Synthesis of MnFe$_2$O$_4$ hollow microspheres via a sacrificial templates approach

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Abstract. Manganese ferrite (MnFe$_2$O$_4$) hollow microspheres were synthesized through a sacrificial template approach using manganese carbonate (MnCO$_3$) microspheres as sacrificial templates. Different from the literatures, the synthesis of MnFe$_2$O$_4$ hollow spheres was achieved through a one-pot hydrothermal process without subsequent calcination process. The temperature and reaction time of the hydrothermal process were set to be 180 ℃ and 8 h. The formation mechanism of the MnFe$_2$O$_4$ hollow microspheres was also investigated. Results indicate that the average diameter of the as-synthesized MnFe$_2$O$_4$ hollow microspheres is 1.2 μm. The shells of the hollow microspheres are composed of nanoparticles. During hydrothermal process, Mn$^{2+}$ ions diffused outward and resulted in shell materials of MnFe$_2$O$_4$, thus MnCO$_3$ templates were consumed and MnFe$_2$O$_4$ hollow microspheres were obtained.

1. Introduction

Magnetic hollow structured ferrites are very attractive due to their well-defined interior voids, low density, large surface area, stability in fluids, and surface permeability. These properties make them much suitable for microencapsulation, drug delivery, magnetic separation [1-3], etc. As an important category of magnetic hollow structured ferrites, spinel structured ferrites (MFe$_2$O$_4$, M =Zn, Mg, Co, Ni, Cd) hollow spheres have been reported to be synthesized through a two-steps template method [4, 5], where precursors of MFe$_2$O$_4$ are then deposited on the surfaces of the templates to form core-shell structures that will be subsequently calcinated to remove the templates and obtain hollow microspheres. Besides the above method, sacrificial template approach is a one-pot template method for hollow structure synthesis, where the template is actually one of the reactants of the synthesis reaction for shell materials and will be consumed in the process [6]. However, the synthesis of MnFe$_2$O$_4$ hollow microspheres via a sacrificial template approach in wet chemistry systems is seldom reported. So it would be interesting to apply sacrificial template approach to the synthesis of MnFe$_2$O$_4$ hollow microspheres.

Herein, we report the synthesis of MnFe$_2$O$_4$ hollow microspheres via a sacrificial templates approach using MnCO$_3$ microspheres as sacrificial templates. It will be demonstrated that MnCO$_3$ templates can be consumed and transformed to MnFe$_2$O$_4$ shell materials during hydrothermal process,
thus the hollow microspheres are obtained. MnFe$_2$O$_4$ is chosen because it is one of the most important magnetic materials and is widely used in electronic applications [7], as contrast-enhancement agents in magnetic resonance imaging (MRI) technology [8], and as magnetic recording media [9], etc.

2. Experimental

All chemicals involved in the experiment were analytical grade and used without further purification.

Preparation of MnCO$_3$ Templates: The typical procedure to prepare the template of MnCO$_3$ microspheres can be referred to Fei’s work in the literature [10]. NH$_4$HCO$_3$ (10 mmol) and MnSO$_4$·H$_2$O (1 mmol) were dissolved respectively in 70 mL water. Ethanol (21 mL) was then added to the MnSO$_4$ solution with stirring. When the two solutions were mixed and maintained at room temperature for 3 h, the MnCO$_3$ particles were precipitated and suspended in this water-ethanol mixed solvent. After being separated from the reaction mixture by vacuum filtration, washed several times with distilled water and dried at room temperature in a vacuum oven (ca. 0.1 MPa) for 6 h, the template of MnCO$_3$ microspheres were obtained.

Preparation of MnFe$_2$O$_4$ hollow spheres: In a typical procedure, appropriate FeSO$_4$·7H$_2$O (2 mmol) was dissolved in water (40 mL), and then the as-prepared MnCO$_3$ particles were dispersed in the FeSO$_4$ solution by ultrasonic treatment for 5 min. Then the obtained mixture were transferred into 60 mL stainless steel autoclave and heated at 180 °C for 8 h, followed by cooling to room temperature naturally. After the hydrothermal reaction, the black solid was centrifuged, and sequentially washed with distilled water repeatedly to remove the residual reactant. Then, the product was dried in air at 60 °C for 6 h before characterization.

Characterizations of samples: The XRD patterns were recorded on a powder X-ray diffractometer (Rigaku D/max-2500/PC) equipped with Cu K$_{\alpha}$ radiation source ($\lambda$=1.5406 Å) at a step width of 0.02°. The transmission electron microscopy (TEM) images were captured on a JEM-2000EX transmission electron microscope. The scanning electron microscopy (SEM) images were taken with a JEOL-JSM6700F scanning electron microscope.

