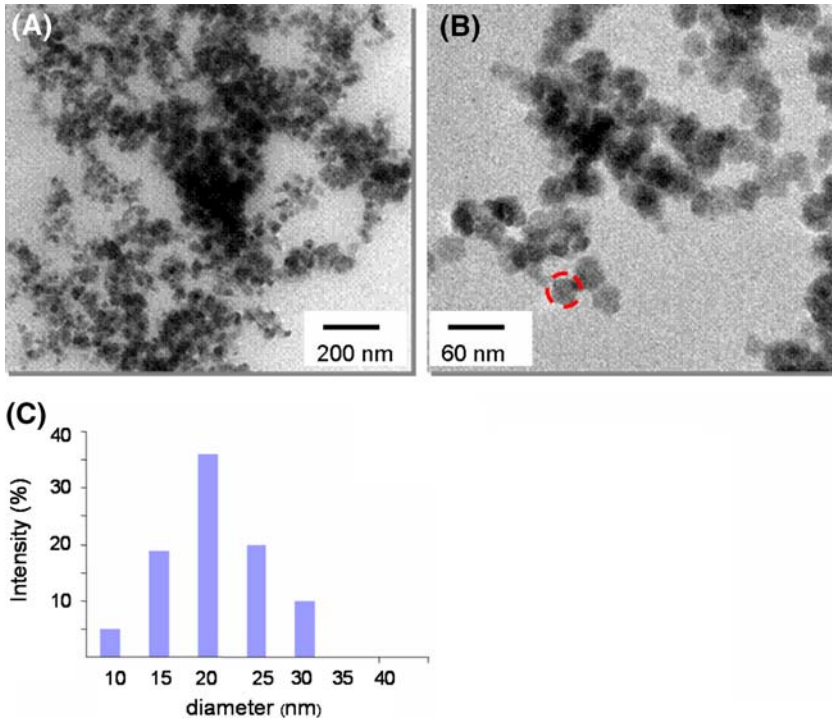
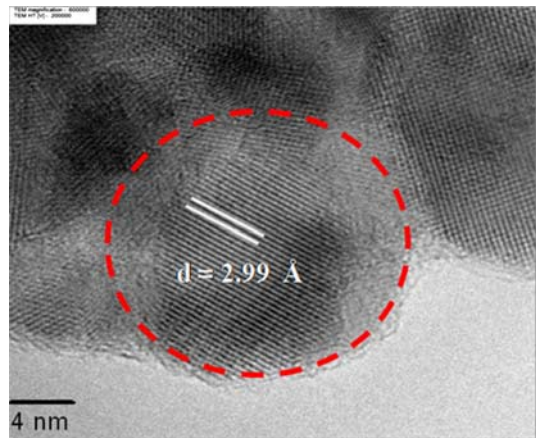


Fig. 4 **a, b** TEM bright field images of magnetite nanoparticles at two different magnifications, and **c** particle size distribution with average diameter = 18.8 ± 3.8 nm

Fig. 5 An HRTEM image of magnetite nanoparticles showing the distance between two adjacent planes of 2.99 Å and polymer shell surrounding the particles



planes in the particles, indicating that these particles are single crystal. The distance between two neighboring planes was approximately 2.99 Å which is comparable to those of the (220) planes in the spinel-structured magnetite nanoparticles (2.97 Å) [18].

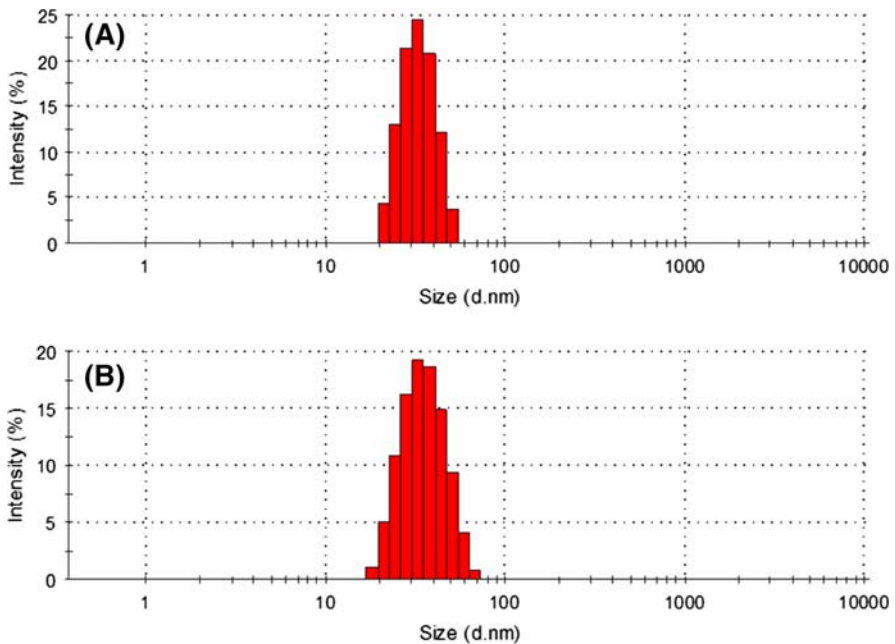


Fig. 6 Particle size distributions of nanoparticles in aqueous dispersions determined from PCS technique, **a** before and **b** after redispersion

PCS was conducted to investigate hydrodynamic volume and size distribution of the particles in aqueous dispersions (Fig. 6). The average size of the particles observed in PCS was 32 nm in diameter. The size was larger than those observed in TEM and XRD techniques, indicating that the particles might occupy large volume of water due to the presence of hydrophilic polymers in the complexes. In addition, it was also reasoned that there was some nanoscale agglomeration of the particles in aqueous dispersions. The nanometer-size agglomeration can also be observed from TEM images in Figs. 4 and 5.

