

Simple synthesis of superparamagnetic magnetite nanoparticles and ion effect on magnetic fluids

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Simple and low cost synthesis of superparamagnetic fine magnetite (Fe_3O_4) nanoparticles can be done by co-precipitation method in air atmosphere. The effects of the air or nitrogen atmosphere combined with the molar ratio of $\text{Fe}^{+2}/\text{Fe}^{+3}$ and the stirring rate on the size and magnetic properties of nanoparticles have been comparatively studied. The average particle size and size-distribution of nanoparticles were measured by nano-zeta sizer. Results showed that the smallest particle size was found to be 44.7 nm with the narrowest size-distribution of 0.211 in air atmosphere. The x-ray patterns indicated that all nanoparticles have face-centred cubic structure confirming the characteristic peaks of magnetite. The magnetic properties of magnetite nanoparticles studied by vibrating sample magnetometer exhibited typical superparamagnetism. It is revealed that molar ratio of 2/3 for $\text{Fe}^{+2}/\text{Fe}^{3+}$ in air atmosphere can be preferred to the one of 1/2 in nitrogen medium at the stirring rate of 2000 rpm. Magnetic properties of nanoparticles dispersed in different acid medium were also studied, and the highest saturation magnetisation, M_s was observed at HClO_4 medium.

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1. Introduction

In recent years, synthesis of superparamagnetic magnetite nanoparticles in powder form and preparation of their magnetic liquids has been a field of intense study due to its extraordinary magnetic and optical properties in biomedical and information storage applications [1]. Among reported synthesis methods of Fe_3O_4 [2-4], the chemical co-precipitation of Fe^{2+} and Fe^{3+} salts by addition of a base in aqueous media may be the most promising one because of its simplicity and productivity. The co-precipitation method quite often was performed under nitrogen atmosphere and the dependence of solution parameters on the control size and composition of nanoparticles investigated [5-7].

The main interest of this study was focused on a simple and low cost synthesis of superparamagnetic magnetite nanoparticles. Therefore, magnetite (Fe_3O_4) nanoparticles were synthesised to comparatively study in air and nitrogen atmosphere and then characterised to understand how the properties of nanoparticles varied with the molar ratio of $\text{Fe}^{+2}/\text{Fe}^{+3}$ and the stirring rate. It is seen that the smaller particle size and higher saturation magnetisation can be obtained in air atmosphere providing simplicity and low cost production. Furthermore, the ion effects on magnetic properties of nanoparticles dispersed in different acid medium were studied and significant influence on saturation magnetisation of fluids was observed.

2. Experimental

The solution of FeCl_3 and FeCl_2 was mixed with certain molar ratio in total 50 mL volume. The

corresponding phase NH_3 was quickly added into this mixture under vigorous stirring. However, in nitrogen atmosphere, the mixture of iron solution was purged with nitrogen for one hour and continued during synthesis of nanoparticles. The reaction (stirring) time was kept constant as 30-minute in all synthesis processes. All reagents used in this work are in analytical grade. After precipitation, the particles were repeatedly washed and filtered before drying at room temperature in air atmosphere to form powders. To obtain the magnetic fluids, the precipitate was stirred within the aqueous 2M acid (HCl , HNO_3 , HClO_4) and was then isolated by centrifugation. After this process was repeated twice, its peptisation was merely accomplished by adding water.

The average particle diameter (size) and polydispersity index, PDI, (size-distribution) of nanoparticles dispersed in HClO_4 were directly measured by Nano-Zeta Sizer (Malvern Instruments, Model 3000 HSA, France) and listed in Table 1. The crystalline structure of magnetite nanoparticles were investigated with PANalytical's X'Pert PRO X-ray diffractometer system (XRD) in powder state. The magnetic properties of nanoparticles and fluids were studied by vibrating sample magnetometer (VSM-ADE EV9 Model).

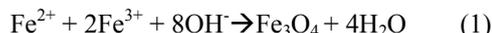
3. Results and discussion

In this study, the effect $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and stirring rate on the particle size and size-distribution of nanoparticles synthesised in air and nitrogen atmosphere were studied in the first section. This is followed by the structural analysis of the nanoparticles. Finally, the magnetic properties of the

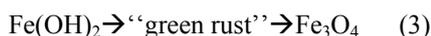
particles in powder and fluid form were presented and discussed.

