



A Facile Method for Preparation and Characterization of Fe₃O₄ Magnetic Nanoparticles

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Article history

Received: 16-June-2016

Revised: 04-July-2016

Available online: 04-Aug-2016

Keywords:

Fe₃O₄ magnetic Nanoparticles, Co-precipitation, Characterization, Super paramagnetic.

Abstract

In this study, Fe₃O₄ magnetic nanoparticles (MNPs) were successfully synthesized by a chemical co-precipitation of ferric and ferrous salts in an alkaline medium. The phase structures, morphologies, particle sizes and chemical composition of MNPs have been characterized by XRD, SEM, TEM, X-ray Photoelectron Spectroscopy (XPS), Energy-dispersive X-ray (EDS), Fourier Transformed Infrared Spectrophotometry (FT-IR), and Thermogravimetric analysis (TGA). It showed that the nanoparticles have an average diameter of 14 nm. The magnetization property of the as-synthesized sample using a superconducting quantum interference device magnetometer (SQUID) measurements. Finally, from the obtained results it is expected that these nanoparticles are a promising for biomedical applications.

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Introduction

Recently, Fe₃O₄ magnetic nanoparticles (MNPs) has much attention in the field of biomedical because of their biocompatibility, injectability, chemical stability over physiological circumstances, and substantial accumulation at the diseased site [1]. As a prospective candidate, MNPs can be employed for both the diagnosis and targeted therapy of cancer [2]. It is also used for the controlled release of a drug from caged drug delivery systems [3, 4].

A number of reports have been focused on the preparation of Fe₃O₄ with nano size and the effect of size and surface charge on various physical properties of MNPs has been studied. Fe₃O₄ with nano size is important for improving its properties. For example, with its reduced magnetic dipole–dipole interaction, MNs can as a potential and suitable drug delivery system for clinical applications [1]. To address this issue, capping agents such as oleic acid, polyethylene glycol (PEG), and citric acid has usually been employed for selective control of size and morphology of Fe₃O₄ [5–7]. However, we have to remove agents adsorbed on the surfaces of crystals to obtain its application by complex treatments. Thus, the fabrication of Fe₃O₄ with nanoscale exposed and without capping agents is still a great challenge.

In this study, Fe₃O₄ magnetic nanoparticles (MNPs) was easy synthesized by a chemical method without any surfactant. The phase structure and morphology of MNPs sample were characterized by X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM), and Fourier Transformed Infrared Spectrophotometry (FT-IR). We also investigated the magnetization property of the as-synthesized sample using a superconducting quantum interference device magnetometer (SQUID).

Experimental

Ferrous sulphate, anhydrous ferric chloride, ammonium hydroxide, and all solvents were purchased from Aldrich and used

as received. Fe₃O₄ magnetic nanoparticles (MNPs) was synthesized by a chemical method, according to the reported procedure [8, 9]. Typically, ferrous sulphate (6.22 mmol, 1.76 g) and anhydrous ferric chloride (12.44 mmol, 2.04 g) were dissolved in 50 mL of water, respectively. These two solutions were mixed together and exposed to ultrasound irradiation for 1 h at 25 °C. Then, the pH of the mixed solution was adjusted to 10 with an ammonia solution to prepare a homogeneous solution. After stirring for 30 min, the resultant suspension was centrifuged at 10000 rpm Fe₃O₄ for 10 min and the Fe₃O₄ solids at the bottom of the tube were rinsed with water for five times, followed by dried at 25 °C overnight.

