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Modified solvothermal synthesis of magnetic microspheres with multifunctional surfactant cetyltrimethyl ammonium bromide and directly coated mesoporous shell

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ABSTRACT

The Fe_3O_4 magnetic microspheres were prepared by a cetyltrimethyl ammonium bromide (CTAB) modified solvothermal process. Then CTAB-modified Fe_3O_4 microspheres were directly coated by mesoporous SiO_2 and γ-AlOOH shell, respectively, and the $SiO_2@Fe_3O_4$ and γ-$AlOOH@Fe_3O_4$ magnetic core–shell composites were obtained. The samples were characterized by FT-IR, XRD, Raman spectroscopy, SEM, TEM, N_2 adsorption–desorption technology, and vibrating sample magnetometer (VSM). The results indicate that CTAB molecules play the roles of capping agent, dispersant, and crystal growth oriented agent during the high-temperature solvothermal process. Thus as-prepared Fe_3O_4 microspheres are assembled by small primary nanocrystals with uniform crystal orientation, and exhibit narrow size distribution, monodispersity, and superparamagnetism with high saturation magnetization (*Ms*). The formation of Fe_3O_4 microspheres combines oriented attachment and Ostwald ripening mechanisms. Furthermore, the adsorbed CTAB molecules can serve as nucleation seeds for precipitation of SiO_2 and γ-AlOOH, and as templates for growth of mesoporous SiO_2. In $SiO_2@Fe_3O_4$ the mesoporous SiO_2 shell presents short-range ordered pores with mean pore size of 2.1 nm. The shell of γ-$AlOOH@Fe_3O_4$ is composed of many irregular γ-AlOOH nanosheets with thickness of 3.0–5.0 nm. The BET surface areas of $SiO_2@Fe_3O_4$ and γ-$AlOOH@Fe_3O_4$ reach up to 441 m^2/g and 289 m^2/g, respectively.

1. Introduction

Magnetic nanoparticles, such as metal, alloy, ferrite and ferrate, have attracted much attention due to their potential applications in information storage, magnetic resonance imaging (MRI), catalysis, bioprocess, drug delivery, and so on [1,2]. Among these magnetic nanomaterials, magnetite (Fe_3O_4) nanoparticles have been widely studied because of their excellent superparamagnetism and biocompatibility [3,4]. During the past decade, Fe_3O_4 nanoparticles have been prepared by various approaches such as coprecipitation [5], micelle synthesis [6], sol–gel method [7], thermal decomposition [8,9], and solvothermal synthesis [10–12]. Among these synthetic methods, the solvothermal process is superior to others in controllable synthesis, including controlling the primary nanocrystals and secondary aggregates [10], which are closely related to the further applications of Fe_3O_4 particles.

Recently, some modified solvothermal methods were applied to fabricate monodispersed Fe_3O_4 nanoparticles with secondary structure because of their outstanding application values in magnetic separation and carrier [2,4]. Generally, using all kinds of multifunctional surfactants during the solvothermal process was the most commonly and effectively modified method. For instance, Deng et al. [13] had successfully prepared monodispersed Fe_3O_4 microspheres using polyethylene glycol (PEG) as protective agent, and the diameter of microspheres varied from 200 to 800 nm. Ge et al. [14] had fabricated Fe_3O_4 particles with controllable diameter using polyacrylic acid (PAA) as surfactant. Similarly, nanoporous and monodispersed Fe_3O_4 spherical aggregates with high surface area and oriented attachment structure had been successfully prepared in the presence of polyvinylpyrrolidone (PVP) [15]. In addition, some other surfactants, such as oleic acid and sodium dodecyl sulfate (SDS) [16–20], were used as modifiers during the solvothermal preparation of monodispersed Fe_3O_4 particles. However, the purpose of using these surfactants was only to obtain the superparamagnetism by reducing the size of Fe_3O_4 nanocrystals or improve the monodispersion of secondary aggregates. The multifunctionality of surfactants had not been displayed. Furthermore, it should be noted that those aforementioned Fe_3O_4 particles, obtained by surfactant-modified solvothermal methods, usually could not be directly coated by inorganic mesoporous materials to further synthesize magnetic core–shell mesostructured composites [2,21]. In recent years, these core–shell mesostructured composites were widely applied as catalyst supports, drug/gene/RNA delivery carriers, and water treatment adsorbents due to their high thermal and chemical stability, favorable biocompatibility and superparamagnetism, simple functionality, high available surface area, and large pore volume [21,22]. In general, an additional pretreatment or precoating to the Fe_3O_4 particles was

