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Preparation of Carboxyl Group Functionalized Magnetite Nanoparticles with High Magnetization

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A new route of the emulsifier-free emulsion polymerization was performed to prepare surface-functionalized magnetic nanoparticles. The Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy images confirm the formation of poly methacrylic acid (PMAA) layers and the existence of free carboxylicacid groups on the surface of magnetite particles. The poly methacrylic acid layer thickness which is estimated by thermal gravity analysis (TGA) increases from 6.5 to 10.6 nm with increasing mass ratio of monomer to magnetite from 3/1 to 16/1. The increase in thickness of the polymer cover results in the decrease in magnetization saturation of polymeric coated magnetic particles. However this reduction of about 20 emu g^{-1} is impressive lower compared to that in the other studies with the presence of surfactants or emulsifiers.

Keywords: Magnetite, Polymeric coated nanoparticles, Magnetic materials.

INTRODUCTION

Magnetic nanoparticles with carboxyl group functionalized surface have potential utilization in medical and biological applications. Besides improving the dispersion of magnetic nanoparticles in biological environments, the carboxyl group has been used for immobilization of oligonucleotides and proteins on polymer surfaces *via* covalent bonding[1,2]. However, only limited literature can be found for the synthesis of carboxyl group functionalized magnetic nanoparticles. In these studies, the core-shell structured composite particles with magnetite (or maghemite) as a core and poly(methacrylic acid) as a shell were prepared by polymerization of acrylic acid or methacrylic acid monomers in the iron oxide colloid solutions with emulsifier or stabilizer[2-4]. The formation of the composite particles was shown. As the results reported, however, the magnetization values of the obtained particles are much lower than the bulk. This result was attributed not only to the non magnetic polymeric coating but to the surfactant layer covering magnetic particles. It is noted that the presence of surfactant leading to a reduction of the magnetization was also found in other works where magnetic particles encapsulated by different polymers were synthesized[5-7]. For resolving this problem, emulsifier-free emulsion polymerization can be consider as a suitable way to prepare polymer coated magnetic particles. In such polymerization systems, however, in order to enhance the interaction between magnetic nanoparticles and polymers, the studies also had to use some added components such as emulsifiers, costabilizers or crosslinking agents. Therefore, to improve the magnetization, a new method of the emulsifier-free emulsion-polymerization with only four main components: magnetite nanoparticles, methacrylic acid, initiator and water will be carried out in this study. In addition, the effect of monomer concentration to the formation of the polymer shell will also be investigated.

EXPERIMENTAL

Ferrous chloride tetrahydrate ($FeCl_2·4H_2O$, AR) and ferric chloride hexahydrate ($FeCl_3·6H_2O$, AR) were procured from BDH Chemicals Ltd. England. Ammonium hydroxide [AR, 25 % (by mass) NH_3 in water] was purchased from Guangdong Xilong Chemical Co. Ltd. China. Initiator potassium persulfate ($K_2S_2O_8$) and monomer methacrylic acid (MAA) of 99 % purity were supplied by Merck

Preparation of poly methacrylic acid coated particle: The PMAA coated particles were prepared through two phases. In the first phase, the magnetite nanoparticles (MNPs) were prepared by reacting iron (II) and iron (III) ions in an aqueous ammonia solution as follows.

$$2FeCl_3 + FeCl_2 + 8NH_3 + 4H_2O \rightarrow Fe_3O_4\downarrow + 8NH_4Cl \quad (1)$$

This preparation has been carried out with the standard conditions as reported by Huang and Nguyen[8]. The prepared precipitate after rinsing several times with deionized water until the pH value decreased to 7 was dispersed in water at the concentration of 2 % wt. by ultrasonication. In the second phase, the dispersion was heated to 60 ± 2 °C in a thermoregulator. Then, the appropriate amount of the initiator $K_2S_2O_8$ (5 % of monomer weight) was added to. After that the solution of methacrylic acid was added into the reaction vessel during 4 h with a constant rate. The mass ratio of methacrylic acid to magnetite was consequently altered: 3/1, 8/1, 11/1 and 16/1. The stir rate of 300 rpm and nitrogen gas were kept throughout the polymerization. This process was continued after the monomer addition has been completed for more than 1 h. The formed polymer coated particles were extracted from the solution by a magnetic particle concentrator to remove the free monomers and polymer. These isolated particles were free dried for the characterization.

