Synthesis and Characterization of Uniform and Crystalline Magnetite Nanoparticles via Oxidation-precipitation and Modified co-precipitation Methods

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Magnetite (Fe₃O₄) nanoparticles have been prepared by oxidation-precipitation method using Monoethanolamine (MEA) as precipitation agent and by modified co-precipitation method using the mixture of isomeric-branched primary alcohol (A1416) and kerosene as stabilizing agent, respectively. X-Ray Diffraction (XRD) patterns and Transmission Electron Microscopy (TEM) images indicate the formation of magnetite with cubic phase consisting of crystalline, near-to-spherical particles with sizes around 10 nm. At high PH values or elevated temperature the precipitated particles possess larger crystallite sizes. Magnetic diameters are obtained by using Chantrell's equations from the magnetic hysteresis loops. The proportion of spin disorder layer in nanocrystalline diameter decreases with an increase in crystallite size.

Keywords: Magnetite nanoparticles, Chemical synthesis, Magnetism.

1. INTRODUCTION

Nanoscaled magnetite (Fe₃O₄) is a kind of magnetic functional nanomaterial, and it has cubic inverse spinel structure with oxygen forming a fcc closed packing and Fe cations occupying interstitial tetrahedral sites and octahedral sites. The electrons can hop between Fe²⁺ and Fe³⁺ ions in the octahedral sites at room temperature; therefore, it is an important class of spintronics material [1]. Magnetite nanoparticles have unique physiochemical, magnetic, and optical properties due to surface effect and finite-size effect. These promising magnetite nanoparticles have been widely used as

microwave radiation absorbers [2, 3], spin-based devices [4], cathode materials of lithium battery [5], ferrofluids [6, 7], drug-targeting and cell separation carriers [8].

Over the past decades, synthesis techniques of magnetite and iron oxides nanoparticles have always been the scientific and technological interest. These methods include chemical co-precipitation [9], thermal decomposition [10], microemulsion [11], Sol-Gel [12] and the method of oxidation of precipitation [13]. However, uniform physical and chemical properties of magnetite nanoparticles greatly depend upon the synthesis route, and how to develop a simplistic and effective way to synthesize magnetite particles with high dispersion and narrow size distribution remains a challenge.

The aim of our work is to explore new routes for synthesis of magnetite nanoparticles. Here we report an organic-phase and an aqueous-phase synthesis of magnetite nanoparticles, both of which have not been reported so far. Firstly, co-precipitation method is the most commonly used method in preparation of magnetite nanoparticles, but it has several disadvantages, such as extensive agglomeration, poor morphology and particle size distribution. In order to overcome these shortcomings, the modified co-precipitation method used the organic mixture of A1416 and kerosene as a stabilizing agent to control the process of nucleation, consequently to control particles size distribution and improve the dispersion. Meanwhile, this synthesis method doesn't use the aqueous solution, so it could reduce the conglutination of the nanoparticles. Secondly, FeCl₂-MEA-H₂O₂ aqueous system was first engaged to synthesize magnetite particles in an oxidation-precipitation method. It is remarkable that this synthetic approach is facile and effective with mild reaction conditions. The main reaction equations can be expressed as:

$$Fe(OH)_2 - FeOH^+ + OH^-$$
 (1)

$$4\text{FeOH}^{+}+\text{O}_{2}+2\text{H}_{2}\text{O} \rightarrow 2[\text{Fe}_{2}(\text{OH})_{3}]^{3+}+2\text{OH}^{-}$$
(2)

$$[Fe_2(OH)_3]^{3+} + FeOH^+ + 4OH^- \rightarrow Fe_3O_4 + 4H_2O$$
(3)

The reaction mechanism is based on the conversion of ferrous hydroxide with hexagonal structure to magnetite with cubic structure. It can be explained that in alkaline solution with high PH value, $Fe(OH)_2$ precipitates, and then dissolution take places by formation of $FeOH^+$ followed by a slow oxidation to magnetite in the air.