3. Results and discussion

The X-ray diffraction (XRD) pattern of the as-synthesized MnCO$_3$ microspheres (see Figure 1a) shows sharp diffractions characteristic of simple cubic MnCO$_3$ (JCPDS card No. 44-1472). No other impurities were detected in the synthesized products. SEM image shows that the MnCO$_3$ crystals have a solid spherical morphology (Figure 1b). The sizes of the microspheres, typically ranges from 1.2 to 1.7 μm, with an average size of about 1.4 μm and standard deviation of 0.3 μm. High magnification image of a single microsphere (the insert in Figure 1b) shows that the surface of the as-prepared MnCO$_3$ microsphere is composed of triangular edges and corners. A BET specific area of 6.7 m$^2$/g has been measured, suggesting that the MnCO$_3$ microspheres are solid inside.

![Figure 1. XRD patterns (a) and SEM images (b) of the MnCO3 templates. The inset in (b) is a high magnifications TEM image of a single microsphere.](image_url)
The X-ray diffraction pattern of the resulted products after hydrothermal treatment is presented as Figure 2a. All diffraction peaks can be readily indexed to cubic MnFe$_2$O$_4$ (JCPDS card No.73-1964) without impurity phases detected. SEM image (Figure 2b) of the as-synthesized MnFe$_2$O$_4$ shows that the sample is composed of microspheres with an average diameter of about 1.2 $\mu$m. A high magnification SEM image of the microsphere surface inserted in Figure 2b shows that the microsphere is composed of nanoparticles with average particles size of about 70 nm. TEM image (Figure 2c) reveals the hollow structure of the microspheres. The hollow structure can also be confirmed by the SEM image of a broken hollow sphere inserted in Figure 2c. It can be found from the cross section that the shell of the hollow microsphere is composed of nanoparticles with size typically ranges from 50 nm to 80 nm. The results indicate that MnFe$_2$O$_4$ hollow microspheres have been synthesized. The magnetic hysteresis curve of the MnFe$_2$O$_4$ hollow microspheres (Figure 2d) shows ferromagnetic behavior with saturation magnetization (Ms), remanent magnetization (Mr), and coercivity (Hc) values of the MnFe$_2$O$_4$ hollow microspheres are 33.96 emu/g, 3.38 emu/g and 85 Oe, respectively (based on the magnified image of the central part of Figure 2d). The relatively lower Ms value of the MnFe$_2$O$_4$ hollow microspheres can be contributed to the small grain size of the nanoparticles constitute the hollow microspheres.

![Figure 2. XRD pattern (a), SEM images (b), TEM images (c) and Magnetic hysteresis curve (d) of the MnFe2O4 hollow microsphere. The scale bars in the two insets stand for 1 $\mu$m.](image)

To study the phase and structure transitions from MnCO$_3$ microsphere to MnFe$_2$O$_4$ hollow microsphere, products obtained at different stages of the hydrothermal process were collected and subjected to XRD and TEM analysis. Figure 3 presents the XRD patterns and TEM images of microspheres obtained at different stages of the hydrothermal process. The microspheres obtained at 5 h are mainly composed of solid cores and loose outer layers. The corresponding XRD pattern reveals a combination of MnCO$_3$ and MnFe$_2$O$_4$. It can be deduced that the solid cores are MnCO$_3$ templates and the loose outer layers are newly formed MnFe$_2$O$_4$ that are transformed from the MnCO$_3$ templates. In this case, an interface between MnCO$_3$ template and MnFe$_2$O$_4$ outer layer existed in the microsphere. Driven by the concentration gradient, Mn$^{2+}$ ions diffused outward and Fe$^{3+}$ ions diffused inward. Reactions occurred at the interface and resulted in MnFe$_2$O$_4$ shell materials. The mechanism details can be proposed as follow.

When dissolved in water, FeSO$_4$ will undergo oxidation and hydrolysis reactions which can be described as equation (1). Oxygen in equation (1) comes from the dissolved O$_2$ in water. Then Fe$^{3+}$ resulted from reaction (1) will partly undergo further hydrolysis reaction (equation (2)) resulting in slightly decrease of pH value. It should be noted that part of Fe$^{2+}$ in the present work might undergo reaction (1) and even reaction (2) before hydrothermal treatment, as the solution was found to have turned yellow before transferred into the autoclave. The rest of Fe$^{2+}$ might be transformed to Fe$^{3+}$ during hydrothermal process. As pH value decreased at the beginning of hydrothermal process, MnCO$_3$ dissolved according to reaction (3). However, reaction (3) occurred at very low speed and
only on the surface of the MnCO₃ templates, because the pH value would not be very low in the present experiment. In fact, the pH value of the resulted mixture after hydrothermal process was measured to be around 4.0. The speed of reaction (3) was so low that the resulted Mn²⁺ could not diffuse from the surface of the MnCO₃ templates before reacted with Fe³⁺ to form MnFe₂O₄ (reaction (4)) at elevated temperature and pressure (saturated vapor pressure of water at 180 °C is about 1.0 MPa). It should be emphasized that reaction (4) can only occur at elevated temperature and pressure. Under ambient conditions, precursors (frequently complex hydroxide) will be formed instead, and then subsequent calcinations are required to get MnFe₂O₄. The driven force of reaction (4) comes from the elevated temperature and pressure that favour the formation of MnFe₂O₄ because MnFe₂O₄ is more stable than the precursors at elevated temperature and pressure. After the outmost layer of MnCO₃ templates had been transformed to MnFe₂O₄, reaction (3) and subsequently reaction (4) continued towards the centre of MnCO₃ templates. It should be noted that MnFe₂O₄ was formed as nanoparticles with tunnel in between, thus ions and molecules could diffuse in and out. During this period, the early formed Fe(OH)₃ dissolved at lower pH value (around 4.0), as reaction (5) describes. Fe³⁺ resulted from reaction (5) joined reaction (4) and was then consumed.

