

Preparation of Magnetic Fe₃O₄ Microspheres Using Different Surfactant and Silica-coated Magnetic Particles

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Abstract—Magnetic nanomaterials have received tremendous attention in the past years due to their unique magnetic responsiveness and corresponding wide applications in many fields. Herein this paper presents several methods to prepare monodisperse magnetic microspheres through a facile hydrothermal technique. The added surfactants were sodium dodecyl benzene sulfonate (SDBS), poly(vinylpyrrolidone) (PVP), trisodium citrate (TSC), and polyethylene glycol (PEG). Transmission electron microscopy (TEM) reveals the monodispersed magnetite (Fe₃O₄) microspheres with narrow size distribution can be obtained using SDBS as the surfactant. In addition, Fe₃O₄@SiO₂ was prepared by modified Stöber methods resulting in the microspheres with more smooth surface and better dispersion.

Keywords—magnetic nanomaterials; preparation; capping

I. INTRODUCTION

With the development of nano-material technology, magnetic nanoparticles had become a hot spot of scientific research. A lot of research on magnetic material had been done in the past report [1, 2]. Some most important magnetic materials, such as spinel ferrites (MFe₂O₄; M = Fe, Mn, Zn, or Co), had been widely used in electronic devices, information storage, and drug-delivery technology [3, 4]. Magnetite (Fe₃O₄) had recently been considered an ideal candidate for sensing, imaging and activity agent for antitumor therapy in biological applications [5, 6, 7]. Since the excellent magnetic properties and good application in a lot of fields, Fe₃O₄ nanoparticles with abundant resources in nature and low cost in their processing were very important magnetic materials. There were many polymerization methods to synthesize Fe₃O₄ nanoparticles, described below: precipitation method, solvothermal method, sol gel method [8], and microemulsion method [9], etc. The typical syntheses of Fe₃O₄ microspheres were carried out in a solvothermal system by modified reduction reactions between FeCl₃ and ethylene glycol. Deng et al. [7] synthesized Fe₃O₄ microspheres ranged from 200 to 800 nm via solvothermal method by the introduction of polyethylene glycol (PEG). Then, Yan et al. [1] modified the above solvothermal procedure by using the mixed

surfactants containing sodium dodecyl sulfate and polyethylene glycol, and the obtained Fe₃O₄ particles ranged from 15 to 190 nm. More recently, Bai et al. [2] reported the preparation of Fe₃O₄ spheres with diameters of 150—450 nm in the presence of oleic acid by controlling the reaction time. These studies suggested that the particle size of Fe₃O₄ nanoparticles can be well controlled by the solvothermal method in the presence of surfactants with varied reaction time. As the high surface energy was responsible for the agglomeration of Fe₃O₄ nanoparticles, it was necessary to reduce the surface energy. Xi et al. [10] had demonstrated that oleic acid, which was acted as surfactant, could lower the surface energy.

Therefore, this paper intends to study the effect of several surfactants on the synthesis of Fe₃O₄ nanoparticles. And Fe₃O₄ nanoparticles were coated by silica to obtain core-shell structured Fe₃O₄@SiO₂ with larger-diameter and chemical stability.

II. EXPERIMENTAL SECTION

A. Chemicals

Ferric chloride (FeCl₃), polyethylene glycol (PEG-4000), anhydrous sodium acetate (NaAc), ethylene glycol (EG), tetraethylorthosilicate (TEOS, 98%), absolute ethanol, concentrated ammonia solution (25-28 wt.%), trisodium citrate (TSC), poly(vinylpyrrolidone) (PVP) K30 (Mw~40000), and sodium dodecyl benzene sulfonate (SDBS) were purchased from Tianjin Guangfu Chemical Co. All chemicals were of analytical grade and used without further purification. Double distilled water was used for all experiments.

B. Synthesis of Fe₃O₄ in the Absence of Any Surfactants

Briefly, FeCl₃ (5 mmol), NaAc (43.8 mmol) were dissolved in EG (40 mL) under magnetic stirring. After stirring for 30 min, the obtained solution was transferred into a Teflon-lined stainless steel autoclave (100 mL in capacity) under 200 °C for 10 h. After cooling to room temperature, the black precipitate was collected by magnetic separation and washed thoroughly several times under ultrasound with water and ethanol, and subsequently dried under ambient condition.