Characterization of synthesized particles: The crystalline structure of the magnetic nanoparticles was characterized by X-ray diffraction. The measurements were performed on powder samples obtained after evaporation of the liquid carrier, using a Siemens diffractometer D5000 with CuK_α radiation at 1.5406 Å.

The formation of the magnetite particles with PMAA coatings was studied by FTIR (model Impact 400, Nicolet, USA) and by TEM technique with the instrument JEOL EM 1010. Assuming that each magnetite particle was coated by the polymer layer, the polymer layer thickness may be predicted from TGA that was done by a thermogravimetric analyzer (TGA, DuPont Instruments, TGA 2950) under nitrogen gas with a heating rate of 5 °C/min from room temperature to 600 °C. The weight ratio of the polymer and magnetite from TGA can be expressed as

$$\chi = \frac{\rho_2\left[\sum_{i=1}^{N}(a_i^t)^3 - \sum_{i=1}^{N}(a_i^0)^3\right]}{\rho_1\sum_{i=1}^{N}(a_i^0)^3} =$$

$$\frac{\rho_2\sum_{i=1}^{N}(a_i^0+t)^3}{\rho_1\sum_{i=1}^{N}(a_i^0)^3} - \frac{\rho_2}{\rho_1} = \frac{\rho_2}{\rho_1}\left[\frac{\sum_{i=1}^{N}(a_i^0+t)^3}{\sum_{i=1}^{N}(a_i^0)^3} - 1\right] \qquad (2)$$

where t is the polymer layer thickness, a_i^0 is the radius of ith uncoated particle and N is the total particles taken account. The densities of magnetite and PMMA are $\rho_1 = 5.20$ g/cm^3 and $\rho_2 = 1.18$ g/cm^3, respectively.

As Eqn. (2), from the particle size distribution determined by the TEM image of the original magnetite dispersion the polymer shell thickness t was calculated with the total particles N of 1000.

Vibrating sample magnetometer (VSM) DMS 880 was used for magnetization measurements. These measurements were taken from 0 to 12 kOe field. From this field *versus* magnetization curve patterns, saturation magnetization values of the samples were measured.

RESULTS AND DISCUSSION

The XRD pattern (Fig. 1) of the as synthesized nanoparticles shows the characteristic peaks (220), (311), (400), (422), (511) and (440) corresponding to magnetite from JCPDS card 11-0614. The existence of any impurity other than magnetite is not detected. It can be proposed that magnetite is the main precipitate in our experiments. The magnetization value of 78 emu/g obtained for these particles that are very close to the bulk Fe_3O_4 (90 emu/g) also confirm this conclusion. The average radius of magnetic nanoparticles that is estimated from the TEM image (Fig. 2a) is about 6.6 nm.

