Preparation of Fe$_3$O$_4$ Spherical Nanoporous Particles Facilitated by Polyethylene Glycol 4000

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Abstract Much interest has been attracted to the magnetic materials with porous structure because of their unique properties and potential applications. In this report, Fe$_3$O$_4$ nanoporous particles assembled from small Fe$_3$O$_4$ nanoparticles have been prepared by thermal decomposition of iron acetylacetonate in the presence of polyethylene glycol 4000. The size of the spherical nanoporous particles is 100–200 nm. Surface area measurement shows that these Fe$_3$O$_4$ nanoporous particles have a high surface area of 87.5 m$^2$/g. Magnetization measurement and Mössbauer spectrum indicate that these particles are nearly superparamagnetic at room temperature. It is found that the morphology of the products is greatly influenced by polyethylene glycol concentration and the polymerization degree of polyethylene glycol. Polyethylene glycol molecules are believed to facilitate the formation of the spherical assembly.

Keywords Nanoporous · Magnetite · Polyethylene glycol · Transmission electron microscopy · Magnetic measurement

Introduction

In the past decade, a variety of methods have been developed to form highly structure-controlled materials of functionalized metal, semiconductor, and copolymer nanoparticles on the nano- or microscale. As a versatile kind of material, magnetite has attracted much attention in recent years. Magnetite is a common ferrite that has a cubic inverse spinel structure [1]. The compound has exhibited unique electric and magnetic properties based on the transfer of electrons between Fe$^{2+}$ and Fe$^{3+}$ in the octahedral sites. Besides having practical applications in industry such as in ferrofluids [2, 3], catalysis [4], ceramics [5], and energy storage [6], properly coated or surface-modified magnetite nanoparticles can be applied in clinical diagnosis and used as a medicine transporter [7–10].

Magnetite nanoparticles are usually synthesized in aqueous solutions [11, 12] via coprecipitation of Fe$^{2+}$ and Fe$^{3+}$ ions by a base. During these reactions, several parameters have to be controlled carefully, including pH value, mixing way of raw materials, temperature, nature, and concentration of anions. Other synthesis methods such as polyol-mediated sol–gel [13] and sonochemical [14] are also proposed. To overcome the limitations introduced by aqueous precipitation reactions, several groups have developed nonaqueous approaches for the production of magnetite [15–18]. Monodispersed magnetite nanoparticles with tunable size can be produced by these nonaqueous approaches.

Mesoporous Fe$_3$O$_4$ nanostructures with strong enough magnetization strength are especially interesting for high capacity drug loading and targeted drug delivery as well as other biomedical and catalytic applications. To our knowledge, several researches reported the successful preparations of mesoporous Fe$_3$O$_4$. Zhu et al. [19] successfully prepared nanoporous and monodispersed Fe$_3$O$_4$ aggregated spheres by hydrothermal method. Hou et al. [20] reported a route to assemble magnetic particles into size-controlled 3D spheres with cyclodextrins as surfactants by solvothermal method. Here, we report a new-route preparation of Fe$_3$O$_4$ nanoporous particles assembled from the small Fe$_3$O$_4$ nanoparticles by thermal decomposition of iron acetylacetonate in the presence of polyethylene glycol 4000.
acetylacetonate [Fe(acac)₃]. Polyethylene glycol 4000 (PEG-4000), an easily available chemical, was introduced in the reactions. The effect of PEG on the morphology of products is investigated.

Experimental

Chemicals

[Fe(acac)₃] and octadecyl amine were purchased from Alfa Aesar Company. PEG 4000, oleic acid, and diphenyl ether were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without further treatment.

Synthesis of Fe₃O₄ Spherical Nanoporous Particles

The synthesis was carried out using airless procedures. The synthesis of magnetic Fe₃O₄ spherical nanoporous particles was developed from previous method [16]. In a typical synthesis, Fe(acac)₃ (2 mmol), PEG 4000 (6 mmol), oleic acid (6 mmol), and octadecyl amine (6 mmol) were mixed into 40 mL of diphenyl ether in a N₂ atmosphere under vigorous stirring. The mixture was stirred at 70 °C until PEG 4000 melted, then heated to 265 °C, and refluxed for 30 min. The product was black. The black powder was collected with a permanent magnet, then redispersed in ethanol by supersonic for 15 min. The washing process was repeated three times. At last, the powder was dried at 40 °C in vacuum.