3.1. The effect of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and stirring rate on nanoparticles

The chemical reaction of magnetite precipitation is expected as follows:



It means that the co-precipitation reaction requires 1 mol of Fe^{2+} ions and 2 mol of Fe^{3+} ions (or an $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 0.5) for stoichiometric conversion. However, if the reaction was done in air atmosphere, the molar ratio must be larger than 0.5, because of oxidative instability of Fe^{+2} [8]. Therefore, the molar ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ was selected as 2/3 in the initial stage of this study. The magnetite nanoparticles (sample 1) were synthesised in air atmosphere at the stirring rate of 1500 rpm. The particle size and size-distribution was measured as 62.5 nm and 0.272, respectively. The synthesis conditions and the properties of nanoparticles were listed in Table 1. In order to comparatively study the effect of atmosphere on size and properties of nanoparticles sample 2 was synthesised at 1500 rpm under nitrogen atmosphere. It is seen that the particle size increased to 143.0 nm and size-distribution of nanoparticles was PDI:0.388 which is higher than sample 1. As reported [9], the excess of Fe^{+2} ions in the nitrogen medium may occur in the following reactions and produce to yield magnetite usually with larger sizes:



Hence, the increase of particle size not only confirmed the statements made in [9] but also showed that 2/3 molar ratio is inconvenient for nitrogen atmosphere. Therefore, magnetite nanoparticles (sample 3) were synthesised in 1/2 molar ratio in nitrogen medium at the same stirring rate. The average particle size then becomes 60.4 nm. It is seen that the ideal molar ratio of $\text{Fe}^{+2}/\text{Fe}^{+3}$ should be 1/2 and 2/3 for nitrogen and air atmosphere, respectively.

By looking at the PDI of samples synthesised in air and nitrogen atmosphere was compared in size-distribution point of view. The size-distribution of sample 1 (PDI: 0.272) is narrower than sample 3 (PDI:0.422) having almost the same particle sizes, see Table 1. Thus, the results revealed that the air medium provides more favourable particle distribution.

The optimisation of synthesis conditions is not only concentrated on the effect of molar ratio but also the stirring rate. Therefore, the effect of stirring rate on particle size and size-distribution was also examined using ideal molar ratios of $\text{Fe}^{2+}/\text{Fe}^{3+}$. Sample 4 and 5 were

synthesised at the stirring rate of 2000 rpm in air and nitrogen atmosphere, respectively. The average particle sizes and size-distribution dropped down to 44.7 nm and 0.211 with the increase of the stirring rate from 1500 to 2000 rpm under air atmosphere. As an example, particle size-distribution diagram of sample 4 was shown Fig. 1. It is worth noting that the value of 0.211 for PDI is lower than 0.234 [9] and also the other studies [10, 11] for the conventional chemical co-precipitation technique. On the other hand, the particle size also reduced to 55.1 nm but the size-distribution is still very large (PDI: 0.413) for nitrogen atmosphere. The latter result may come from the difficulties of keeping the molar ratio of 1/2 for $\text{Fe}^{+2}/\text{Fe}^{3+}$ constant in practise since it needs an oxygen-free medium. It can be concluded that the smallest particle size and the best monodisperse size-distribution can be obtained in air atmosphere.

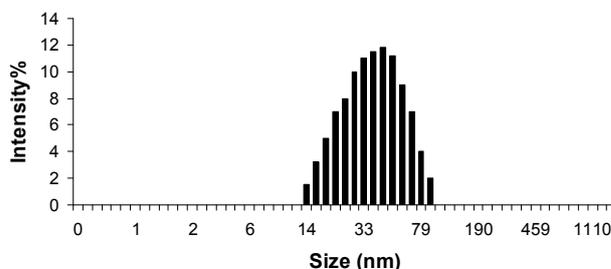


Fig. 1. Particle size distribution of nanoparticles synthesised at stirring rate of 2000 rpm in air atmosphere.