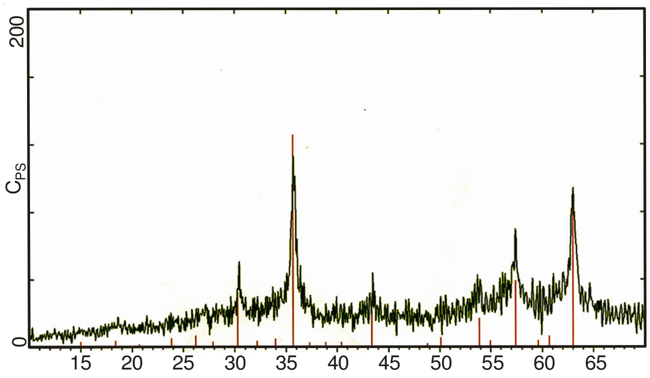

Fig. 1. X-ray diffractogram of synthesized precipitates

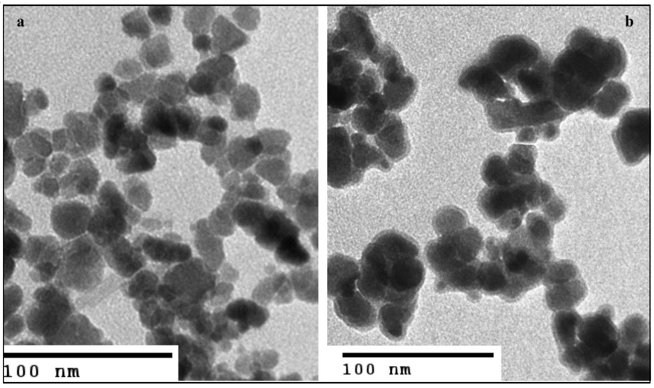

Fig. 2. TEM image of magnetite particles uncoated (a) and coated (b) PMAA

FTIR spectra of magnetite nanoparticles before and after coating with PMAA are presented in Fig. 3. The absorption band of magnetite at 570 cm^{-1} can be found in both spectra. Meanwhile, the observed C-H stretching bands at just below 3000 cm^{-1} indicate the presence of PMAA on the surface of the magnetite. The symmetrical C=O stretching band that appears at 1402 cm^{-1}, similar to the observation for the PMAA coated maghemite nanoparticles[2], suggests here that the carboxylate might symmetrically bind to the magnetite nanoparticle surface and the carboxylate is connected to the surface through two oxygen atoms. Moreover, the evident C=O stretch at 1656 cm^{-1} indicates the existence of free carboxylic acid groups.

Fig. 2b shows a typical TEM image of the PMAA coated Fe_3O_4 nanoparticles synthesized with different mass ratios of monomer/magnetite. The observation at the TEM image confirms the formation of polymer coated magnetite nanoparticles. Most magnetite particles are covered by PMAA and the polymer shells have a uniform thickness. In addition, the

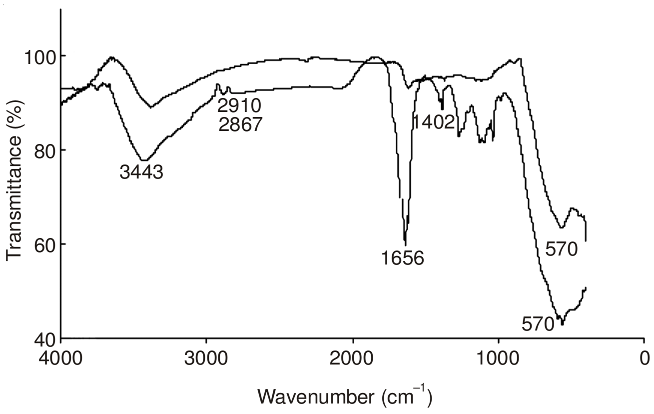

Fig. 3. FTIR spectra of magnetite particles uncoated and coated by PMAA

coated particles are dispersed in water at a degree much higher than the original dispersion. It is concluded that the polymer shells improve the dispersion stability of the magnetic nanoparticles. From the obtained result, the polymer layer thickness can be calculated by eqn. (2) from TGA measurements. As seen in Fig. 4, where thermogravimetric charts of PMAA coated particles of the samples from S1 to S4 are presented, the loss of mass is gradual. An endothermal peak in DTA corresponding to the PMAA degradation is observed around 180 °C. The PMAA weight can be estimated by the mass loss from 180 °C to 450 °C revealing the complete decomposition of PMAA. The residual mass is considered as the amount of magnetite in the PMAA coated particles. The thicknesses of the polymer layers obtained at the samples are