2. EXPERIMENTAL SECTION

2.1. Materials and methods

All chemicals were of analytical grade and were used as received without further purification. In this work, sample 1 was synthesized by the oxidation-precipitation method at room temperature. Namely, 0.67 M/L FeCl₂·4H₂O was titrated to the mixture of de-ionized water (320 ml), MEA (12 ml), and H₂O₂ (8 ml, 30%) with a pump. The initial PH value of the mixture was 10-11. Pumping velocity

was about 1 ml/min. During the reaction process, we detected PH value of the mixture with a PH meter. After titrating and aging for 1 hour, the black precipitates were rinsed with absolute ethyl alcohol and de-ionized water repeatedly by using a magnet to separate the particles from the liquid until the used alcohol and de-ionized water could mix a settled solution, and then dried in a vacuum oven at 70 °C for 8 hours. According to the final PH value of the mixture when stopping titrating (PH= 9.2, 8.0, 7.3), the samples were labeled as S1, S2, and S3, respectively. In addition, sample 2 was prepared by a modified co-precipitation method. The organic solvent consisting of A1416 (75% volume) and kerosene (25% volume) was used as a stabilizing agent. The products synthesized by FeCl₃·6H₂O and FeCl₂·4H₂O at molar ratios of 2:1.1 to 2:1.5 at room temperature were compared. In the end, the molar ratio of 2:1.4 was fixed according to the XRD data of the as-synthesized samples. In detail, the ethanol solution mixture (61.87 ml) of 0.0133M FeCl₂ and 0.0093M FeCl₃ (molar ratio: 2:1.4) was mixed with the organic solvent (137.15 ml), then 2 M/L ammonia solution (43.88 ml) was added quickly into the mixture at 25 °C, 40 °C and 55 °C while vigorously stirring for 10 minutes. The reaction solution turned black immediately. Afterwards, the black precipitates were rinsed and dried by the same method as sample 1. The samples were labeled as S4, S5, and S6 according to the reacting temperature of the mixture (T=25 °C, 40 °C and 55 °C).

2.2. Characterization

The crystalline phase of the prepared nanoparticles was identified by XRD using a XD-2 diffract meter (PuXi TongYong Instrument Co. Ltd., Beijing) equipped with $Cu_{K\alpha}$ radiation (λ =0.15406nm). The morphologies of the samples dispersed in absolute ethyl alcohol were examined by TEM (JEM-3000F, JEOL Ltd., Japan). A vibrating-sample magnetometer (VSM, BHV-50HTI, Riken Denshi) was used to study the magnetic properties. Parameters such as saturation magnetization (m_s), coercive field (H_c) and remnant magnetism (M_r) were measured.

3. RESULTS AND DISCUSSION

The XRD results indicate typical X-ray powder diffraction patterns of magnetite nanoparticles at different PH values (9.2, 8.0 and 7.3) for sample 1(Figure 1a) and different temperatures (25, 40 and 50 °C) for sample 2 (Figure 1b). The experiment results are compared with standard magnetite patterns. In all cases, the XRD patterns show characteristic peaks at 2θ =18.2°, 30.0°, 35.4°, 43.0°, 53.4°, 56.9°, 62.5°, and 74.0°, marked by (111), (220), (311), (400), (422), (511), (440), and (533) with lattice spacing *d* and lattice parameters a_0 as shown in Table 1.

It is found that the position and relative intensity of the peaks in the obtained XRD patterns match well with the standard magnetite samples according to JCPDS cards No. 89-0691 and 88-0866. This demonstrates that these samples are in inverse spinel structure with a face-centered cubic phase. Lattice parameters of the representive samples S2 and S6 are 0.83894 and 0.83848 nm, which are closed to the ones of standard Fe₃O₄ samples.



Figure 1. X-ray powder diffraction patterns of sample 1 (a) and sample 2 (b).