The crystal structures of Fe₃O₄ samples were examined by powder X-ray diffraction (XRD) patterns with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) in the 2θ range of 5–80° (Philips X'pert-MPD, Netherlands). Surface composition was analyzed using an X-ray Photoelectron Spectroscopy (XPS) (Thermo VG Multilab 2000) in an ultra-high vacuum with Al K α radiation. The changes in the surface chemical were investigated by Fourier Transformed Infrared Spectrophotometry (FT-IR) using a BOMEM Hartman & Braun FT-IR Spectrometer in the frequency range of 4000–400 cm⁻¹. Thermogravimetric analysis (TGA) carried out at a heating rate of 10°/min under an air flux up to 700 °C using a Perkin-Elmer Pyris 1 analyzer. Transmission Electron Microscopy (TEM) images were recorded using a Joel JEM 2010 instrument with an accelerating voltage of 200 kV. Magnetic measurements of the synthesized Fe₃O₄ sample was performed at 300 °K using a superconducting quantum interference device magnetometer (SQUID) (Quantum design MPMS-XL7).

Results and Discussion

TGA characterization of MNPs was shown in Figure 1. As seen from Figure 1, a weight loss of about 4 % from room temperature to 500 °C was observed, result from the evaporation of physisorbed water. In addition, when increasing over 500 °C, the weight loss

remains unchanged indicates that no more volatile substances are to be evaporated. This result indicates that our as-prepared sample is pure without organic compounds.

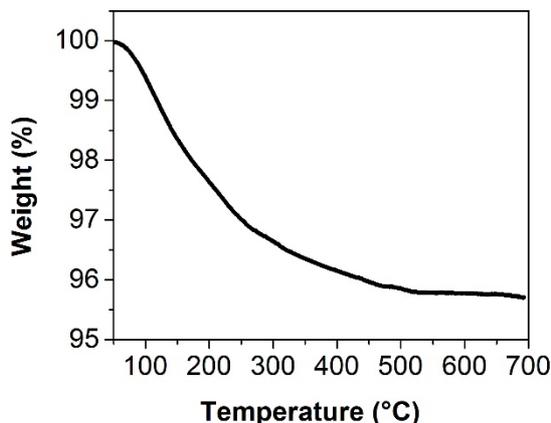


Figure 1: TGA characterization of MNPs

Figure 2 shows the XRD spectrum of MNPs. From the XRD result, the diffraction peaks appeared at $2\theta = 30.23^\circ$, 35.16° , 43.22° , 53.64° , 57.54° and 62.38° which can be assigned to the (220), (311), (400), (422), (511) and (440) crystal planes of Fe₃O₄, respectively, corresponding to the patterns reported earlier [1, 4, 5]. The result indicates that the shape of the MNPs is inverse spinel Fe₃O₄ with a face-centered cubic (fcc) structure, suggesting the sample has a cubic crystal system. Moreover, no impurity peak was detected in the MNPs, suggesting that the obtained samples were single phase Fe₃O₄.

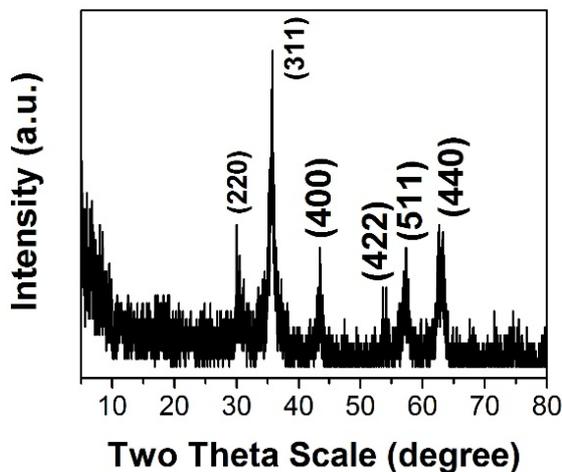


Figure 2: XRD pattern of MNPs.

The surface chemical composition of MNPs was investigated by the survey XPS spectra as shown in Figure 2(A). The wide scan spectrum of the MNPs surface is dominated by signals attributable to the Fe, O, and C elements. As shown in Figure 2(B), the high-resolution XPS pattern for the Fe element in the sample shows the binding energies of Fe 2p_{3/2} and Fe 2p_{1/2} at 711.8 eV and 724.7 eV, respectively, which suggests that both Fe²⁺ and Fe³⁺ should be existed showing the formation of Fe₃O₄ [10]. The XPS spectrum of C 1s was shown in Figure 2(D), the C 1s peak at 288 eV may attribute to the signal from carbon in the instrument or environmental disturbance [11].