An important property of nanoparticles for use in medical applications is their ability to redisperse in aqueous medium. To study this property, the as-prepared dispersion was freeze-dried to obtain the particles in a powder form and they were then redispersed in refresh water. It was found that there was no observable magnetite powder remaining in the dispersion upon redispersion. In addition, according to PCS measurements, the particle size and its distribution of the redispersed particles in water were comparable to those before redispersion (Fig. 6), indicating that the complexes had good redispersibility in aqueous dispersions. In addition, this also indicated the formation of a polymer layer surrounding the particles and preventing them from further aggregation during the drying process.

Magnetic behavior of dried magnetite–polymer complexes was investigated using vibrating sample magnetometry (VSM). The particles had saturation magnetization (M_s) about 23 emu/g sample (Fig. 7a). M_s in the unit emu/g magnetite was calculated by taking percent of Fe_3O_4 in the polymer–magnetite

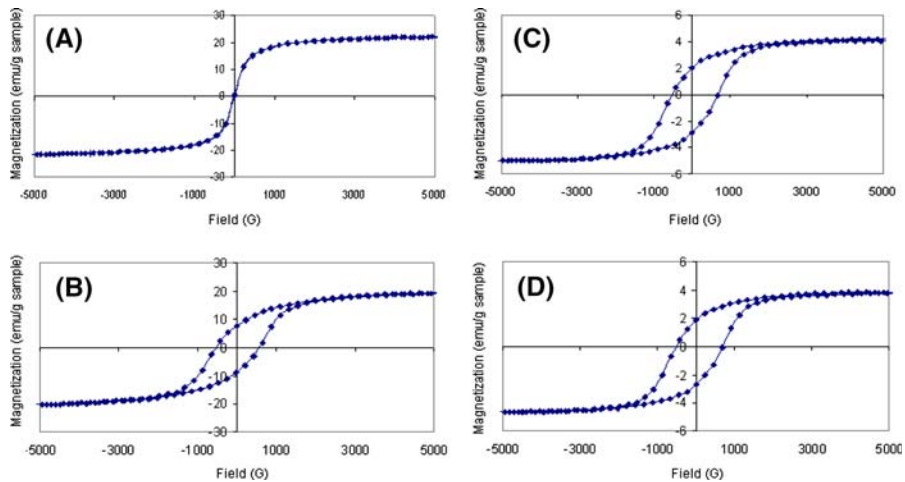


Fig. 7 Hysteresis curves of nanoparticles made from the reactions **a** using 1:0.7:5 molar ratio of COOH:NH₂:OH functional groups, respectively, **b** without NH₂, **c** without COOH and **d** without OH groups

complexes (42% Fe₃O₄) into account and it was about 54 emu/g magnetite. This number is a typical M_s value of magnetite nanoparticles. The particles showed superparamagnetic behavior as indicated by the absence of magnetic remanence (M_r) and coercivity (H_c). It should be noted that the as-synthesized magnetite particles were made from the reaction using 1:0.7:5 molar ratio of COOH:NH₂:OH functional groups, respectively. The particles made from the reaction having only COOH and OH functional groups (without NH₂) resulted in the particles with the same M_s value but having magnetic hysteresis as indicated by the presence of magnetic remanence and coercivity (Fig. 7b). This was probably due to the formation of large particles or clusters, which in turn influenced their magnetic properties. It should be mentioned that large aggregation was visually observed in this reaction. The decomposition reactions of the particles in the absence of mPEG acid (without COOH group) or PVA (without OH group) and having the other two components were also carried out. Similarly, there were some aggregations visually observed in these two dispersions. Additional experiments were performed to observe the aggregate size of the dispersions without mPEG acid using TEM and PCS techniques. The aggregate sizes determined from these two techniques were larger than 100 nm with some micron-scale aggregate (larger than 1,000 nm). The reactions without PVA and having the other two components exhibited particle aggregation similar to the ones without mPEG acid. These aggregates did not or insignificantly respond to an external magnetic field ($M_s \sim 4$ emu/g sample) and exhibited magnetic hysteresis probably due to the formation of large particles (Fig. 7c, d). This suggested that COOH in mPEG acid and OH in PVA might play an important role on the nanoparticle formation and their crystal structure, which affected their magnetic properties.

Conclusions

Magnetite nanoparticles were successfully prepared by thermal decomposition of $\text{Fe}(\text{acac})_3$ in organic solution phase in the presence of hydrophilic polymers. These polymers containing COOH , NH_2 or OH reactive functional groups influenced the particle formation and in turn their magnetic properties. FTIR and TEM confirmed the existence of the polymers in the complex. These particles were single crystal with some nano-scaled agglomeration and possessed polymeric shell coating on their surface and thus enhanced their dispersibility as well as their stability in aqueous dispersions. The preparing process of this polymer–magnetite complex is facile and possible to scale up, so it might be potentially used in magnetically targeted biomedical applications.

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