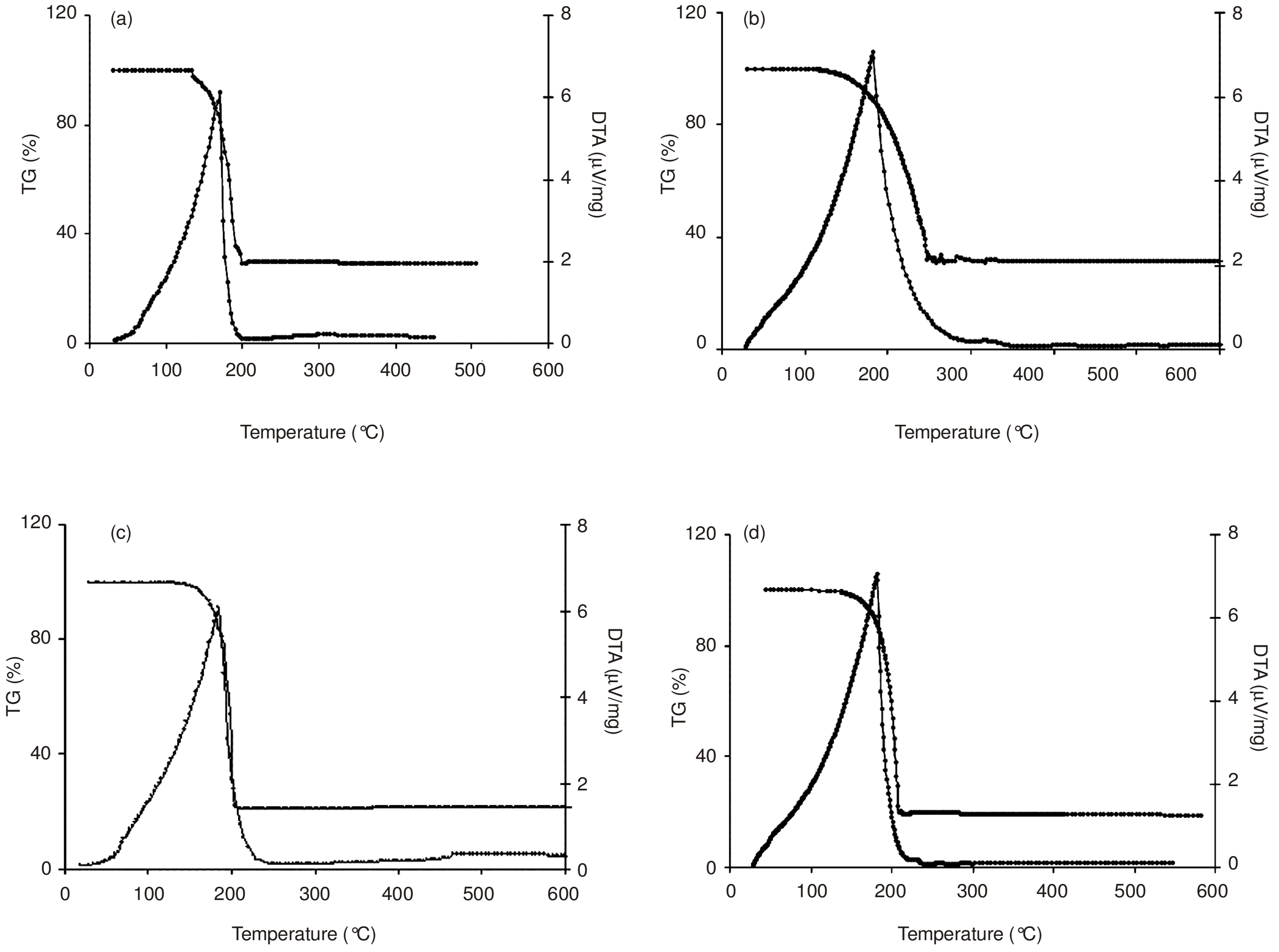

Fig. 4. Weight loss curves of PMAA coated particles prepared at different ratios of MAA/magnetite: (a) S1, (b) S2, (c) S3, (d) S4

TABLE-1
PMAA LAYER THICKNESS DETERMINED BY TGA

Sample	Weight ratio MAA/MNPs	Initial avg. size α_N^0 (nm)	TGA analysis		Polymerization yield (%)
			PMAA/MNPs	t (nm)	
S1	3	6.6	1.42	6.5	47
S2	8		1.80	7.5	23
S3	11		2.88	9.7	26
S4	16		3.48	10.6	22

reported in Table-1. These values are quite good in agreement with the observation in the TEM image.