Sample	d_{111}	d_{220}	<i>d</i> 311	d_{400}	d_{422}	d_{511}	d_{440}	d ₅₃₃	a ₀	PDF
S2	4.9115	2.9608	2.5295	2.0999	1.7145	1.6141	1.4813	1.2781	8.3894	
Fe ₃ O ₄ (Standard)	4.8424	2.9654	2.5289	2.0968	1.7120	1.6141	1.4827	1.2790	8.3874	#89-0691
S6	4.8761	2.9692	2.5291	2.0978	1.7217	1.6125	1.4823	1.2788	8.3881	
Fe ₃ O ₄ (Standard)	4.8409	2.9644	2.5281	2.0962	1.7115	1.6136	1.4822	1.2787	8.3848	#88-0866
Fe ₂ O ₃ (Standard)	4.8220	2.9530	2.5177	2.0886	1.7045	1.6073	1.4758	1.2730	8.3503	#39-1346

Table 1. Crystallite parameters of S2 and S6 calculated from XRD patterns.

In the XRD patterns, there are no typical γ -Fe₂O₃ peaks, such as (110), (210), (211), the intensities of which are stronger than the one of (111). The sample black colors, lattice spacing and lattice parameter suggest that it is significant that the nanoparticles mainly consist in magnetite. Further, to confirm the result above, a well known standard Fe²⁺ and Fe³⁺ content test was performed for the as-synthesized samples [14], which also indicated the minority of γ -Fe₂O₃.

The mean crystallite size of the sample is determined by using the Debye-Scherrer's formula following standard procedures [15, 16]. The Calculated average crystallite sizes are 10.6, 9.8 and 8.9 nm with PH values ranging from 9.2 to 7.3 for sample 1, and are 6.7, 7.7 and 8.6 nm with the temperature varying from 25 °C to 55 °C for sample 2, suggesting that at high PH values or elevated temperature the precipitate particles possess larger crystallite sizes. This arises from the fact that, according to Oswald ripening theory [17], small particles are preferred in reaction dynamics with larger surface energy, while large particles are thermodynamically favored with larger volume energy. In the growth process nuclei smaller than the critical nuclear size dissolve and transform into large particles to attain a lower total energy state of the entire system. Thus, the critical size of the particles increases with reaction temperature. On the other hand, the effect of PH value can be understood that at a low PH value, an increase of the concentration of Fe²⁺ ions results in a decrease in oxidation ratio. In this case, smaller magnetite crystallites are more likely to form and precipitate. Therefore, the crystallite size of the magnetite could be controlled by tailoring the final PH value or the reaction temperature.



Figure 2. TEM images of magnetite nanoparticles S2 (a) and S6 (b) with the corresponding SAED patterns inserted. (c) Lognormal distribution functions from fitting the TEM particle size data for S2 and S6.



Figure 3. Magnetic hysteresis loops of S1-S3 (a) and S4-S6 (b) at room temperature. Inset: An enlargement of the region at low magnetic field.

Representative TEM images of the synthesized samples are shown in Figure 2a and 2b. It can be seen that sample S2 and S6 are composed of a large number of congeries with a near-to-spherical shape. The selected area electronic diffraction (SAED) patterns (inset shown in Figure 2a and 2b) recorded on a nanoparticle assembly show spotty diffraction rings that can be attributed to S2 and S6 with crystalline feature. Determined by statistical analysis of the TEM images, the particle diameters of S2 and S6 are 10.7 ± 2.0 and 9.6 ± 1.9 nm, which are consistent with the XRD data and suggest that each particle is a single crystal. The TEM particle size data are fitted assuming a lognormal distribution and the resulting curves are shown in Figure 2c. Logarithmic standard deviations of around 0.13 (S2) and 0.14 (S6) support narrow size distribution of the particles prepared by these two methods. Furthermore, sample S6 is relatively monodisperse and more spherical than sample S2, which can be attributed to the effects of the organic stabilizing agent and high reaction temperature.