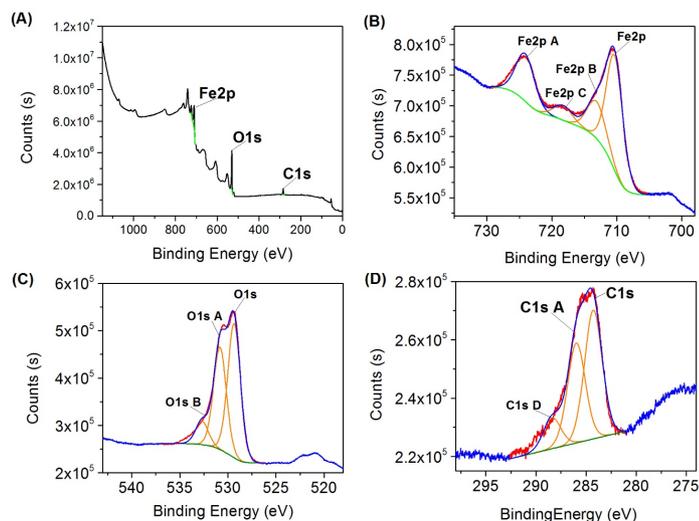


Figure 3: XPS spectra of MNPs: full spectrum (A); Fe 2p (B); O 1s (C); C 1s (D).

FT-IR analysis of the MNPs was shown in Figure 4. From Figure 4, the characteristic band at 3431 cm^{-1} is attributed to the stretching vibration of OH which is originated from OH-group on MNPs and the absorption band at 584 cm^{-1} is attributed to the Fe-O bond of bulk magnetic [12].

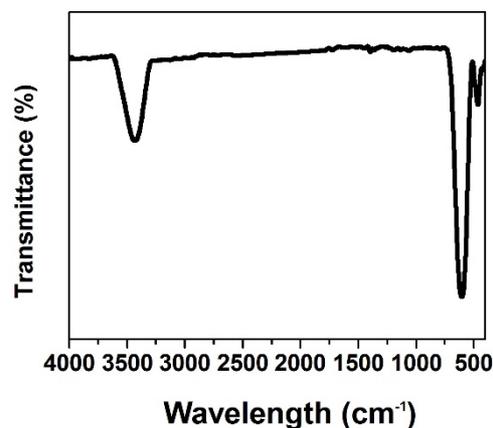


Figure 4: FT-IR spectra of MNPs.

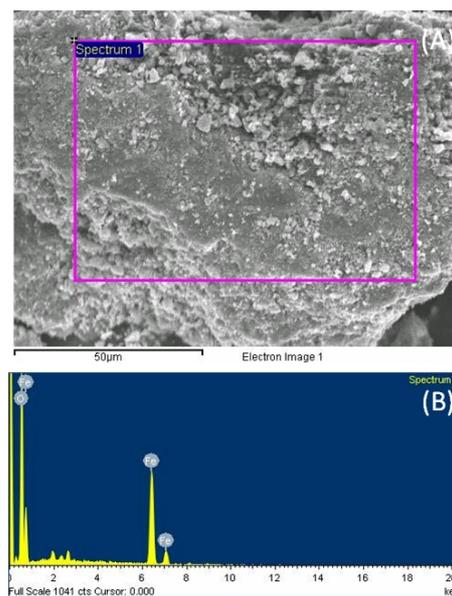


Figure 5: SEM image (A) and EDS (B) of MNPs.

