Polym. Bull. (2012) 68:1305–1314
DOI 10.1007/s00289-011-0614-9

ORIGINAL PAPER

Effect of surface modification of Fe_3O_4 nanoparticles on the preparation of Fe_3O_4/polystyrene composite particles via miniemulsion polymerization

Feng Yan · Xiuwen Zheng · Zhaomei Sun · Aihua Zhao

Received: 29 June 2011 / Revised: 19 August 2011 / Accepted: 20 August 2011 /

Abstract Fe_3O_4 nanoparticles were modified by *n*-octadecyltrimethoxysilane (C18TMS) and 3-trimethoxysilylpropylmethacrylate (MPS). The modified Fe_3O_4 nanoparticles were used to prepare Fe_3O_4/polystyrene composite particles by miniemulsion polymerization. The effect of surface modification of Fe_3O_4 on the preparation of Fe_3O_4/polystyrene composite particles was investigated by transmission electron microscopy, Fourier transform infrared spectrophotometer (FT-IR), contact angle, and vibrating sample magnetometer (VSM). It was found that C18TMS modified Fe_3O_4 nanoparticles with high hydrophobic property lead to the negative effect on the preparation of the Fe_3O_4/polystyrene composite particles. The obtained composite particles exhibited asymmetric phase-separated structure and wide size distribution. Furthermore, un-encapsulated Fe_3O_4 were found in composite particles solution. MPS modified Fe_3O_4 nanoparticles showed poor hydrophobic properties and resulted in the obtained Fe_3O_4/polystyrene composite particles with regular morphology and narrow size distribution because the ended C=C of MPS on the surface of Fe_3O_4 nanoparticles could copolymerize with styrene which weakened the phase separation distinctly.

Keywords Fe_3O_4/polystyrene · Composite particles · C18TMS · MPS · Surface modification · Miniemulsion polymerization

---

F. Yan (✉) · X. Zheng · Z. Sun · A. Zhao (✉)
School of Chemistry & Chemical Engineering, Linyi University, Linyi 276000, Shandong, People's Republic of China
e-mail: fyanchem@gmail.com

A. Zhao
e-mail: zhaoah@126.com

Introduction

In recent years, magnetic polymer particles have been extensively studied due to their wide applications in the fields of biotechnology, for example, drug delivery, magnetic resonance imaging, selective separation of biomolecules, hyperthermia therapy, and so on [1–4]. Magnetic polymer composite particles could be prepared by encapsulated magnetic nanoparticles (Fe_3O_4 and γ-Fe_2O_3) into polymer via emulsion polymerization [5, 6], soapless emulsion polymerization [7, 8], inverse emulsion polymerization [9, 10], miniemulsion polymerization [11–14], and atom transfer radical polymerization (ATRP) [15, 16]. Miniemulsion polymerization has been considered as one of the most advantageous methods to prepare magnetic polymer composite particle with moderate diameter and high saturation magnetization [11–14]. However, the magnetic polymer composite particles with irregular morphology and wide size distribution were often obtained [11–14, 17–19]. Furthermore, there was existence of un-encapsulated Fe_3O_4 nanoparticles in the prepared magnetic polymer composite particles. In order to prepare magnetite/polymer composite particles with regular morphology and narrow size distribution, Montagne et al. [13] investigated the detailed encapsulation condition and found that the use of water-soluble initiator, crosslinker, and amphiphilic functional copolymer as stabilizer would drastically prevented the phase separation and obtain Fe_3O_4/polystyrene composite particles with core–shell morphologies. Lu and Forcada [17] found that un-encapsulated Fe_3O_4 and free polymer particles could be reduced distinctly by the selection of the optimized condition (2–3% sodium dodecyl sulfate (SDS) on the total amount of styrene and Fe_3O_4, 10% Fe_3O_4 with respect to total amount of styrene and Fe_3O_4, 5% polyvinylpyrrolidone co-stabilizer, and 4% methacrylic acid comonomer). Yan et al. [18] reported that the monolayer OA modified Fe_3O_4 nanoparticles was more hydrophobic than that of the multilayer coated ones, thus would reduce the free polymer particles. Though much progress has been made by optimized encapsulating conditions, the problem was existent.