The classification of a material's magnetic property is based on magnetic susceptibility. Magnetite is a typical kind of ferromagnetic material. Magnetizations M versus applied magnetic field

H for powders of these six samples are measured at room temperature by cycling the magnetic field between -15k to 15k Oe with sweep speed of 5 min/loop. The magnetization curves in Figure 3 show hysteresis behavior in the low field region with the coercive field and remnant magnetism around 50 Oe and 5 emu/g, respectively. As small particles are difficult to saturate, the saturation magnetization is obtained by extrapolation to infinite field of the experimental data in which the magnetization varies linearly with the inverse of the applied field. In addition, based on the low field and high field portions of magnetization curves at room temperature, the mean magnetic diameter (D_{mag}) and its standard deviation σ can been obtained from Chantrell's equations [18], derived for zero interaction between magnetic nanoparticles and assuming a lognormal distribution of particle sizes. The canting layer is estimated from the formula: $2e=(1-m_s/M_s)^{1/3}D$, where m_s and M_s are the saturation magnetization of the nanoparticles and bulk state, *e* is the canting layer thickness, and *D* is the average particle size. The obtained parameters of the samples from magnetic measurement including saturation magnetization, mean magnetic diameter, surface canting layer thickness, and the ratio ($2e/D_{xrd}$) are listed in Table 2.

Sample	S1	S2	S 3	S4	S5	S6
m_s (emu/g)	68.9	66.6	64.1	57.4	60.9	61.9
D_{mag} (nm)	5.8	6.5	6.2	5.5	5.6	5.5
<i>e</i> (nm)	0.49	0.50	0.50	0.49	0.49	0.53
$2e/D_{xrd}$	0.09	0.10	0.11	0.15	0.13	0.12

 Table 2. Magnetic measurement parameters of S1-S6.

The saturation magnetization of the bulk phase of magnetite is about 92 emu/g, but here for sample S2 and S6, the m_s values are 66.6 and 61.9 emu/g. The difference can be most likely attributed to several factors including the finite size effect and large surface- to-volume ratio, the spin canting effect found at a grain boundary, and the incomplete crystallization of magnetite particles; all of which may lead to decrease in the effective magnetic moment [19]. For sample 1, the saturation magnetization increases with the final PH value; meanwhile the particle size increases gradually, so the increase of saturation magnetization is mainly due to finite size effect. While for sample 2, the saturation magnetization increases with the reaction temperature, thus elevated crystallization and finite size effect may both be responsible for this result. The calculated magnetic diameters of magnetite nanoparticles with a standard deviation σ around 0.4 are shown in Table 2. It is known that the critical dimension for a single- to multi-domain structure in magnetite particles is about 30nm [20], so single domain structures of these samples are expected. It is obvious that the magnetic diameters are smaller than the average crystallite sizes estimated from XRD and particle diameters from TEM measurements. The cause for this observation is 2-fold: first, there is a spin canting layer on the particle surface, and second, taking into account the equation used to calculate the D_{Mag} , the interaction between particles may also cause this deviation. In light of the data from Table 2, the thicknesses of the surface spin layer of these samples are around 0.5 nm, which are consistent with the experimental

results obtained by Dutta [21]. TEM images of Figure 2a and 2b demonstrate significant magnetostatic interaction between nanoparticles, as reflected in formation of congeries of particles. So this deviation is mainly due to the interaction between nanoparticles. Additionally, it is clear from Table 2 that the ratio of $2e/D_{xrd}$ which corresponds to the proportion of spin disorder layer in nanocrystalline diameter, decreases with an increase in crystallite size. This may be a general phenomenon for very small nanoparticles.

