

One pot method synthesis of magnetic Fe_3O_4 /polyacrylamide (Fe_3O_4 /PAM) composite nanoparticles

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In this paper, we proposed novel ideas to synthesize Fe_3O_4 /PAM composite nanoparticles (Fe_3O_4 /PAM CNPs). Taken each water-drop in W/O emulsion system as a mini-reactor and based on the coprecipitation and inverse emulsion polymerization, we obtained magnetic composite nanoparticles using cheap raw materials and simple working procedure. At the same time, compound emulsifiers were used to improve the stability of W/O emulsion system. Fe_3O_4 /PAM CNPs were quasi-sphere with the size range of 70-600 nm around and exhibited superparamagnetic character at room temperature. The saturation magnetization value of Fe_3O_4 /PAM CNPs was 28.9 emu/g.

(Received January 31, 2012; accepted April 11, 2012)

Keywords: Composite nanoparticles, Superparamagnetism, Mini-reactor, Compound emulsifiers

1. Introduction

Magnetic nanoparticles are of great interest to researchers for their wide range a board of applications, including magnetic fluid, magnetic storage, microwave absorption [1-3], owing to their unique magnetic properties such as superparamagnetic, low Curie temperature, high coercivity, and high susceptibility.

Recently, magnetic nanoparticles, mainly Fe_3O_4 , also have generated a lot of interest in biomedical applications for magnetic resonance imaging, magnetic separation, and targeted drug delivery [4]. Magnetic polymer nanoparticles are usually composed of the magnetic cores that could ensure a strong magnetic response and the polymeric shells that could provide favorable functional groups to prevent particle aggregation.

In the past few years, several methods have been developed for the synthesis of these composites, including dispersion polymerization, suspension polymerization, and miniemulsion polymerization [5-7]. However, some methods involved high cost of materials and complex working procedure when extrapolated to industrial production for technological applications.

In this paper, we proposed novel ideas to synthesize magnetic Fe_3O_4 /PAM composite nanoparticles

(Fe_3O_4 /PAM CNPs) via inverse emulsion polymerization using cheap raw materials and simple working procedure. X-ray diffractometer, transmission electron microscopy, and vibrating-sample magnetometer were respectively adopted to characterize the appearance and property of Fe_3O_4 /PAM CNPs. The synthesis method is also as a good candidate to prepare magnetic polymer nanoparticles quickly and simply.

2. Experimental section

2.1. Materials

AM, Iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were purchased from the Tianjin Fu-chen Chemical Reagent Factory, China (AR), and AM was recrystallized once from water. Toluene, ammonium hydroxide (NH_4OH) and potassium persulphate (KPS) were obtained from the Beijing Chemical Plant, China (AR), and KPS was recrystallized once from water. Sorbitan monooleate (Span80) and alkylphenol polyoxyethylene ether (Op10) were obtained from the Tianjin Guang-fu Fine Chemical Research Institute, China (CP), were used as received. In

this study, only distilled water was used.

2.2. Synthesis of Fe₃O₄/PAM CNPs

At first, oil phase, which was composed of 1.2g Span80 and 24 ml toluene, was vigorously stirring for 30 min at room temperature. Aqueous phase, which was composed of 1M 2.6 ml FeCl₂ and 1M 5.2 ml FeCl₃, 3.8g AM and 0.13g Op10, was slowly dropped into the oil phase with continuous stir to form stable W/O emulsion system. Then emulsion was heated to 50°C. Based on the coprecipitation [8], the black Fe₃O₄ nanoparticles in the W/O emulsion system was prepared by adding 4.2 ml NH₄OH in the emulsion. Then emulsion was sequentially stirred for 2 h at 50°C. After adding initiator 0.05g KPS in emulsion, PAM was obtained via inverse emulsion polymerization in the black emulsion. Then emulsion was vigorously stirred for 4 h. Now black Fe₃O₄/PAM CNPs in the W/O emulsion system were obtained. Nitrogen (N₂) was purged all along during the whole reaction. Fe₃O₄/AM (wt/wt) was about 16.5%.

There were two key points existed in the reaction course. There were many mini-reactors, namely every water-drop in the W/O emulsion system. A schematic diagram of synthesizing steps of Fe₃O₄/PAM CNPs is presented in Fig. 1. Picture (a) shows Fe²⁺, Fe³⁺ and AM were scattered in a water-drop of W/O emulsion system by vigorous stir. According to the principle of “like dissolves like”, with adding NH₄OH into emulsion step by step, OH⁻ permeated into surface of the water-drop. Then OH⁻ and Fe²⁺, Fe³⁺ together generated Fe₃O₄ nanoparticles in the water-drop based on the coprecipitation. Picture (b) shows the formation of Fe₃O₄ nanoparticles in the water drop. Similarly, with adding KPS into emulsion, KPS also permeated into surface of the water-drop again and initiated polymerization reaction to form PAM encapsulating Fe₃O₄ nanoparticles. Picture (c) shows the formation of Fe₃O₄/PAM CNPs.

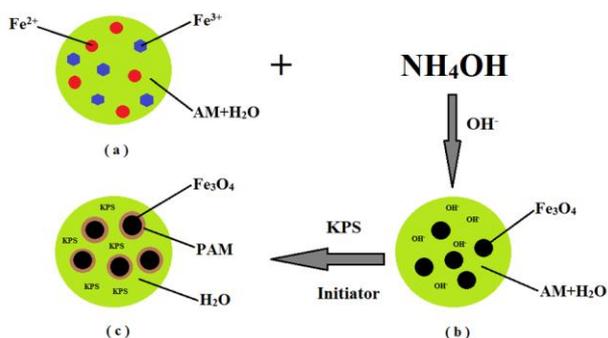


Fig. 1. Schematic diagram of synthesizing steps for Fe₃O₄/PAM CNPs.