\[
12 \text{Fe}^{2+} + 3 \text{O}_2 + 6 \text{H}_2\text{O} \rightarrow 8 \text{Fe}^{3+} + 4 \text{Fe(OH)}_3
\]  
\[
\text{Fe}^{3+} + 3 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3 \text{H}^+
\]  
\[
\text{MnCO}_3 + 2 \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}
\]  
\[
\text{Mn}^{2+} + 2 \text{Fe}^{3+} + 4 \text{H}_2\text{O} \rightarrow \text{MnFe}_2\text{O}_4 + 8 \text{H}^+
\]  
\[
\text{Fe(OH)}_3 + 3 \text{H}^+ \rightarrow \text{Fe}^{3+} + 3 \text{H}_2\text{O}
\]

As time prolonged, more and more Mn²⁺ ions diffused outward leaving some caves at the center of the microsphere. Such caves can be observed in the TEM image of the microspheres obtained at 6 h. The microspheres obtained at 7 h are mainly hollow structures with a few individual small cores inside. The corresponding XRD pattern shows a dominant MnFe₂O₄ phase with minor peak of the main diffraction of MnCO₃. Thus the individual small cores can be explained as the residual of MnCO₃ templates. In the hollow microspheres obtained at 8 h, the individual small cores of MnCO₃ have totally disappeared. The corresponding XRD pattern can be indexed to MnFe₂O₄ phase without any diffraction of MnCO₃ detected. The sacrificial templates of MnCO₃ microspheres have been completely transformed to MnFe₂O₄ hollow microspheres. Theoretically, the diameters of the MnFe₂O₄ hollow microspheres should be slightly larger than that of the MnCO₃ microspheres. However, due to the loose structure of the outer layers, some MnFe₂O₄ nanoparticles dropped from the surface and resulted in similar diameters of the MnFe₂O₄ hollow microspheres.
Figure 3. Conversion from MnCO$_3$ microspheres towards MnFe$_2$O$_4$ hollow microspheres under hydrothermal condition at 180 °C. XRD patterns (left) and TEM images (right) of products collected at different stages of hydrothermal process.

Hydrothermal temperature is critical to the formation of MnFe$_2$O$_4$. In order to determine the appropriate hydrothermal reaction temperature, the hydrothermal temperature was set to be 140 °C, 160 °C, and 180 °C, respectively. The hydrothermal reaction time was prolonged to 12 h thus the reaction would complete. Other conditions were identical to the typical procedure. Figure 4 shows the X-ray diffraction patterns of products obtained at different hydrothermal temperatures. The results support the idea that MnFe$_2$O$_4$ should be synthesized at elevated temperature and pressure. The products obtained at 180 °C is MnFe$_2$O$_4$ without detectable impurity, while the products obtained at 140 °C and 160 °C contain considerable amount of complex impurities. It seems that 180 °C is the appropriate hydrothermal temperature in the present work.

Figure 4. The XRD patterns of the samples obtained at different hydrothermal temperatures

The molar ratio of MnCO$_3$ to FeSO$_4$ is also important and should be controlled severely as 1:2, otherwise diffraction peaks of impurities will appear in the XRD patterns. Figure 5a shows the X-ray diffraction pattern of the sample synthesized with excessive Mn$^{2+}$. Surplus MnCO$_3$ exists in the products when there is excessive Mn$^{2+}$. Figure 5b shows the X-ray diffraction pattern of the sample synthesized with excessive Fe$^{2+}$. The pattern peaks reveal that the hematite Fe$_2$O$_3$ has been synthesized together with MnFe$_2$O$_4$ when Fe$^{2+}$ is excessive.
4. Conclusion
In summary, we report a sacrificial templates approach for the synthesis of MnFe$_2$O$_4$ hollow microspheres using MnCO$_3$ as sacrificial template. We demonstrate that MnCO$_3$ microspheres can be transformed to MnFe$_2$O$_4$ hollow microspheres through hydrothermal process at elevated temperature and pressure. Hydrothermal treatment at 180$^\circ$C for 8 h is the appropriate condition for the formation of MnFe$_2$O$_4$ hollow microspheres. The as-synthesized MnFe$_2$O$_4$ hollow microspheres exhibit ferromagnetic behaviour with slightly lower saturation magnetization value than their solid counterparts.

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