3.2. Crystalline structure of nanoparticles

The XRD patterns were taken from 10 to 80 (2θ value) using $\text{Cu K}\alpha$ radiation at room temperature. Fig. 2 illustrated that x-ray powder diffraction patterns of nanoparticles synthesised in presence of air (sample 1) and nitrogen (sample 2) atmosphere. As it can be seen in Fig. 2, all magnetic powders have a face-centred cubic spinel structure having the characteristic (311), (400), (220), (551) and (440) peaks of magnetite. There is no other phase of Fe_2O_3 caused by oxygen and the peaks of sample 1 were broadened owing to smaller particle size. When Scherrer equation [12] was used to calculate the size of magnetite nanoparticles from the highest peak intensity (311) of XRD patterns, the sizes were calculated as 35 nm and 25 nm for sample 1 and sample 2, respectively. The results are in consistent with the one measured by using Nano-Zeta Sizer. It should be noted that the value for the particle diameter obtained from XRD pattern means the particle core size, whereas the size detected using Nano-Zeta Sizer system refers to a hydrodynamic diameter of particles.

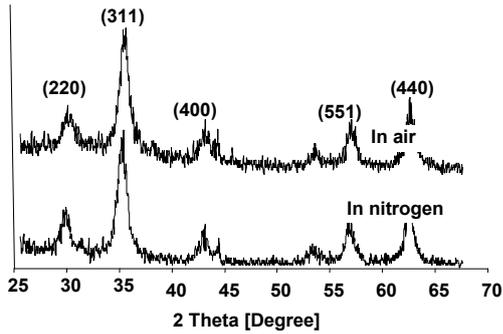


Fig.2. X-ray powder diffraction patterns of nanoparticles synthesised in presence of air and nitrogen atmosphere.

3.3. Magnetic properties of nanoparticles

The study is not only based on obtaining the smallest size and the best size-distribution but also finding the superparamagnetic nanoparticles with the high saturation magnetisation, M_s . The hysteresis curves of magnetite nanoparticles in powder state were measured and shown in Fig. 3. The typical characteristics of superparamagnetic behaviour were observed for all samples. Almost immeasurable coercivity and remanence can be also seen in the inset of Fig. 3. Superparamagnetic magnetite nanoparticles synthesised in air atmosphere exhibit higher M_s expect for sample 2 synthesised in nitrogen medium, as seen Table 1. As reported in [12], if there is no change observed in structural properties of nanoparticles, the decrease of particle size results in the decrease of M_s because of large deformations occurred on the surface of very small particles. This is most probably the case seen in this study. Therefore, synthesis of sample 4 is the most suitable process for the benefit of the better quality in an easy and low cost production.

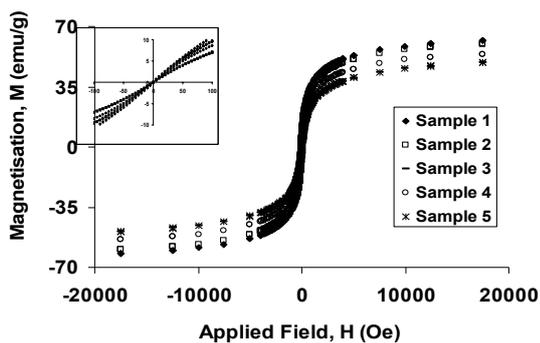


Fig.3. Hysteresis loops of powder Fe_3O_4 nanoparticles samples, inset shows zero coercivity.

3.4. Magnetic properties of fluids

The magnetic fluids of synthesised nanoparticles were prepared using different acids. Since low polarising anions, such as NO_3^- , Cl^- , and especially ClO_4^- is weak flocculating agents [2], HCl, HNO_3 and $HClO_4$ were selected to prepare stable magnetic fluids. The fluids have the same pH=2.0 and the percentage of magnetite dispersed in fluid was settled 0.5% (w/w).