During preparation of Fe_3O_4/polystyrene composite particles via miniemulsion polymerization, oleic acid was often used to make Fe_3O_4 nanoparticles be compatible with styrene monomer [11–14, 17–19]. Silane coupling agents *n*-octadecyltrimethoxysilane (C18TMS) and 3-trimethoxysilylpropylmethacrylate (MPS) were widely used to modify inorganic nanoparticles during the preparation of SiO_2/polystyrene, ZnO/polystyrene, Al_2O_3/polystyrene composite particles [20–24]. The morphology and encapsulation effect of inorganic polymer composite particles could be influenced by the type of silane coupling agent modified for the inorganic particles. In this article, Fe_3O_4 nanoparticles were modified by C18TMS and MPS and then used to prepare Fe_3O_4/polystyrene composite particles by miniemulsion polymerization. Transmission electron microscopy (TEM), Fourier transform infrared spectrophotometer (FT-IR), contact angle, and vibrating sample magnetometer (VSM) were used to characterize magnetic particles to investigate the effect of surface modification of Fe_3O_4 on the morphology and encapsulation effect for the Fe_3O_4/polystyrene composite particles.

Experimental

Materials

Ferric chloride ($FeCl_3{\cdot}6H_2O$) and ferrous chloride ($FeCl_2{\cdot}4H_2O$) were purchased from ACROS. MPS (98%) and C18TMS were purchased from Aldrich. Styrene from Beijing Chemical Reagents Company was purified upon distillation under reduced pressure and kept refrigerated before use. SDS, potassium persulfate (KPS), sodium bicarbonate ($NaHCO_3$), cyclohexane, anhydrous ethanol, and ammonium hydroxide ($NH_3{\cdot}H_2O$, 25%) were all analytical grade obtained from Beijing Chemical Reagents Company and used without further purification. OA (90%) was obtained from Shanghai Chemical Reagents Company and used as received. Deionized water was used in all the experiments.

Preparation of Fe_3O_4 nanoparticles by coprecipitation method

The Fe_3O_4 nanoparticles were prepared by coprecipitation of $FeCl_2/FeCl_3$ (mol ratio 1:2) according to Massart's method [25]. An aqueous solution (150 mL) containing 0.06 M $FeCl_2$ and 0.12 M $FeCl_3$ in a 250-mL three-necked flask was heated to 50 °C with the deaeration of O_2 by N_2 bubbling. Then, 12.5 mL $NH_3{\cdot}H_2O$ was added under vigorous stirring. After 30 min, the precipitate was collected on the vessel wall by a magnet and washed three times with water.

Modified Fe_3O_4 nanoparticles by silane coupling agents

0.5 g of Fe_3O_4 nanoparticles were redispersed in anhydrous ethanol (100 mL) by ultrasound. 0.5 mL of silane coupling agents was added. The suspension was stirred for 12 h. The modified Fe_3O_4 nanoparticles were separated with a magnet, washed three times with anhydrous ethanol to remove excess silane coupling agents.

Preparation of Fe_3O_4/polystyrene composite particles by miniemulsion polymerization

Miniemulsion polymerization was used to prepare Fe_3O_4/polystyrene composite particles according to the following procedure. 0.1 g of modified Fe_3O_4 nanoparticles was dried with N_2, and dispersed in the solution of 1 mL of styrene and 0.1 g of cyclohexane with the aid of ultrasound to form the oil phase. 0.08 g of SDS and 0.01 g sodium bicarbonate were dissolved in 30 mL of water to form the water phase. Mixture of the oil phase and the water phase was ultrasonicated for 10 min to form miniemulsion and transferred to a four-necked flask equipped with a condenser, a nitrogen inlet, and a stirrer. 0.015 g of KPS dissolved in 0.5 mL of water was added to initiate the polymerization at 70 °C with continual stirring at 300 rpm. After 12 h, the Fe_3O_4/polystyrene composite particles were obtained.