Characterization

X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku D/max 2550V diffractometer equipped with a Cu KR (1.5418 Å) X-ray source. The morphology and chemical composition of the products were examined by transmission electron microscopy (TEM, JEM-2100F). Samples were dispersed in ethanol by supersonic for 15 min and then dropped onto carbon film-coated grids. Magnetization measurements were taken with a vibrating sample magnetometer (VSM) at room temperature. The surface area of the products was measured by nitrogen adsorption–desorption isotherms using the Brunauer–Emmett–Teller (BET) method (Micromeritics Tristar3000). The samples were degassed under vacuum at room temperature before measurements were taken. Mössbauer spectrum of the product at room temperature was recorded on a Wissel spectrometer with the ⁵⁷Co in Pd matrix as the source moving in constant-acceleration regime. Hyperfine interaction parameters were derived from the Mössbauer spectrum using a least-squares method. The spectrometer was calibrated using a standard 25-μm z-Fe foil.

Results and Discussion

The crystalline structure of the black product was characterized by the powder XRD technique. As shown in Fig. 1, the product displays several relatively strong diffraction peaks in the 2θ region of 20°–70°. These strong peaks are at the 2θ angles of 30.1° (d = 2.967 Å), 35.4° (d = 2.532 Å), 43.0° (d = 2.101 Å), 53.4° (d = 1.714 Å), 56.9° (d = 1.616 Å), and 62.5° (d = 1.484 Å). The pattern can be easily indexed to Fe₃O₄ (ICPDS 19-629) according to the diffraction peak positions and relative intensities, which confirms the magnetite structure of this material. The average size of the Fe₃O₄ nanoparticles deduced from Sherrer’s formula is about 9.6 nm, which is consistent with the result obtained from the TEM observation of the same sample.

The morphology and structures of the black Fe₃O₄ products were investigated by TEM. Figure 2a shows a representative TEM image of the products. It can be found that the Fe₃O₄ product is nearly spherical, and the sizes of the spherical particles are 100–200 nm. The structural details are shown in Fig. 2b, d. It can be observed clearly from Fig. 2b that large Fe₃O₄ spherical particles have rough surfaces and are composed of many small Fe₃O₄ nanoparticles. It demonstrates that the small Fe₃O₄ nanoparticles have self-assembled into Fe₃O₄ spherical aggregated particles. The size of these small Fe₃O₄ nanoparticles is less than 10 nm. The size values of the small Fe₃O₄ nanoparticles got from XRD and TEM are very close. It also can be seen that the disordered pores exist among the primary nanoparticles within the spherical assembly. Therefore, these assembled particles have a nanoporous structure. Energy-dispersive X-ray spectroscopy (EDS)
spectrum (Fig. 2c) shows the expected presence of Fe and O. Element analysis (inset table in Fig. 2c) shows the ratio of Fe to O is very close to the standard value of Fe$_3$O$_4$. High-resolution transmission electron microscopy (HRTEM) analysis provides more detailed structural information. A representative HRTEM image took from the edge of an assembled particle is shown in Fig. 2d. The parallel lattice fringes across almost all the primary nanoparticles are clearly visible. The lattice planes of (2 2 0) (0.297 nm), (3 1 1) (0.254 nm), and (4 0 0) (0.210 nm) for Fe$_3$O$_4$ are easily distinguished. It should be accentuated that these samples were kept at least 2 weeks and underwent supersonic for about 1 h discontinuously in the washing process before TEM measurement. To further investigate the stability of the assemblies, the porous sample was dispersed by supersonic for one more hour. Figure 2e shows the morphology of the sample after the supersonic treatment. It is clear that the morphology maintained without breakdown into constituent Fe$_3$O$_4$ nanoparticles. So the morphology is considered to be stable.
Nitrogen adsorption–desorption measurements were carried out for Fe$_3$O$_4$ spherical assemblies (Fig. 3). The particles display a characteristic hysteresis in the desorption isotherm at relative pressure ($P/P_0$) in the range 0.4–1.0. This behavior is indicative of mesoporous structure of the tested sample [21–23]. The pore size distribution (Fig. 3 inset) indicates that most of the nanopores is less than 4 nm in the sample. The surface area of the Fe$_3$O$_4$ assemblies is 87.5 m$^2$/g calculated from the linear part of the BET plot. The single-point adsorption total volume at $P/P_0 = 0.978$ is 0.324 cm$^3$/g. The high BET surface area and large pore volume support the fact that the Fe$_3$O$_4$ assembled particles have a nanoporous structure.