An increase of the polymer film thickness with increasing ratio of monomer/magnetite is found. In order to explain this result, it should be noted that in the current work the methacrylic acid addition rate is only 0.13 % wt. per minute at the highest level (S4) and with the polymerization rate reported[9] where the time for the complete conversion of 0.1 M methacrylic acid was about 15 minutes, the dynamic concentration of methacrylic acid in the continuous phase was always lower its the aqueous solubility of 9.7 % wt.[10]. Hence the polymerization may be considered as a solution polymerization. At the beginning time of the reaction, since the amount of methacrylic acid is much smaller than initiator concentration, the radical capturing is accelerated to form oligomeric radicals with sulfate end groups. These elements are surface active and absorb on the surface of magnetic particles. The subsequent polymerization occurs in incorporation of the added monomers to the particle surface and the structure core-shell is formed. According to this supposition, the degree of polymerization as well as the molecular weight of polymer that determines the polymer layer thickness is increased with increasing monomer concentration. However, for high water-soluble monomers such as methacrylic acid, the growth of the polymer layers coating magnetite particles is strongly competed by the polymer particles that are formed in the medium by the precipitation of growing chains upon achievement of a critical chain length[9]. Besides, the interaction between magnetite particles and PMAA as found at the FTIR may be considered as a chain transfer agent leading to diminish molecular weight of the coated polymer. Thus, the preferred formation of the free polymer particles rather than the polymer covering magnetite explains for the fact that the polymerization yield is quite lower than that of the polymerization for poly-methyl methacrylate (PMMA) under similar reaction conditions[11]. The polymerization yields (except sample S1) fluctuate around the value of 25 % although the monomer concentration is increased up to 5 times (Table-1). This result also implies that the mass ratio of monomer/magnetite should be equal or lower than 3/1 to obtain the sythesis with high efficiency.

It is striking that the polymerization method used in this study allows preparing PMAA coated particles with the structure core-shell and the polymer coating thickness can be simply adjusted by changing monomer concentration. Furthermore, the prepared particles show magnetic property significantly higher than similar studies[2,6,7]. As illustrated in Fig. 5 the saturation magnetization at 12 kOe of bare Fe_3O_4 nanoparticles is 78 emu g^{-1} and of PMAA coated magnetite particles are 62 and 58 emu g^{-1} for samples S2 and S4, respectively. It is clearly observed that the higher the polymer layer thickness the lower the saturation magnetization is. This result can be simply attributed to the non-magnetic polymer. The existence of the Fe-O-C bonds supported by the FTIR measurements is a possible reason causing the decrease in magnetization of PMAA coated particles[2]. Nevertheless, compared to the magnetic particles coated different polymers such as PMAA, PMMA, PS, the magnetization reduction in this study is much lower than the others. For magnetic particles coated by PMMA, Hong *et al.*[6] found that the magnetization down from 65.6 emu/g to 23 emu/g by the existence of PMMA and oleic acid (emulsifier). In addition, the poly ethylene glycol methacrylate (PEG-MA) coated particles of Utkan *et al.*[7] showed the sharp reduction in magnetization after polymer coating (from 23 emu g^{-1} to 2.5 emu g^{-1}). A similar result also observed in[2]. The main difference between our research and the others comes from either too thick polymer layer (165 nm)[7] or the presence of surfactant layer[2,6].