Characterization

Magnetic particles were characterized by TEM (Hitachi H-8100). The sample for TEM observation was prepared by dipping a few drops of a dilute dispersion on carbon coated copper grids.

Magnetic particles were characterized by FT-IR (PerkinElmer, Spectrum One) in the transmission mode. The sample was palletized with KBr powder for the FT-IR study.

The wettability of modified Fe_3O_4 was characterized by FTÅ200 according to the reported method [18, 26, 27].The wettability of modified Fe_3O_4 was reflected by the advancing contact angle of water on the surface of modified Fe_3O_4 nanoparticle films. The films were prepared by spreading the ferrofluid on a clean microscope glass slide, dried at room temperature, and finally placed in a vacuum desiccator for 24 h before measurements. C18TMS modified Fe_3O_4 nanoparticles were dispersed in cyclohexane to form the ferrofluid by ultrasound. MPS modified Fe_3O_4 nanoparticles were dispersed in anhydrous ethanol to form the ferrofluid by ultrasound. Hydrophilic Fe_3O_4 were dispersed in water to form the ferrofluid by ultrasound.

VSM Controller Model 7300 (Lakeshore) was used to measure the magnetic properties of the magnetic particles. The field dependence of the magnetization was investigated over the range from -10 to $+10$ kOe at 300 K.

Results and discussion

Modified Fe_3O_4 nanoparticles

Figure 1a showed the TEM of Fe_3O_4 nanoparticles prepared by coprecipitation method. The diameter of the Fe_3O_4 nanoparticles was in the range from 6 to 15 nm with average size of 9.5 nm and a polydispersity (PDI) of 0.15. C18TMS and MPS modified Fe_3O_4 nanoparticles were shown in Fig. 1b, c. As shown in the TEM images, the modification of C18TMS and MPS did not make an obvious difference in the morphology and distribution of the nanoparticles size.

FT-IR was used to characterize Fe_3O_4 nanoparticles, shown in Fig. 2. In Fig. 2, the strong vibrations at 632 and 580 cm^{-1} observed was assigned to Fe–O stretch of the Fe_3O_4 nanoparticles [28]. In Fig. 2a, the bands at 3300–3540 cm^{-1} and 1623 cm^{-1} were due to the stretching vibration and binding vibration of –OH in water [29]. In Fig. 2b, the strong peaks at 2922 ($\upsilon_{as}CH_2$), 2853 ($\upsilon_{s}CH_2$), and 1465 ($\delta_{s}CH_2$) cm^{-1} were attributed to the presence of C18TMS on the particle surfaces. The broad peaks between 1150 and 900 cm^{-1} were attributed to Si–O, Si–O–Fe group [28, 30]. The existence of CH_2 and Si–O–Fe indicated that Fe_3O_4 nanoparticles were modified with C18TMS. In Fig. 2c, the strong peaks at 1630 and 1704 cm^{-1} were attributed to the C=C bond and C=O of MPS, which indicated that Fe_3O_4 nanoparticles were modified with MPS [31, 32]. The broad peaks between 1105 and 900 cm^{-1} were attributed to Si–O, Si–O–Fe group [28, 30]. This suggested that MPS modified Fe_3O_4 nanoparticles by formation of Fe–O–Si bonds.

