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A facile single-step approach for preparing water-based Fe_3O_4@PFR magnetic nanofluids

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Abstract : A water-based magnetic nanofluid is constructed by directly dispersing Fe_3O_4 @ phenol formaldehyde resin (PFR) nanocomposites into pure water without adjusting pH value or adding additives. The turbid liquid including Fe_3O_4 nanoparticles with size around 20 nm are firstly prepared via a co-precipitation route. When hexamethylene tetramine and phenol are put into the mixture, it is demonstrated by hydrothermal process at 120° C for 2h. The nanocomposites are characterized by XRD, FTIR, SEM, TEM and VSM instruments. The hydrophilic branch-like PFR coating paramagnetic Fe_3O_4 nanoparticle is accomplished via a hydrothermal approach. The nanofluid exhibits excellent magnetism and high stability. The formational mechanism is discussed.

Keywords : Magnetism; Nanocomposites; Nanofluids; Nanoparticles; Nanosynthesis.

INTRODUCTION

Fe_3O_4 magnetic nanofluids have been paid more attention upon their important perspective applications including industrial field, biological technology field and medical field, and so on[1,2]. A based-water magnetic nanofluids plays an important role in biological technology and medical field due to their advantages on chemical stability, exact targeting property, good biocompatibility and biodegradation. So this kind of magnetic nanfluid have been used in protein/cell separation[3,4], drug delivery[5,6], hyperthermia[7,8], biological detection[9,10] and magnetic resonance imaging (MRI)[11,12], and so on.

Recently, many methods have been developed to prepare diverse nanofluid, which can be divided into two categories: two-steps approach and single-step method[13]. The two-steps method as a widespread adopting approach includes two main stages: synthesis of nanoparticles and dispersion of them into based liquid. The procedure of the method is fussy and time-consuming. Ladislau et al. had obtained some nanofluids via this method[14]. The single-step method combines preparation nanoparticles and nanofluids by one pot process, which is difficult to accomplish, because nanoparicles must be modified simultaneously in synthesis procedures to keeping its stability in water or oil solvent. Peng et al. had synthesized oil-based PEG-PEI/Fe_3O_4 nano-magnetic fluid by co-precipitation method[15]. Recently, our group found that Fe_3O_4 nanoparticles coated phenol formaldehyde resin (PFR) can be facilely obtained via a given one-step solvothermal route[16]. Meanwhile, the hydrophily of PFR can be easily controlled by change of reaction conditions[17]. So we conceive that a two-step method may be simplified by introducing PFR into the system for preparing water-based Fe_3O_4 nanofluid.

In the study, a novel hydrothermal route is demonstrated for obtaining nanofluid. After some hexamethylene tetramine and phenol are directly added into the suspension mixture produced Fe_3O_4 nanoparticles, the obtained mixture is performed in hydrothermal process. Then the hydrophilic PFR can be produced and replaced some organic molecular on the surface of Fe_3O_4 nanoparticles to form nanocomposite. As-obtained nanocomposites show good hydrophilic and form nanofluids in water without tuning pH value or adding other dispersing reagent. The as-obtained black Fe_3O_4 nanocomposites possess excellent super-paramagnetic properties at room temperature with size around 20 nm. Meanwhile, the nanofluid exhibits outstanding stability. Compared to general two-steps approaches, this method just like a one-step route because the separating and re-dispersing procedures of nanoparticles are leaved out in its procedures. By this study, an alternative idea maybe provides to improve two-steps approach for preparing nanofluids. Meanwhile, is so the method may show good applicable perspective for it is facile to operate and bring out in future.

EXPERIMENTAL

Reagents and materials

$FeCl_3 \cdot 6H_2O$ (AR), $FeSO_4 \cdot 7H_2O$ (AR), hexamethylene tetramine (HMTA, AR), NaOH (AR), C_6H_5OH (AR), ethylene glycol (AR) and absolute ethanol (AR) were all purchased from China National Medicines Corporation Ltd. and used as received without further purification. De-ionized water used in all experiment is self-made with the electric conductivity round 5μS.