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indispensable, making the preparation of magnetic core–shell mesostructured composites complex. Therefore, it was very necessary to find a new multifunctional surfactant which could simultaneously contribute to modifying the solvothermal synthesis of Fe_3O_4 particles and simplifying the further synthesis of magnetic core–shell mesostructured composites.

Cetyltrimethyl ammonium bromide (CTAB), a kind of common cationic surfactant, was widely used for preparing noble metal nanoparticles [23] and transition metal oxides [24–26] due to its good solvent compatibility and thermal stability. Becker et al. [23] had synthesized Au nanorods with controllable size and shape using CTAB as surfactant. Similarly, PbO_2 and Pb_3O_4 single-crystalline nanorods were obtained in the presence of CTAB [25]. In these cases, the CTAB molecules played the roles of capping agent, dispersant, crystal growth oriented agent and/or surface modifier. Moreover, CTAB itself was a good template for preparation of mesoporous molecule sieves, such as MCM-41 and MCM-48 [27]. Hence, we conceived that CTAB should be a great multifunctional modifier for the solvothermal preparation of Fe_3O_4 particles. On the one hand, the grain size of Fe_3O_4 nanocrystals might be reduced to achieve superparamagnetism and the crystal growth of that might be enhanced because of the capping and crystal growth oriented functions of CTAB; on the other hand, the dispersity and stability of the Fe_3O_4 particles would be improved greatly. What's more, without any other templates and pretreatments, these CTAB-modified Fe_3O_4 particles could be used conveniently for preparation of magnetic core–shell mesostructured composites.

In this study, we report, for the first time, a CTAB-modified solvothermal synthesis of monodispersed Fe_3O_4 microspheres with narrow size distribution (230–250 nm) and high *Ms* value (86.3 emu/g). The influences of initial concentration of CTAB and preparation time to the structural properties of Fe_3O_4 microspheres were investigated systematically. The roles of CTAB during the solvothermal process were discussed and the formation mechanism of monodispersed Fe_3O_4 microspheres was presented. Furthermore, as-prepared CTAB-modified Fe_3O_4 microspheres were facilely coated by mesoporous SiO_2 and γ-AlOOH without any other additional pretreatments and templates, and two kinds of magnetic core–shell mesostructured composites, SiO_2@Fe_3O_4 and γ-AlOOH@Fe_3O_4, were prepared.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), cetyltrimethyl ammonium bromide (CTAB), anhydrous sodium acetate (NaAc), glycol, tetraethoxysilane (TEOS), aluminum isopropoxide (AIP), ammonia aqueous solution (28 wt.%), and absolute ethyl alcohol were of analytical grade and used without further purification. Deionized water was used throughout the experiments.

2.2. Synthesis of Fe_3O_4 microspheres

Briefly, 10.8 g of $FeCl_3 \cdot 6H_2O$, 28.8 g of NaAc, and a certain amount of CTAB were dissolved in 400 mL of glycol under stirring. The obtained homogeneous yellow solution was transferred to a Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated at 200 °C under 400 rpm speed. After heating for a certain time, the autoclave was naturally cooled to room temperature. The obtained black magnetite particles were separated with a permanent magnet, washed with ethanol 6 times, and dried in vacuum at 60 °C for 24 h. When the initial concentration of CTAB (C_{CTAB}) was varied from 0 mol/L to 0.136 mol/L, the autoclave was heated at 200 °C for 12 h. Similarly, the initial C_{CTAB} was kept at 0.102 mol/L as the autoclave was heated at 200 °C for 2, 6, 12, and 24 h, respectively.