Figure 5(A) shows the SEM images of MNPs. As shown in Figure 5(A), the morphologies and shapes of MNPs sample is the aggregate of nanoparticles. Besides, the TEM analysis (Figure 6(A)) indicated that the MNPs are almost nanocrystals although their shape is somewhat irregular from oval to spherical. The nanoparticles have an average diameter of 14 nm. The electron diffraction pattern (Figure 6(B)) consisting of rings indicates the good crystal structure of the nanoparticles. EDS was carried out to further identify the elemental composition of samples. The EDS data analysis in Figure 5(B) revealed the presence of the element Fe and O in the sample. The atomic ratio of Fe and O from the ED S spectrum is approximately 3:4 atomic ratio.

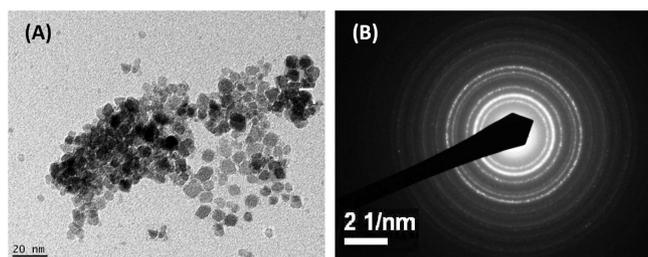


Figure 6: TEM images of MNPs (A) and diffraction pattern of a single MNP (B).

The magnetization measurement of MNPs was carried out by a vibrating sample magnetometer at room temperature, as shown in Figure 7. From Figure 7, there is no hysteresis curve at the low magnetic field in the case of MNPs and it was completely reversible at room temperature. In addition, the saturation magnetization value of the MNPs was estimated to be 59.4 emu/g, which indicated the superparamagnetic nature of the as-synthesized MNPs. The magnetizations versus applied magnetic field (*M*–*H* loop) curves of the MNPs show zero coercivity and remanence, which clearly suggests their superparamagnetic behavior. The observed level of saturation magnetization of MNPs is well suitable for magnetic materials which enhance its susceptible property applying for the magnetic fields and eventually facilitates for the solid-liquid phase separation [13].

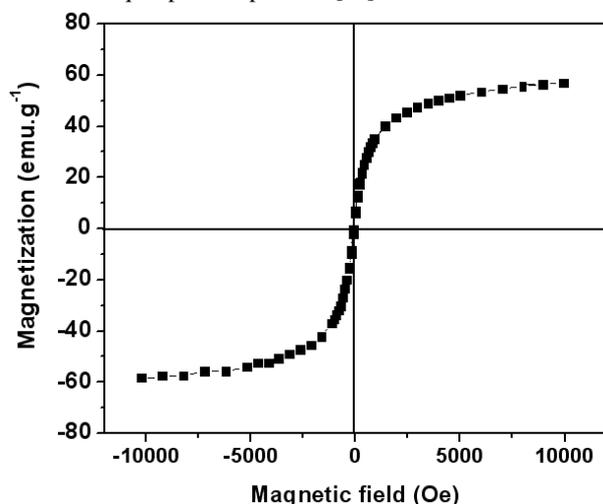


Figure 7: Magnetization curve of (A) MNPs.

Conclusions

In this work, the efficiency and simplicity of the chemical method for the preparation of Fe₃O₄ magnetic nanoparticles by co-precipitation of Fe²⁺ and Fe³⁺ with NH₄OH with the required properties for technological applications is described. Fe₃O₄ magnetic nanoparticles with 14 nm average diameter and single phase with a good crystallinity were prepared and characterized by

TEM, XRD, FT-IR, and SEM-EDS. Additionally, SQUID measurements confirm the ferromagnetic behavior of the nanoparticles with a saturated magnetization of 59.4 emu/g at room temperature. The observed level of saturation magnetization of MNPs is well suitable for magnetic materials which enhance its susceptible property applying for the magnetic fields and eventually facilitates for the solid-liquid phase separation.

Acknowledgements

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.02-2014.53.

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