4. CONCLUSION

We have developed two solution-phase routes for the synthesis of magnetite nanoparticles. Average crystallite sizes of the powder range from 8.9 to 10.6 nm for sample 1 synthesized by oxidation-precipitation method and from 6.7 to 8.6 nm for sample 2 synthesized via modified coprecipitation method. The nanoparticles possess larger crystallite sizes at high PH values or high temperature. TEM measurements demonstrate that the particles obtained by these two methods are near-to-spherical and uniform in particle size. Because of the interaction between nanoparticles, the particle diameters calculated from hysteresis loops are smaller than the average diameters estimated from XRD and TEM measurements. For sample 1, the saturation magnetization increases with the final PH value due to finite size effect. For sample 2, the saturation magnetization. In addition, the proportion of the spin disorder layer in nanocrystalline diameter decreases with an increase in crystallite size.

References

- 1. M.E. Fleet, Acta Cryst., B37 (1981) 917.
- 2. J. L.Kirschvink, *Bioelectromagnetics.*, 17 (1996) 187.
- 3. D.K. Kim, M.S. Amin, S. Elborai, S.H. Lee, Y. Koseoglu, M. Zahn and M. Muhammed, *J. Appl. Phys.*, 97 (2005) 10J510.
- 4. S. Wang, F.J. Yue, D. Wu, F.M. Zhang, W. Zhong and Y.W. Du, *Appl. Phys. Lett.*, 94 (2009) 012507.
- 5. S. Ito, K. Nakaoka, M. Kawamura, K. Ui, K. Fujimoto and N. Koura, *J. Power Sources.*, 146 (2005) 319.
- 6. S. S.Nair, J. Thomas, C.S. Suchand Sandeep, M.R. Anantharaman and R. Philip, *Appl. Phys. Lett.*, 92 (2008) 171908.
- 7. X.F. Wang and L.Q. Shi, Chin. Phys. B., 19 (2010) 107502.
- 8. H.M. Chen, C.H. Deng and X.M. Zhang, Angew. Chem. Int. Ed., 49 (2010) 607.
- 9. H. El Ghandoor, H.M. Zidan, Mostafa M.H. Khalil and M.I. M. Ismail, *Int. J. Electrochem. Sci.*, 7 (2012) 5734.
- 10. S.H. Sun and H. Zeng, J.Am. Chem. Soc., 124 (2002) 8204.
- 11. Z.L. Liu, X. Wang, K.L. Yao, G.H. Du, Q.H. Lu, Z.H. Ding, J. Tao, Q. Ning, X.P. Luo, D.Y. Tian and D. Xi, *J. Mater. Sci.*, 39 (2004) 2633.
- 12. H.Z. Qi, B. Yan, W. Lu, C.K. Li and Y.H. Yang, Curr. Nanosci., 7 (2011) 381.
- 13. Z. Li, M. Kawashita, N. Araki, M. Mistumori, M. Hiraoka and M. Doi, *J. Biomater. Appl.*, 00 (2010) 1.

- 14. Sivasankar, Engineering Chemistry, Tata McGraw-Hill Education, New Delhi, (2008).
- 15. X.C. Chen, J.P. Zhou, H.Y. Wang, P.S. Xu and G.Q. Pan, Chin. Phys. B., 20 (2011) 096102.
- 16. F. Pan, Y. Guo, F.F. Cheng, T. Fa and S.D. Yao, Chin. Phys. B., 20 (2011) 127501.
- 17. G. Madras and B. J.McCoy, J. Chem. Phys., 115 (2001) 6699.
- 18. R.W. Chantrell, J. Popplewell and S.W. Charles, IEEE Trans. Magn., 14 (1978) 975.
- 19. M. Mandal, S. Kundu, S.K. Ghosh, S. Panigrahi, T. K.Sau, S.M. Yusuf and T. Pal, J. Colloid Interface Sci., 286 (2005) 187.
- 20. M. Andres Verges, R. Costo, A.G. Roca, J.F. Marco, G.F. Goya, C.J. Serna and M.P. Morales, J. Phys. D: Appl. Phys., 41 (2008) 134003.
- 21. P. Dutta, S. Pal, M.S. Seehra, N. Shah and G.P. Huffman, J. Appl. Phys., 105 (2009) 07B501.
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