2.3. Synthesis of SiO_2@Fe_3O_4 composites

0.1 g of Fe_3O_4 microspheres was dispersed into the mixture solution of 60 mL of ethanol, 80 mL of deionized water, and 1.0 mL of concentrated ammonia aqueous solution (28 wt.%). After this, the mixture solution was homogenized by ultrasonication for 30 min to form a uniform dispersion. Subsequently, 0.25 mL of TEOS was added dropwise into the solution with vigorous stirring. After stirring at room temperature for 6 h, the product was separated with a permanent magnet, washed with deionized water 3 times, and dried in vacuum at 50 °C for 12 h.

2.4. Synthesis of γ-AlOOH@Fe_3O_4 composites

0.1 g of Fe_3O_4 microspheres was dispersed in 60 mL, 0.016 mol/L of AIP ethanol solution. After ultrasonication for 30 min, the above solution was transferred to a three neck flask and stirred overnight at 45 °C to allow a saturated adsorption of AIP on the surface of Fe_3O_4 particles. After that, ethanol/water (5/1, v/v, 50 mL) was added into the solution for 1 h under stirring. Later, the mixture solution was transferred to a Teflon-sealed autoclave and kept at 80 °C for 20 h. The obtained particles were separated with a permanent magnet, washed several times with ethanol, and then dried in vacuum at 50 °C for 12 h.

2.5. Characterization of samples

Fourier transform infrared (FT-IR) spectra were obtained on a Bruker (TENSOR-27) spectrophotometer by using a KBr pellet method. The X-ray diffraction (XRD) patterns were collected on a D/Max 2500 VB2+/PC diffractometer with Cu Kα irradiation ($\lambda = 1.5418$ Å, 200 kV, 50 mA) in the range of 2θ value between 10° and 90°. The Raman spectra were recorded at the room temperature on a HORIBA (LabRAM ARAMIS) Raman spectrometer with an argon-ion laser at an excitation wavelength of 532 nm. Transmission electron microscopy (TEM) and high-resolution (HR) TEM were performed on a JEOL (JEM-2100) transmission electron microscope operated at 200 kV accelerating voltage. Scanning electron microscopy (SEM) images were taken on a Zeiss (SUPRA-55) field emission scanning electron microscope and the energy-dispersive X-ray (EDX) measurement was carried out on an Oxford Instruments INCAx-act EDX detector using a 15 kV electron beam and 60 s acquisition time. The N_2 adsorption–desorption analysis was tested on an ASAP 2020M automatic specific surface area and aperture analyzer. Magnetic properties of the samples were measured using a vibration sample magnetometer (VSM; Lake Shore Model 7400) under magnetic fields up to 20 kOe.

3. Results and discussion

3.1. Structural and textural features of Fe_3O_4 particles obtained at different initial C_{CTAB}

In order to characterize the presence of CTAB molecules on the surface of products, FT-IR characterization was used. Typical FT-IR spectra of samples in the range of 4000–400 cm^{-1} are shown in Fig. 1. All samples exhibit the broad strong peaks at about 580 cm^{-1}, which are related to the Fe–O stretching mode of the magnetite (Fe_3O_4) [3,19]. In the presence of CTAB (Fig. 1b–e), the peaks in the region of 2800–3200 cm^{-1} can be attributed to the CTAB molecules, corresponding to the asymmetric (2918 cm^{-1}) and symmetric (2846 cm^{-1}) stretching vibrations of $C-CH_2$ in the methylene chains [28]. Because cationic surfactant CTAB can ionize completely into CTA^+ cations and Br^- anions in polar solvent glycol, we believe that CTA^+ cations with a long-chain hydrophobic tail adsorb on the surface of particles through the electrostatic attraction interaction between $-N(CH_3)_3^+$ in CTA^+ and surface Fe-OH groups on iron oxides [1,2]. Moreover, with the C_{CTAB} increasing from 0.034 mol/L to 0.102 mol/L, the intensity of characteristic peaks in the region of