C. Synthesis of Fe₃O₄ Using SDBS as Surfactant

FeCl₃ (4 mmol), SDBS (0.92 mmol), and NaAc (22.6 mmol) were dissolved in EG (32 mL) under vigorous stirring. The obtained yellow solution was then transferred and sealed into a Teflon-lined stainless-steel autoclave. The autoclave was heated at 180 °C for 12 h, and then allowed to cool to room temperature. Processing method as described above.

D. Synthesis of Fe₃O₄ in the Presence of PVP

Briefly, FeCl₃ (5 mmol), NaAc (43.8 mmol), and PVP (0.025mmol) were dissolved in EG (40 mL) with magnetic stirring. The obtained solution was then transferred into a Teflon-lined stainless steel autoclave for hydrothermal treatment at 200 °C for 20 h. Processing method as described above, the black precipitate was collected by magnetic separation and washed several times under ultrasound with water/ethanol, and then dried in air at temperature.

E. Synthesis of Fe₃O₄ Using TSC as Surfactant

Similar to section 2.2: FeCl₃ (7.22 mmol), NaAc (48.6 mmol), and TSC (1.7 mmol) were dissolved in EG (40 mL) under vigorous stirring. The obtained yellow solution was then transferred and sealed into a Teflon-lined stainless-steel autoclave. The autoclave was heated at 200 °C for 10 h, and then allowed to cool to room temperature. The products were processed in the same way as above.

F. Synthesis of Fe₃O₄ in the Presence of PEG as Surfactant

The Fe₃O₄ particles were prepared through a high-temperature hydrolysis reaction according to the method reported previously [11]. Typically, FeCl₃ (5 mmol), NaAc (43.8 mmol), PEG (0.25mmol), were dissolved in EG (40 mL) under vigorous stirring. The obtained solution was then transferred into a Teflon-lined stainless steel autoclave for hydrothermal treatment at 200 °C for 10 h, and allowed to cool to room temperature. The black precipitate was collected by magnetic separation and dealt in the same method as described above before characterization and application.

G. Preparation of Fe₃O₄@SiO₂ Microspheres

The Fe₃O₄@SiO₂ microspheres were prepared through a versatile solution sol-gel method as follows: An aqueous solution (16 mL) containing Fe₃O₄ particles (50 mg) was mixed with absolute ethanol (80 mL) in a three-neck round-bottom flask, aqueous ammonia (2 mL) by vigorous mechanical stirring for 10 min. Afterward, tetraethylorthosilicate (TEOS) (0.2 mL) was added dropwise. And the reaction proceeded for 6 hours under continuous mechanical stirring. The resultant Fe₃O₄@SiO₂ microsphere product was separated and collected with a magnet, followed by washing with double distilled water and absolute ethanol 3 times, respectively.

H. Characterization

Transmission electron microscopy (TEM) images were taken with a JEOL-1400 microscopy (Japan) operated at 100 kV. Samples for TEM were prepared on copper grids (size 200 mesh) coated with a carbon. Samples were first dispersed in ethanol and then prepared by placing a drop of a solution of the nanoparticles on a grid placed on filter paper and allowing the solvent to evaporate. The poly dispersity index (PDI) of the microspheres was calculated from the following statistical formulas: [12]

$$PDI = D_w / D_n$$
$$D_n = \frac{\sum_{i=1}^k n_i D_i}{\sum_{i=1}^k n_i}$$
$$D_w = \frac{\sum_{i=1}^k n_i D_i^4}{\sum_{i=1}^k n_i D_i^3}$$

Where PDI is the polydispersity index, D_n is the number-average diameter, D_w is the weight-average diameter, D_i is the diameter of the microspheres, and n_i is the number of microspheres. In each case, about 10-30 microspheres in the TEM image were used for the analysis.