Preparation of nanofluid

In a typical procedure, 15 mmol $FeCl_3 \cdot 6H_2O$, 12 mmol $FeSO_4 \cdot 7H_2O$, 250 ml de-ionized water with 50 ml ethylene glycol were poured into a three-necked bottle and the mixture was quickly stirred with mechanical whisk at 65 ºC about 30 minutes. before the aqueous NaOH (1M) 50 ml was injected into the bottle. Though the black suspension was formed at once, the mixture was constantly stirred at 65 ºC about 90 minutes. After that, the mixture was transferred into a 500 ml hydrothermal autoclave with Teflon inner. When 0.50 g C_6H_5OH and 1.00 g HMTA were added into the mixture, the autoclave was sealed and kept in a thermostatically controlled oven at 120 ºC for 4 h. Then the autoclave was cooled naturally. The black precipitate was washed by ethanol and de-ionized water several times in turn. Finally, the Fe_3O_4@PFR nanocomposites were re-dispersed into de-ionized water to form nanofluids.

Characterization

The crystal phase of as-obtained samples is identified by X-ray diffraction instrument (XRD, Bruker, D8 Focus, Germany) equipped with graphite monochromatized Cu k_a radiation ($\lambda = 1.54056$ Å). The XRD patterns were acquired in the range from 10º to 70º of 2θ at scanning rate of 0.05 º/s. Fourier transform infrared spectra were recorded from 4000 to 400 cm^{-1} using a Nicolet 5DX FTIR spectrometer (USA). The morphologies of the as-synthesized products were studies by scanning electron microscopy (SEM, Philip XL30, Holland) at an accelerating voltage of 20 kV, and transmission electron microscope (TEM, Hitachi, H800EM, Japan) at an accelerating voltage of 200 kV. Magnetic measurements were performed by vibrating sample magnetometer (VSM, Lake Shore 735 VSM, USA) from -10000 to 10000 Oe.

RESULTS AND DISCUSSION

A XRD pattern of a typical as-obtained Fe_3O_4@PFR nanocomposite is shown in Figure 1A. The pattern reveals the crystal structure of sample is belonged to F-centered cube type. All diffraction peaks are easily indexed as Fe_3O_4 given in JCPDS (No. 65-3107) with lattice constants a= 8.383(9) Å. The average crystallite size of samples is estimated about 20 nm by the Scherrer equation. Concurrently, a widen peak appeared in the region between 20º and 30º indicate that some amorphous materials is presented in the product, which should be attributed to PFR. The above results suggest that the Fe_3O_4 @ PFR nanocomposite can be synthesized via the given hydrothermal method. The typical FTIR spectrum of the sample is measured and shown in Figure 1B. The FTIR spectrum demonstrates some characteristic absorbance bands of groups contained in the samples, which can be divided into four parts including 560–600 cm^{-1}, 1000–1650 cm^{-1}, 2850–3000 cm^{-1}, and 3200–3600 cm^{-1}. The first part proves the sample contain Fe_3O_4 due to Fe-O group characteristic absorbance at 578 cm^{-1}. Other parts further confirm the component of PFR for its characteristic peaks appeared in the 1000-1650 cm^{-1}, 2850-3000 cm^{-1}, and 3200-3600 cm^{-1}. Meanwhile, the powerful absorbance bands in region of 3200-3600 cm^{-1} and 1600-1650 cm^{-1} also provide the information of OH group plentifully presented in the samples. So FTIR results further verifies Fe_3O_4 and PFR exist in the product.