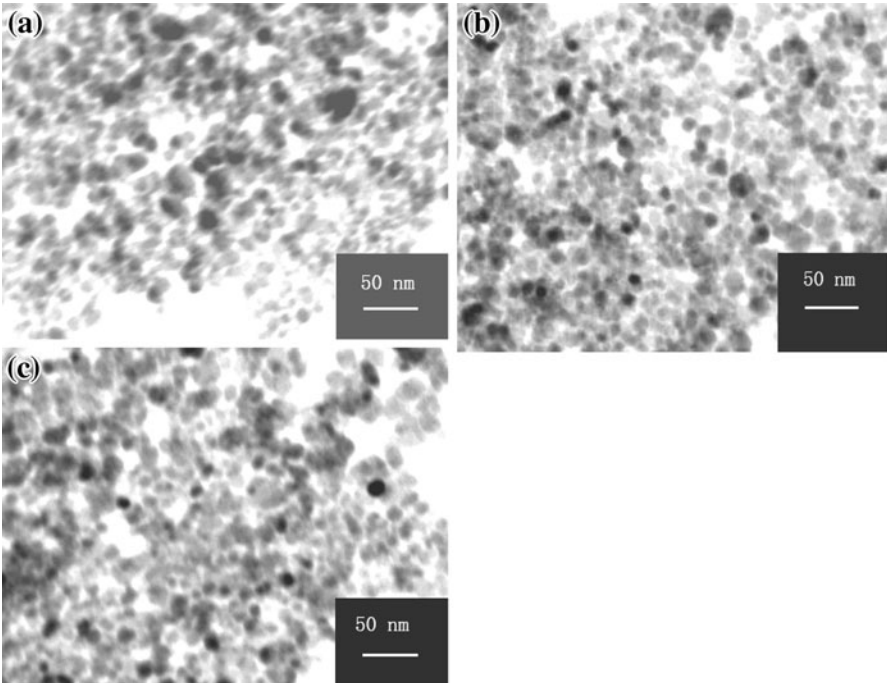

Fig. 1 TEM images of **a** Fe_3O_4 nanoparticles, **b** C18TMS modified Fe_3O_4 nanoparticles, and **c** MPS modified Fe_3O_4 nanoparticles

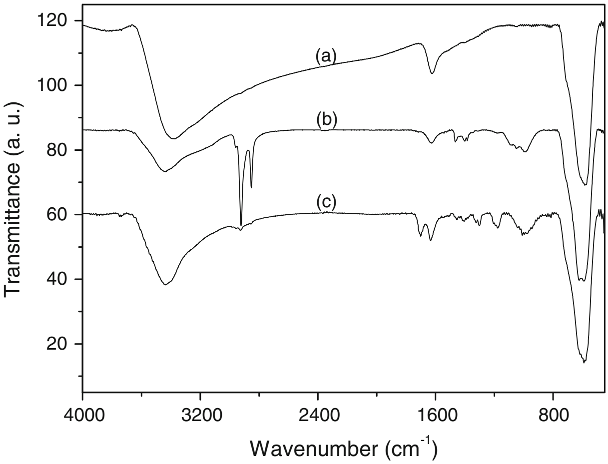

Fig. 2 FT-IR spectra of *a* Fe_3O_4 nanoparticles, *b* C18TMS modified Fe_3O_4 nanoparticles, and *c* MPS modified Fe_3O_4 nanoparticles

The surface properties of the modified Fe_3O_4 nanoparticles were characterized by contact angle measurements and the results were tabled in Table 1. The advancing water contact angle on the films of the Fe_3O_4 nanoparticles is about 9.6°. The

Table 1 The advancing contact angle of magnetic nanoparticles

Sample	Fe_3O_4	C18TMS modified Fe_3O_4	MPS modified Fe_3O_4
Contact angle of water	9.6°	128°	78°

C18TMS modified Fe_3O_4 nanoparticles were more hydrophobic which the advancing water contact angle was 128° and could be dispersed in styrene by ultrasound. The MPS modified Fe_3O_4 nanoparticles was more hydrophilic than C18TMS modified Fe_3O_4 nanoparticles, which advancing water contact angle was 78°. MPS modified Fe_3O_4 nanoparticles could also be dispersed in styrene by ultrasound, but the dispersibility in styrene was poorer than C18TMS modified Fe_3O_4 nanoparticles.