Using compound emulsifiers - Op10 and Span80 was the other key point. Appropriate emulsifier blends will improve emulsion stability. The HLB values of compound

emulsifiers were calculated with the following formula:

$$HLB=4.3e+13.9 \times (1-e)$$

Here e stands for the mass fraction of Span80. When the HLB values were about 5.0 - 5.74, inverse emulsion system of AM and toluene was very stable [9]. The HLB values were 5.23 in this experiment and W/O emulsion system was very stable. Inverse emulsion polymerization of AM for obtaining PAM can finish successfully under the circumstances.

2.3. Analytical methods

Fe₃O₄/PAM CNPs were subjected to heat treatment at 500 °C for 10 h, N₂ was purged all along. The black iron oxides powder was obtained for testing. An X-ray diffraction measurement was recorded using a Rigaku X-ray diffractometer (XRD, Cu radiation, $\lambda = 0.15418$ nm) so as to acquire information about the crystal structure of the black powder.

Transmission electron microscopy (TEM) images were obtained using electron microscopes JEM-1200EX (JEOL, Japan).

A vibrating-sample magnetometer (VSM, Lake Shore 7410, USA) was used to study the magnetic properties of the powder of Fe₃O₄/PAM CNPs.

3. Results and discussion

The crystal structure of the sample prepared had been confirmed by XRD analysis in Fig. 2. The (220), (311), (400), (422), (511), and (440) diffraction peaks observed at curves can be indexed to the cubic spinel structure, and all peaks were in good agreement with the Fe₃O₄ phase (JCPDS card 19-0629). It can be concluded that the iron oxides particles in the W/O emulsion system were composed of Fe₃O₄.

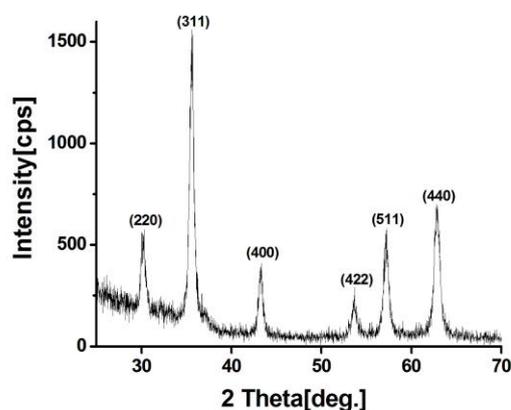


Fig. 2. XRD of black powder from Fe₃O₄/PAM CNPs via heat treatment at 500 °C for 10 h.

Fig. 3 showed the morphology of $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs in the W/O emulsion system. The shapes of $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs were nearly quasi-sphere. In addition, the TEM photo showed that Fe_3O_4 nanoparticles were encapsulated within the PAM matrix and exhibited good dispersion. The size distribution of these $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs was within the range of 70–600 nm around.

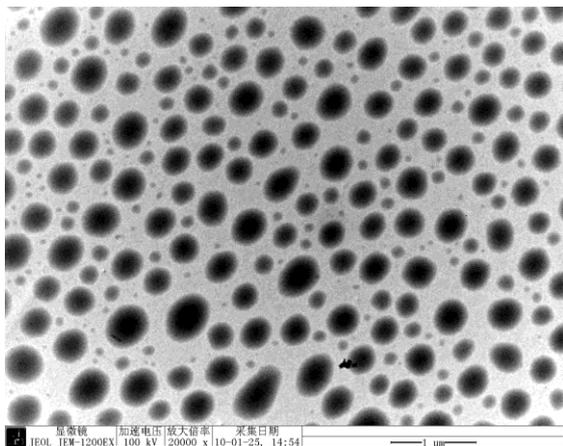


Fig. 3. TEM photo of $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs.

The magnetization curves were shown at 300K for both pure Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs in Fig. 4. The saturation magnetization values of both pure Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs were 58.1 emu/g and 28.9 emu/g, respectively. Moreover, the magnetization curves in two cases exhibited nearly zero remanence, which proved the existence of the superparamagnetic character of $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs at room temperature [10-11]. The reduction of saturation magnetization value of $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs could be partially contributed by PAM coating.

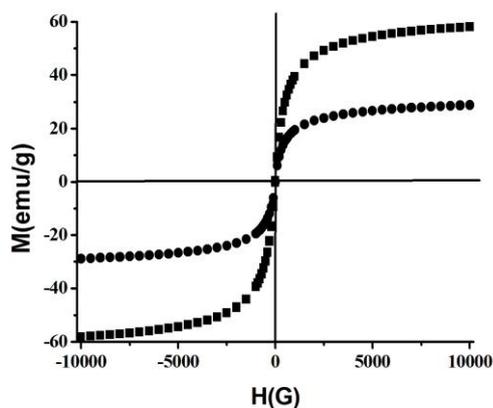


Fig. 4. Magnetization curves of both pure Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs. ■: pure Fe_3O_4 , ●: $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs at room temperature.

4. Conclusions

Taken each water-drop in W/O emulsion system as a mini-reactor and based on the coprecipitation and inverse emulsion polymerization, we obtained $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs using cheap raw materials and simple working procedure. The shape of $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs was quasi-sphere. The size distribution was within the range of 70–600 nm. The saturation magnetization value of $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs was 28.9 emu/g. $\text{Fe}_3\text{O}_4/\text{PAM}$ CNPs exhibited superparamagnetic character at room temperature.

Acknowledgment

I wish to give special thanks to Mr. Zhicheng Li and Gehui Wen for their helps in performing the TEM and VSM.

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