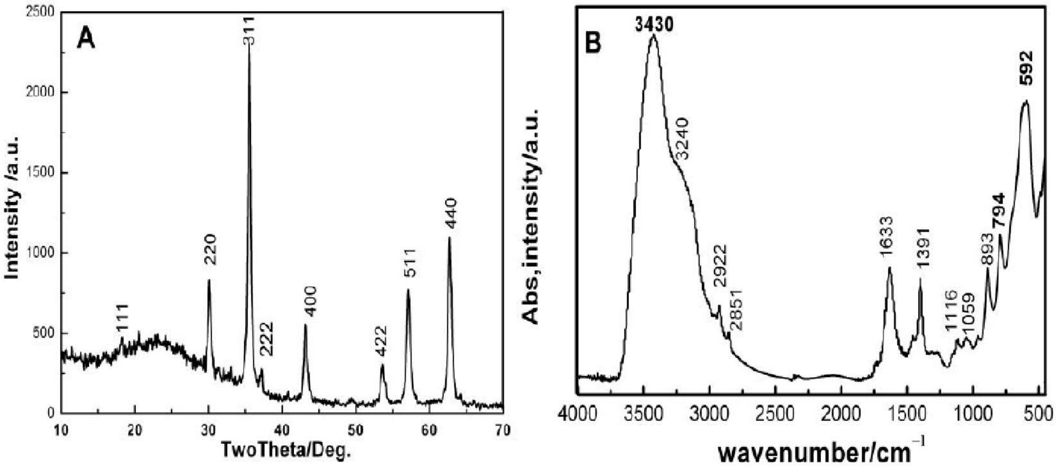

Figure 1 : The typical XRD Pattern (A) and FTIR curve (B) of the as-obtained Fe_3O_4 coated by water-soluble PFR nanoparticles.

The typical SEM and TEM images of as-prepared Fe_3O_4 @ PFR nanocomposite are presented in Figure 2. The SEM image shown in Figure 2A demonstrates agglomerate sample. The TEM image further exhibits the agglomerate sample is composed of nanoparticles with average diameter around 20 nm and the brand-like amorphous organic polymer due to PFR (Figure 2B). These branched PFR macromolecules interact with each other and result into the agglomerate of nanocomposite. The size of Fe_3O_4 nanoparticles obtained by TEM image is accordant with the inferences from XRD pattern. Meanwhile, the TEM image intuitively suggests Fe_3O_4 nanoparticles are covered by amorphous PFR.

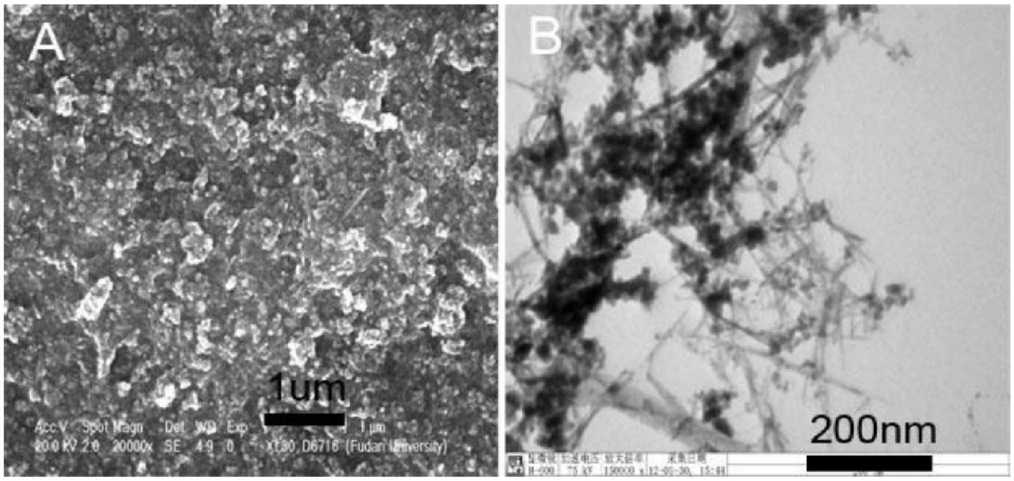

Figure 2 : The SEM image (A) and TEM image (B) of the typical Fe_3O_4 @ PFR sample.