The effect of surface modification of Fe_3O_4 on the prepared Fe_3O_4/polystyrene composite particles

Figure 3 showed the morphology of Fe_3O_4/polystyrene composite particles prepared from modified Fe_3O_4 nanoparticles. From Fig. 3a, the Fe_3O_4/polystyrene composite particles, which were prepared from C18TMS modified Fe_3O_4, were spherical. The average diameter of the composite particles was about 165 nm with a PDI of 0.251. The size distribution of the Fe_3O_4 within the polystyrene particles was quite heterogeneous. Most of Fe_3O_4 particles were located in the side of polystyrene particles, which indicated the Fe_3O_4/polystyrene composite particles exhibited asymmetric phase-separated structure. There were also un-encapsulated Fe_3O_4 nanoparticles dispersed in the solution of Fe_3O_4/polystyrene composite particles. From Fig. 3c, the Fe_3O_4/polystyrene composite particles prepared from MPS modified Fe_3O_4 were also spherical. The average diameter of the composite particles was about 145 nm and PDI of 0.068. Compared with Fe_3O_4/polystyrene composite particles prepared from C18TMS modified Fe_3O_4, the morphology of composite particles from MPS modified Fe_3O_4 were more uniform. Fe_3O_4

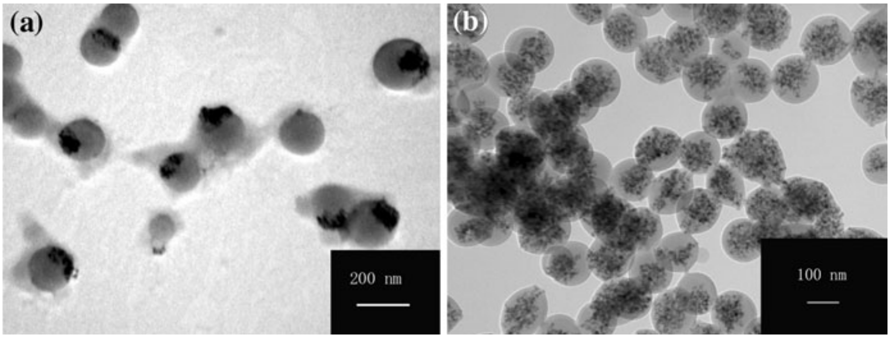

Fig. 3 TEM images of Fe_3O_4/polystyrene composite particles prepared from **a** C18TMS modified Fe_3O_4 nanoparticles and **b** MPS modified Fe_3O_4 nanoparticles

nanoparticles were dispersed in the interior of the composite particles. There was no un-encapsulated Fe_3O_4 nanoparticles found in composite particles solution.

CCl_3 were used to extract polystyrene in Fe_3O_4/polystyrene composite particles. The extracted Fe_3O_4 particles were further characterized by FT-IR, shown in Fig. 4. In Fig. 4a, there were no difference on C18TMS modified Fe_3O_4 nanoparticles before and after polymerization, which indicated that miniemulsion polymerization did not influence the C18TMS modified Fe_3O_4 nanoparticles. In Fig. 4b, the band in 702 cm^{-1} were attributed to the υC–H of benzene ring [31–34]. The bands in 1451, 1493, 1599 cm^{-1} were attributed to υC–C of benzene ring in polystyrene [31–34]. The strong vibrations at 632 and 580 cm^{-1} observed was assigned to Fe–O stretch of the Fe_3O_4 nanoparticles [28]. The existence of polystyrene and Fe_3O_4 nanoparticles proved that the C=C of MPS on the Fe_3O_4 nanoparticles copolymerized with styrene. It is known that the droplet nucleation mechanism is expected to be the dominant nucleation mechanism in miniemulsion polymerization [35, 36]. The droplets consisting of styrene and modified Fe_3O_4 nanoparticles were obtained during miniemulsification process. During the polymerization process of composite particles prepared from C18TMS modified Fe_3O_4 nanoparticles, the phase separation occurred, and the Fe_3O_4 nanoparticles modified with C18TMS were extruded by the polystyrene chain. After polymerization, some of Fe_3O_4 nanoparticles were encapsulated in the side of polystyrene particles and Fe_3O_4/polystyrene composite particles exhibited asymmetric phase-separated structure. During the polymerization process of composite particles prepared from MPS modified Fe_3O_4 nanoparticles, Fe_3O_4 nanoparticles modified with MPS act like huge crosslinking agents and could copolymerize with styrene during polymerization process, which weakened the phase separation distinctly. After polymerization, Fe_3O_4 nanoparticles were encapsulated in the interior of the composite particles and Fe_3O_4/polystyrene