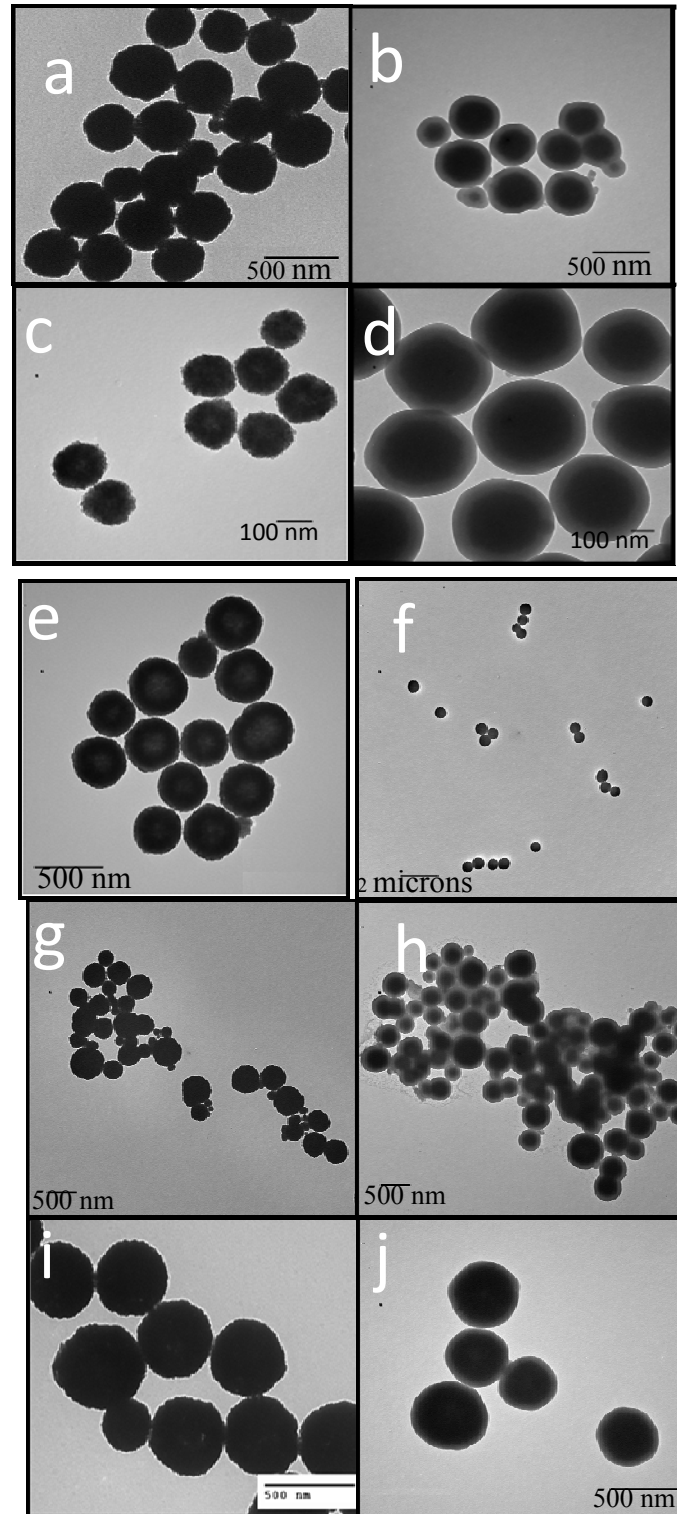


Figure 1. TEM images of (a) Fe_3O_4 -non microspheres, (c) Fe_3O_4 -SDBS microspheres, (e) Fe_3O_4 -PVP microspheres, (g) Fe_3O_4 -TSC microspheres, (i) Fe_3O_4 -PEG microspheres, (b) Fe_3O_4 @ SiO_2 -non microspheres, (d) Fe_3O_4 @ SiO_2 -SDBS microspheres, (f) Fe_3O_4 @ SiO_2 -PVP microspheres, (h) Fe_3O_4 @ SiO_2 -TSC microspheres, (j) Fe_3O_4 @ SiO_2 -PEG microspheres.

III. RESULTS AND DISCUSSION

The Fe₃O₄ microspheres with various sizes were synthesized via the slightly modified solvothermal method. Products prepared based on the above theory named as follows: Fe₃O₄-non, Fe₃O₄-SDBS, Fe₃O₄-PVP, Fe₃O₄-TSC and Fe₃O₄-PEG. The transmission electron microscopy (TEM) images of the Fe₃O₄ nanoparticles were shown in Figure 1, parts a, c, e, g and i, respectively.

The images revealed that the Fe₃O₄ microspheres were narrowly distributed with a smooth surface. When different surfactants were added, Fe₃O₄ microspheres with different size were made (Table I). The Fe₃O₄-non (Figure 1a) and Fe₃O₄-TSC (Figure 1g) showed spherical morphology with particle size of ca. 365 nm and 395 nm (Table I) though a little aggregates observed, while the Fe₃O₄-SDBS, Fe₃O₄-PVP and Fe₃O₄-PEG (Figure 1 c, e, and i) displayed much better dispersity with particle size ca. 149, 368 and 406 nm (Table I), respectively. However, careful inspection of the TEM images indicated that the surface of the Fe₃O₄ microspheres lacked smoothness. As shown in Table I, the polydispersity index (PDI) of Fe₃O₄-SDBS was 1.01, which concluded that sodium dodecyl benzene sulfonate (SDBS) could improve the dispersibility of the magnetic nanoparticles. In contrast, Fe₃O₄-TSC with a relatively high polydispersity index (PDI) 1.18 indicated that the aggregation resistance of trisodium citrate (TSC) was not very good. Overall, these as-prepared Fe₃O₄ microspheres exhibited good dispersibility in polar solvents such as water and ethanol, which favored the subsequent coating or modification with other oxides or polymers.