Hysteresis curves of fluids prepared from powder form of sample 1 were shown in Fig. 4. All magnetic fluids showed typical superparamagnetic behaviour. M_s values obtained from the hysteresis curves of nanoparticles dispersed in HCl, HNO_3 and $HClO_4$ were 31.70, 40.82 and 58.38 emu/g, respectively. It was found that M_s of nanoparticles dispersed in acid medium is smaller than the one in powder state, see Table 1. The decrease in M_s of magnetic fluids may be the result of deformation occurred in the crystal lattice surface of the magnetite nanoparticles. The magnetic moment on the surface of the magnetite will become slanting, and there are many slanting magnetic moments on the surface of the magnetite. When the particle size increases, however, the deformation of the crystal lattice surface of the magnetite nanoparticles is small and the relative portion of atoms on the powder surface decreases. The highest deformation of the crystal lattice surface was observed in HCl solution whereas ClO_4^- showed the lowest effect of deformation. It can be verbalised that Cl^- anion is the most polarising one among the ions used. The ClO_4^- was the most suitable one to prepare magnetic fluids having the lowest M_s in Fig. 4.

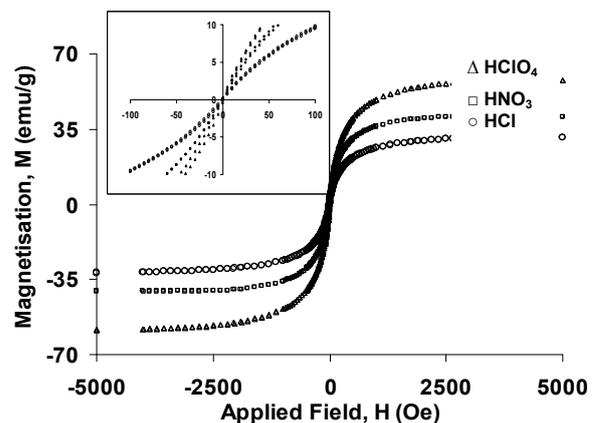


Fig.4. The hysteresis curves of sample 1 in acidic fluid measured by VSM, inset shows zero coercivity

Table 1. Synthesis conditions and properties of magnetite nanoparticles

Synthesis conditions					Properties of magnetite nanoparticles		
Sample	Fe ⁺² /Fe ⁺³ ratio	NH ₄ OH (ml)	Stirring rate (rpm)	Atmosphere	Size ^a (nm)	PDI ^b	M _s ^c (emu/g)
1	2/3	50	1500	Air	62.5	0.272	60.45
2	2/3	50	1500	Nitrogen	143.0	0.388	62.68
3	1/2	50	1500	Nitrogen	60.4	0.422	50.29
4	2/3	50	2000	Air	44.7	0.211	54.81
5	1/2	50	2000	Nitrogen	55.1	0.413	50.07

^aDiameter of nanoparticles measured by Nanosizer ^bPolydispersity Index, ^cSaturation magnetisation

To investigate the effect of the concentration on the fluids, the ClO₄⁻ was used and the percentage of magnetite dispersed in fluid was increased to 3.4% (w/w). M_s obtained from the hysteresis curves is 67.15 emu/g. This value is higher than the highest M_s (58.38 emu/g) obtained from previous fluid (0.5% (w/w)) as well as M_s values of powder form for all nanoparticles. This may be occurred because magnetite nanoparticles have more often collision with increasing their concentration in solution, and behaves like large particles, and consequently M_s increases.

4. Conclusions

Synthesis of superparamagnetic fine magnetite nanoparticles by co-precipitation method was comparatively studied in air and nitrogen atmosphere. Optimal molar ratio of Fe⁺²/Fe⁺³ was determined as 2/3 at the stirring rate of 2000 rpm in air atmosphere. Consequently, the smallest particle size and size-distribution was found to be 44.7 nm and 0.211, respectively. The results point out that the synthesis of magnetite nanoparticles in air atmosphere can be preferred because of its advantages of the simplicity and low cost as well as the better quality of production.

It is also seen that the saturation magnetisation magnitudes of magnetic fluids can be increased with the type of ion used in solution medium and the concentration of dispersed nanoparticles.

A continuation of this study is to prepare the monodisperse and stable superparamagnetic latex to investigate the bio-compatibility of these particles on the biological systems, such as the interaction of cell-nanoparticles.

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