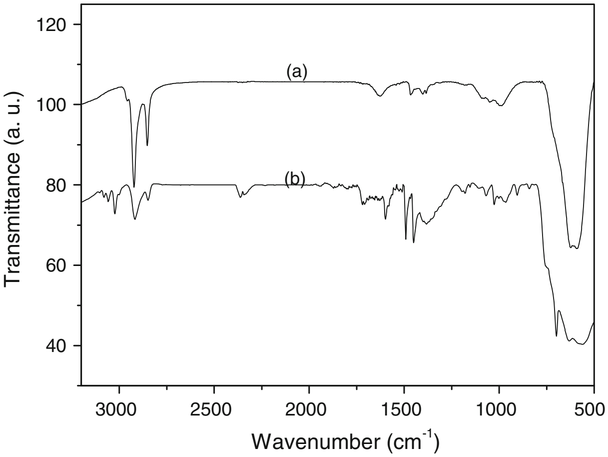

Fig. 4 FT-IR spectra of magnetic particles after extraction of polystyrene in Fe_3O_4/polystyrene composite particles prepared from *a* C18TMS modified Fe_3O_4 nanoparticles and *b* MPS modified Fe_3O_4 nanoparticles

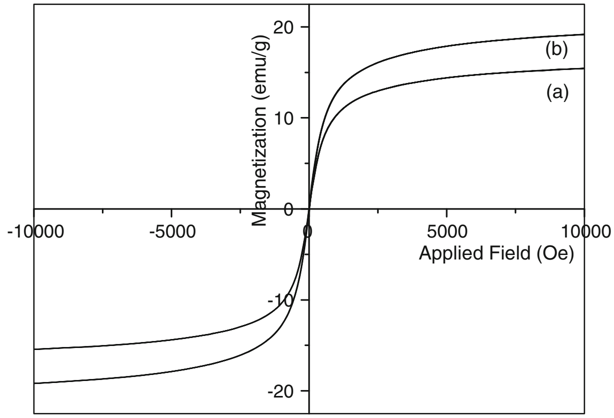

Fig. 5 Magnetization curves of the Fe_3O_4/polystyrene composite particles prepared from *a* C18TMS modified Fe_3O_4 nanoparticles and *b* MPS modified Fe_3O_4 nanoparticles as a function of applied external field *H* at 300 K

composite particles with regular morphology and narrow size distribution were obtained.

The magnetic properties of Fe_3O_4/polystyrene composite particles were characterized by magnetometer. As shown in Fig. 5, both of Fe_3O_4/polystyrene composite particles were superparamagnetic. The saturation magnetization of Fe_3O_4/polystyrene composite particles prepared from C18TMS and MPS modified Fe_3O_4 nanoparticles was 15 and 19 emu/g, respectively.

Conclusions

In this article, C18TMS and MPS were used to modify Fe_3O_4 nanoparticles, respectively. The modified Fe_3O_4 nanoparticles could be dispersed in styrene and then used to prepare Fe_3O_4/polystyrene composite particles by miniemulsion polymerization. When C18TMS was used to modify Fe_3O_4 nanoparticles, the high hydrophobic property of the modified Fe_3O_4 nanoparticles lead to the negative effect on the preparation of the Fe_3O_4/polystyrene composite particles. It was found that the obtained composite particles exhibited asymmetric phase-separated structure and wide size distribution. Furthermore, un-encapsulated Fe_3O_4 were found in composite particles solution. When MPS was used to modify Fe_3O_4 nanoparticles, the modified Fe_3O_4 nanoparticles showed poor hydrophobic properties and resulted in the obtained Fe_3O_4/polystyrene composite particles with regular morphology and narrow size distribution because the ended C=C in MPS on the surface of Fe_3O_4 nanoparticles could copolymerize with styrene which weakened the phase separation distinctly.

Acknowledgments This study was financially supported by the Shandong Province Natural Science Foundation (No. ZR2010BQ030, and No. Y2005B02), Shandong Scientific and Technical Items (GG4402056) and the Doctoral Foundation of Linyi University (No. BS201011).