Figure 4 shows the magnetization of Fe$_3$O$_4$ spherical nanoporous particles at room temperature (300 K). The curves obtained at 300 K are nearly superimposable as the field is cycled between $-5$ and 5 kOe. The magnetic remanence and coercivity of Fe$_3$O$_4$ spherical nanoporous particles are 1.0 emu/g and 1.2 Oe. The curves may imply the superparamagnetic behavior and the nanoscale dimensions of the particles [24, 25]. The magnetization saturation of product is 56.4 emu/g. It has been reported that the magnetic Fe$_3$O$_4$ particles exhibit superparamagnetic behavior when the particle size decreases to below a critical value, generally around 10 nm, and the magnetization saturation values of Fe$_3$O$_4$ of several nanometers are usually low due to the small size.

The room-temperature Mössbauer spectrum of Fe$_3$O$_4$ spherical nanoporous particles is shown in Fig. 5 in the absence of an external magnetic field. The bulk phase Mössbauer spectrum of Fe$_3$O$_4$ is composed of two sets of magnetic sextets at room temperature [26]. The spectrum of our sample is composed of one doublet and two broad sextets. The values of hyperfine parameters are shown in Table 1. The two broad sextets correspond to two sets of Fe ions located in octahedron and tetrahedron sites of spinel-structured Fe$_3$O$_4$ according to the isomer shift and quadrupole splitting [26]. The values of hyperfine field are much smaller than the values of bulk material due to the small nanoparticle size of the sample. When the size of Fe$_3$O$_4$ reduces to less than 10 nm, the particles exhibit the superparamagnetic behavior for the quantum size effect. In Mössbauer spectrum, two sets of magnetic sextets change into superparamagnetic relaxation doublet [27–29]. The large doublet of the sample possesses 73.1% area of the spectrum, which indicates the superparamagnetic behavior of most particles at room temperature. This result is consistent with magnetization measurement of low remanence and coercivity. Superparamagnetic behavior is a character of small magnetic nanoparticles (usually <10 nm).
nearly superparamagnetic behaviors of Fe₃O₄ spherical nanoparticles in Mössbauer spectrum and magnetization measurements at room temperature further confirm that these spherical particles are assemblies of small primary Fe₃O₄ nanoparticles.

In order to investigate the formation process of such Fe₃O₄ spherical assemblies, the products were collected when the reaction solutions were heated for different time periods at 265 °C. Their structures were investigated by TEM. As shown in Fig. 6, when a sample was heated for 10 min at 265 °C, Fe₃O₄ nanoparticles were formed, but they did not self-assemble (Fig. 6a). When heating for 20 min, the small spherical assemblies were partly formed. They were structurally loose, and some dispersed particles remained (Fig. 6b). When the sample was heated at 265 °C for 30 min, all Fe₃O₄ nanoparticles were self-assembled into the spherical particles (Fig. 6c). When the heating time prolonged to 1 h, spherical assemblies still appeared in the sample without obvious change in shape and dimension (Fig. 6d).

Samples of different PEG 4000 amount were also prepared for comparison. The amount of PEG 4000 was found to be effective to the morphology of samples. When PEG 4000 amount reduced to 2 mmol, particles in the sample heated at 265 °C for 30 min were nearly monodisperse with the size of about 8 nm (Fig. 7a). When the heating time prolonged to 1 h, the dispersion of particle was not so good as the sample heated for 30 min, but no obvious

| Fitted spectra | Hyperfine field (KOE) | Isomer shift (mm s⁻¹) | Quadrupole splitting (mm s⁻¹) | Line width (mm s⁻¹) | Area (%) |
|----------------|-----------------------|-----------------------|------------------------------|--------------------|---------|
| Doublet        | 0.35                  | 0.74                  | 0.82                         | 73.1               |
| Sextet1        | 424.35                | 0.38                  | 0.02                         | 1.47               | 15.7    |
| Sextet2        | 218.24                | 0.61                  | 0.01                         | 1.13               | 11.2    |