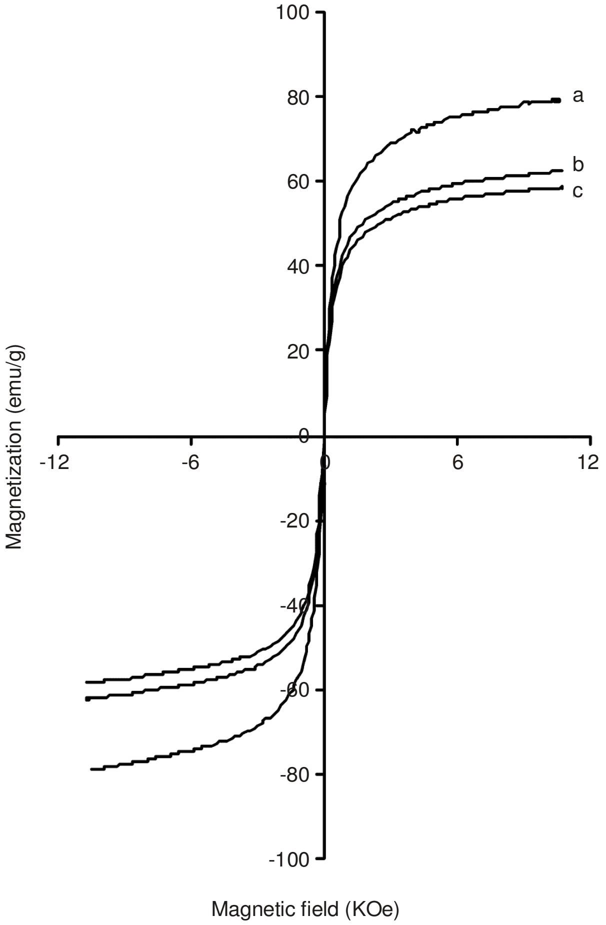

Fig. 5. Magnetization curvers of MNPs (a) and PMMA coated particles synthesized with different MMA/magnetite ratios: (b) 8/1, (c) 16/1

Conclusion

In this study, the magnetic particles surface-functionalized with carboxyl group were prepared by the polymerization of methacrylic acid monomers without surfactants. The experimental investigations indicate that the carboxylic acid groups can chemically adsorb on to the surface of magnetic nanoparticles *via* a possible symmetrical carboxylate binding. The magnetite particles are encapsulated by the thin polymeric layer and this layer can be adjusted by altering mass ratio of monomers to magnetite particles. The PMAA coated nanoparticles retain their magnetic properties at a level much higher than that in other studies.

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REFERENCES

1. E.P. Ivanova, M. Papiernik, A. Oliveira, I. Sbarski, T. Smekal, P. Grodzinskiand and D.V. Nicolau, *Smart Mater. Struct*., **11**, 783 (2002).
2. S. Yu and G.M. Chow, *J. Mater. Chem*., **14**, 2781 (2004).
3. P. Businova, J. Chomoucka, J. Prasek, R. Hrdy, J. Drbohlavova, P. Sedlacek and J. Hubalek, In Proceedings of Nano conference, Czech Republic (2011).
4. L. Charoenmark, D. Polpanich, R. Thiramanas and P. Tangboriboonrat, *Macromol. Res*, **20**, 590 (2012).
5. I. Csetneki, M. Kabai Faix, A. Szilagyl, A.L. Kovacsi, Z. Nemeth and M. Zrinyi, *J. Polym. Sci. A Polym. Chem*., **42**, 4802 (2004).
6. R.Y. Hong, B. Feng, X. Cai, G. Liu, H.Z. Li, J. Ding, Y. Zheng and D.G. Wei, *J. Appl. Polym. Sci*., **112**, 89 (2009).
7. G. Utkan, F. Sayar, P. Batat, S. Ide, M. Kriechbaurnd and E. Piskin, *J. Colloid Interf. Sci*., **353**, 372 (2011).
8. N.Q. Hung and H.T.K. Nguyen, In Proceedings of International Workshop of Nanotechnology and Applications, Vietnam, pp. 528-534 (2011).
9. T. Tanrisever, O. Okay and I.C. Sonmezoclu, *J. Appl. Polym. Sci*., **61**, 485 (1996).
10. C.S. Chern, Principles and Applications of Emulsion Polymerization, John Willey & Sons, 2008.
11. S. Beyaz, T. Tanrisever, H. Kockar and V. Butun, *J. Appl. Polym. Sci*., **121**, 2264 (2011).