References

1. Lee JE, Lee N, Kim H, Kim J, Choi SH, Kim JH, Kim T, Song IC, Park SP, Moon WK, Hyeon T (2010) Uniform mesoporous dye-doped silica nanoparticles decorated with multiple magnetite nanocrystals for simultaneous enhanced magnetic resonance imaging, fluorescence imaging, and drug delivery. J Am Chem Soc 132:552–557
2. Lee H, Lee E, Kim DK, Jang NK, Jeong YY, Jon S (2006) Antibiofouling polymer-coated superparamagnetic iron oxide nanoparticles as potential magnetic resonance contrast agents for in vivo cancer imaging. J Am Chem Soc 128:7383–7389
3. Chen H, Deng C, Zhang X (2010) Synthesis of Fe_3O_4@SiO_2@PMMA core–shell–shell magnetic microspheres for highly efficient enrichment of peptides and proteins for MALDI-ToF MS analysis. Angew Chem Int Ed 49:607–611
4. Fortin JP, Wilhelm C, Servais J, Ménager C, Bacri JC, Gazeau F (2007) Size-sorted anionic iron oxide nanomagnets as colloidal mediators for magnetic hyperthermia. J Am Chem Soc 129: 2628–2635
5. Xu X, Friedman G, Humfeld KD, Majetich SA, Asher SA (2002) Synthesis and utilization of monodisperse superparamagnetic colloidal particles for magnetically controllable photonic crystals. Chem Mater 14:1249–1256
6. Yu S, Chow GM (2004) Carboxyl group (–CO_2H) functionalized ferrimagnetic iron oxide nanoparticles for potential bio-applications. J Mater Chem 14:2781–2786
7. Wang PC, Chiu WY, Lee CF, Young TH (2004) Synthesis of iron oxide/poly(methyl methacrylate) composite latex particles: Nucleation mechanism and morphology. J Polym Sci A 42:5695–5705
8. Gu S, Shiratori T, Konno M (2003) Synthesis of monodisperse, magnetic latex particles with polystyrene core. Colloid Polym Sci 281:1076–1081
9. Deng Y, Wang L, Yang W, Fu S, Elaïssari (2003) A Preparation of magnetic polymeric particles via inverse microemulsion polymerization process. J Magn Magn Mater 257:69–78
10. Hong RY, Feng B, Liu G, Wang S, Li HZ, Ding JM, Zheng Y, Wei DG (2009) Preparation and characterization of Fe_3O_4/polystyrene composite particles via inverse emulsion polymerization. J Alloys Compd 476:612–618
11. Ramírez LP, Landfester K (2003) Magnetic polystyrene nanoparticles with a high magnetite content obtained by miniemulsion processes. Macromol Chem Phys 204:22–31
12. Betancourt-Galindo R, Saldivar R, Rodríguez-Fernández OS, Ramos-de Valle LF (2004) Preparation and characterization of magnetic latexes using styrene monomer. Polym Bull 51:395–402
13. Montagne F, Mondain-Monval O, Pichot C, Elaïssari A (2006) Highly magnetic latexes from submicrometer oil in water ferrofluid emulsions. J Polym Sci A 44:2642–2656
14. Zhang X, Jiang W, Ye Y, Feng Z, Sun Z, Li F, Hao L, Chu J (2011) A facile method to synthesize magnetic polymer nanospheres with multifunctional group. J Magn Magn Mater 323:1440–1444
15. Wang Y, Teng X, Wang JS, Yang H (2003) Solvent-free atom transfer radical polymerization in the synthesis of Fe_2O_3@Polystyrene core-shell nanoparticles. Nano Lett 3:789–793
16. Vestal CR, Zhang ZJ (2002) Atom transfer radical polymerization synthesis and magnetic characterization of $MnFe_2O_4$/Polystyrene core/shell nanoparticles. J Am Chem Soc 124:14312–14313
17. Lu S, Forcada J (2006) Preparation and characterization of magnetic polymeric composite particles by miniemulsion polymerization. J Polym Sci A 44:4187–4203
18. Yan F, Li J, Zhang J, Liu F, Yang W (2009) Preparation of Fe_3O_4/polystyrene composite particles from monolayer oleic acid modified Fe_3O_4 nanoparticles via miniemulsion polymerization. J Nanopart Res 11:289–296
19. Zhang Q, Zhang H, Xie G, Zhang J (2007) Effect of surface treatment of magnetic particles on the preparation of magnetic polymer microspheres by miniemulsion polymerization. J Magn Magn Mater 311:140–144
20. Zhang SW, Zhou SX, Weng YM, Wu LM (2005) Synthesis of SiO_2/Polystyrene nanocomposite particles via miniemulsion polymerization. Langmuir 21:2124–2128
21. Shen Y-D, Zhao Y-N, Li X-R (2009) Polyacrylate/silica hybrids prepared by emulsifier-free emulsion polymerization and the sol-gel process. Polym Bull 63:687–698
22. Yi GR, Manoharan VN, Michel E, Elsesser MT, Yang SM, Pine DJ (2004) Colloidal clusters of silica or polymer microspheres. Adv Mater 16:1204–1208
23. Zhang J, Gao G, Zhang M, Zhang D, Wang C, Zhao D, Liu F (2006) ZnO/PS core-shell hybrid microspheres prepared with miniemulsion polymerization. J Colloid Interface Sci 301:78–84