TABLE I. SIZE AND SIZE DISTRIBUTION OF THE Fe₃O₄ MICROSPHERES

Sample	D_n (nm)	D_w (nm)	PDI
Fe ₃ O ₄ -non	365	406	1.11
Fe ₃ O ₄ -SDBS	149	150	1.01
Fe ₃ O ₄ -PVP	368	381	1.04
Fe ₃ O ₄ -TSC	395	468	1.18
Fe ₃ O ₄ -PEG	406	439	1.08

D_n is the number-average diameter, D_w is the weight-average diameter, and PDI is the polydispersity index.

After coating the Fe₃O₄ particles with silica shells through a modified Stober process in ethanol, core-shell particles with smooth surface were synthesized. The TEM images of the Fe₃O₄@SiO₂ were shown in Figure 1, parts b, d, f, h and j, respectively. The obtained Fe₃O₄@SiO₂-SDBS microspheres exhibited better dispersion (Figure 1d), while Fe₃O₄@SiO₂-TSC exhibited the most poor dispersivity. The surface of Fe₃O₄@SiO₂ showed more slippery and better dispersion compared to Fe₃O₄ microspheres. The diameters of Fe₃O₄@SiO₂ were showed in Table II, which were increased in various degrees compared to Fe₃O₄ microspheres. And the SiO₂ shell thickness (Table II) were, in order, 20 nm, 40 nm, 30 nm, 28 nm, and 27 nm. As seen by comparing Table I and II, the polydispersity index of Fe₃O₄@SiO₂ reduced by

comparison to Fe₃O₄, which demonstrated the dispersibility of magnetic nanoparticles improved by coating a silica layer. The PDI of as-obtained Fe₃O₄@SiO₂-SDBS microspheres was 1.01, which exhibited dispersibility as well as Fe₃O₄-SDBS. While Fe₃O₄@SiO₂-non, Fe₃O₄@SiO₂-PVP and Fe₃O₄@SiO₂-PEG exhibited better dispersion than Fe₃O₄-non, Fe₃O₄-PVP, and Fe₃O₄-PEG. These results suggested that the dispersibility of magnetic nanoparticles (Fe₃O₄) could be improved by coating a layer of silica.

TABLE II. SIZE, SIZE DISTRIBUTION, AND SHELL THICKNESS OF THE Fe₃O₄@SiO₂ CORE-SHELL MICROSPHERES

Sample	D_n ^a (nm)	D_w ^a (nm)	PDI ^a	Shell thickness ^b (nm)
Fe ₃ O ₄ @SiO ₂ -non	407	430	1.05	20
Fe ₃ O ₄ @SiO ₂ -SDBS	230	232	1.01	40
Fe ₃ O ₄ @SiO ₂ -PVP	428	435	1.01	30
Fe ₃ O ₄ @SiO ₂ -TSC	450	522	1.16	28
Fe ₃ O ₄ @SiO ₂ -PEG	460	482	1.05	27

^a D_n is the number-average diameter, D_w is the weight-average diameter, and PDI is the polydispersity index. ^b The shell thickness of the core-shell was measured from the TEM images.

IV. CONCLUSIONS

In summary, a series of nearly monodispersed Fe₃O₄ microspheres with various particle sizes had been successfully synthesized via solvothermal method with different surfactants. And the Fe₃O₄@SiO₂ microspheres were prepared by the Stober method. The diameters of as-obtained Fe₃O₄ particles were about 149 nm to 406 nm. The Fe₃O₄-SDBS microspheres showed the best dispersibility. The dispersibility of Fe₃O₄ microspheres improved after coating a layer of silica. The shell thickness of Fe₃O₄@SiO₂ microspheres, were 20 nm, 40 nm, 30 nm, 28 nm, and 27 nm. Fe₃O₄@SiO₂-SDBS microspheres with smooth surface exhibited more regular spherical shape and better dispersibility. And the magnetite nanoparticles exhibited excellent stability on the silica surface. Such materials have great potential as dual-functional probes in cell imaging, and the synthesis method will also benefit the preparation of many other types of nanofunctional materials.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (NO. 21172171).

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