The room-temperature VSM curve of the samples is presented in Figure 3. The two hysteresis loops are overlapped with each other. The coercive force and residual magnetism of the sample are measured as zero, which suggest the as-obtained sample possesses super-paramagnetic properties at room-temperature. Meanwhile, the saturation magnetization of the sample is detected about 41 emu g^{-1}, which indicates the sample own sufficient magnetic response capability.

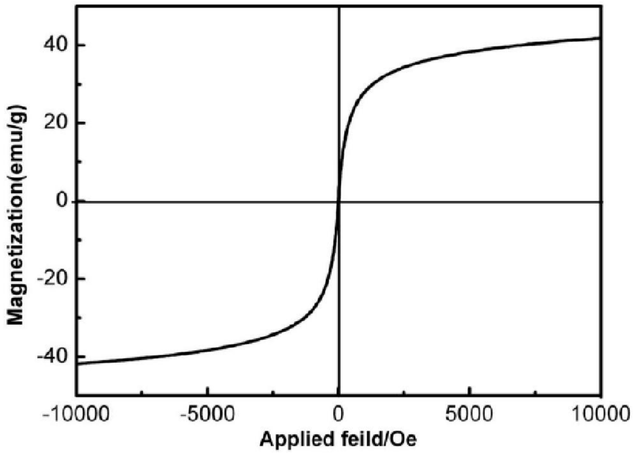

Figure 3 : Room-temperature VSM curves of the typical Fe_3O_4 @ PFR samples.

The nanocomposites are dispersed into de-ionized water to obtain a series of nanofluid with different concentration, including 1wt%, 5wt%, and 10wt% via ultrasonic dispersion process about 120 min. In the system, any accessory dispersing reagent is not added and the pH value of nanofluid is not modified by acid or base. For the stability of the as-obtained nanofluids investigated, they have been statically laid aside in a sealing bottle in room-temperature. The concentration of different location and the nanofluid appearance are detected after some times. It is found that the fluids can keep suspension property and without appearance of deposit sediment after 60 days, but the concentration of the upper-lay nanofluid decreases from 10 wt% to 8.5 wt%. Above results reveal that Fe_3O_4 @ PFR nanofluid possesses excellent stability.

According to above investigations, the good hydrophilic resole type PFR, which covers small paramagnetic nanoparticles, is crucial factor for constructing stable magnetic nanofluid. In this synthesis approach, Fe_3O_4 nanoparticles are firstly form in the precursor's mixture system. The growth of Fe_3O_4 nanoparticles is inhibited due to glycol absorbed on their surface. When precursors solvent are preformed in hydrothermal at 120 °C, HMTA molecules are hydrolyzed into formaldehyde and ammonia. Meanwhile, phenols are reacted with sufficient formaldehyde and synthesize phenolic resin[17]. The small resin molecules are cross-linked into branch-like resole polymers[18,19], which replace glycol molecule and are absorbed on the magnetic nanoparticles. These polymers contain plenty hydroxyl groups derived from phenol and hydroxymethyl due to excess formaldehyde. Because these hydroxyl groups can catch many H_2O molecular by hydrogen bond effect, the obtained nanocompsites demonstrate excellent hydrophilic capacity and increase the dispersity of Fe_3O_4 nanoparticles in water solvent.

CONCLUSIONS

This paper reports a novel hydrothermal method to prepare stable superparamagnetic water-based magnetic nanofluids, where Fe_3O_4 nano-particles are covered by hydrophilic PFR. The nanofluids are constructed via a simply process which make nanocomposites be redispersed into pure water in absence of other procedures, such as adjusting pH value or adding dispersants. The good stable of nanofluids should be attributed to the resole PFR with abundant OH groups are successfully obtained by hydrothermal route. This result provides an alternative approach for constructing water-based nanofluids, but there are many works to do in future. Because PFR is a good biocompatible material, the nanofluids maybe have good application prospective in biological medical field, environmental field, and so upon.

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