24. Zeng Z, Yu J, Guo ZX (2005) Preparation of functionalized core-shell alumina/Polystyrene composite nanoparticles encapsulation of alumina via emulsion polymerization. Macromol Chem Phys 206:1558–1567
25. Massart R (1981) Preparation of aqueous magnetic liquids in alkaline and acidic media. IEEE Trans Magn 17:1247–1248
26. López-López MT, Durán JDG, Delgado AV, González-Caballero F (2005) Stability and magnetic characterization of oleate-covered magnetite ferrofluids in different nonpolar carriers. J Colloid Interface Sci 291:144–151
27. Galindo-González C, Vicente DJ, Ramos-Tjada MM, López-López MT, González-Caballero F, Durán JDG (2005) Preparation and sedimentation behavior in magnetic fields of magnetite-covered clay particles. Langmuir 21:4410–4419
28. Yamaura M, Camilo RL, Sampaio LC, Macêdo MA, Nakamura M, Toma HE (2004) Preparation and characterization of (3-aminopropyl) triethoxysilane-coated magnetite nanoparticles. J Magn Magn Mater 279:210–217
29. Sun G, Sun L, Wen H, Jia Z, Huang K, Hu C (2006) From layered double hydroxide to spinel nanostructures: facile synthesis and characterization of nanoplatelets and nanorods. J Phys Chem B 110:13375–13380
30. Palma RD, Peeters S, Bael MJV, Rul HVD, Bonroy K, Laureyn W, Mullens J, Borghs G, Maes G (2007) Silane ligand exchange to make hydrophobic superparamagnetic nanoparticles water dispersible. Chem Mater 19:1821–1831
31. Chen Z, Peng K, Mi Y (2007) Preparation and properties of magnetic polystyrene microspheres. J Appl Polym Sci 103:3660–3666
32. Yan F, Li J, Fu R, Lu Z, Yang W (2009) Facile preparation of superparamagnetic Fe_3O_4/Poly(St-co-MPS)/SiO_2 composite particles with high magnetization by introduction of silanol groups. J Nanosci Nanotechnol 9:5874–5879
33. Yang JC, Jablonsky MJ, Mays JW (2002) NMR and FT-IR studies of sulfonated styrene-based homopolymers and copolymers. Polymer 43:5125–5132
34. Zhao Y, Urban MW (2000) Polystyrene/poly(n-butyl acrylate) latex blend coalescence, particle size effect, and surfactant stratification: a spectroscopic study. Macromolecules 33:7573–7581
35. Reimers J, Schork FJ (1996) Robust nucleation in polymer-stabilized miniemulsion polymerization. J Appl Polym Sci 59:1833–1841
36. Antonietti M, Landfester K (2002) Polyreactions in miniemulsions. Prog Polym Sci 27:689–757