Fig. 6 TEM images of Fe₃O₄ samples of different heating time: a 10 min; b 20 min; c 30 min; and d 1 h
tendency to form assembled sphere was detected (Fig. 7b). When PEG 4000 amount increased to 4 mmol, particles began to assemble (Fig. 7c). However, the assemblies’ morphology was rough, and disperse particles still existed. The morphology of products prepared using different polymerization degree of PEG was also studied. PEG 2000 and 6000 were chosen. The preparing conditions of two samples were the same as the sample’s in Fig. 2a. The morphologies of the two samples were shown in Fig. 8. Figure 8a is the sample prepared using PEG 2000. We can see from the figure that most of the small particles were dispersed. Only a few particles assembled, and the morphology of them were not so regular. Big spheres emerged in the sample prepared using PEG 6000 (Fig. 8b). These spheres were about 600 nm, much bigger than the particles prepared using PEG 4000. They turned out to be solid investigated from the higher resolution TEM image (Fig. 8c). The morphology of samples prepared using PEG of different polymerization was so various. It is an interesting result that porous structure can be obtained only using PEG 4000 under the same condition.

From these results, the use of PEG 4000 is the key in preparing a sphere-like assembly. When the PEG 4000 amount decreases to 2 mmol, spherical assembly is hard to form even if the heating is prolonged. When the PEG 4000 amount increases to 6 mmol, the particles were from dispersed to assembled as the heating prolonged. Therefore, on the one hand, PEG 4000 prevents the single particle from growing larger by coating on the particle surface. On the other hand, intermolecular cross-link among long chains of PEG 4000 is beneficial to the fabrication of assemblies. So, PEG 4000 may act as a “bridge” among original particles. The effect of PEG 4000 concentration (represented by [PEG]) on the morphology of products is shown in Scheme 1. When [PEG] is low, the TEM image shows that the uniform Fe₃O₄ nanoparticles about 8 nm are obtained. These nanoparticles are well-separated due to the PEG 4000 coating on their surfaces, as well as amine and acid, reducing their tendency to agglomerate. This result is consistent with recent reports [30] suggesting that Fe₃O₄ nanoparticles do not assemble in the presence of a low concentration of polymer. The increase in [PEG] leads to more surface coating. The PEG 4000 molecules on surfaces entangle each other in high [PEG] forming network structure [31, 32]. Further, the spherical particles form together with Fe₃O₄ nanoparticles due to the self-assembly
ability of PEG 4000. The assembly results in the nanoporous structure of product. The high enough surface area of Fe₃O₄ sphere nanoporous particles promises potential applications in chemical industry. The possible reasons are considered why PEG 2000 and PEG 6000 do not lead to the porous structure. The final temperature (265 °C) nearly reaches the boiled temperature of PEG 2000. The reduction of PEG 2000 concentration caused by quick evaporation may be a reason for the failure of porous structure’s fabrication. Decreasing the reaction temperature can be a method to reduce the evaporation. However, once the reaction temperature is below 250 °C, the yield of products sharply decreases. Higher polymerization degree means that PEG 6000 has longer flexural chain than PEG 4000, which can lead to the more intermolecular cross-link, facilitating the bigger assemblies. Whereas, the product prepared using PEG 6000 is solid instead of porous. Further research is needed to find out the exact reasons for the interesting result of PEG 6000.

Conclusions

In summary, the Fe₃O₄ nanoporous particles are synthesized in the presence of polymer PEG 4000 by thermal decomposition of iron acetylacetonate. The morphology of product can be tuned by the amount of PEG 4000. When the concentration of PEG 4000 is decreased, monodispersed Fe₃O₄ nanoparticles around 8 nm are produced. Particles tend to assemble as the PEG 4000 amount increase, and last form spherical nanoporous particles. The size of the spherical nanoporous particles is 100–200 nm. BET measurement shows these Fe₃O₄ nanoporous particles have a high surface area of 87.5 m²/g and a number of porous less than 4 nm. The saturation magnetization of nanoporous particles is 56.4 emu/g. Magnetization measurement and Mössbauer spectrum indicate that these particles are nearly superparamagnetic at room temperature, which confirms that these spherical particles are assembly of small monodisperse Fe₃O₄ nanoparticles. Moreover, polymerization degree of PEG also has great influence on the morphology of the product. We believe that these Fe₃O₄ spherical nanoporous particles will be promising materials for applications in advanced magnetic materials.

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