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Simple polyol route to synthesize heptanoic acid coated magnetite (Fe_3O_4) nanoparticles

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ABSTRACT

Magnetite (Fe_3O_4) nanoparticles were prepared via polyol method by using $FeCl_2$ as only source of iron. As-prepared samples were characterized by powder X-ray diffractometer (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), thermal gravimetric analyzer (TGA) and vibrating sample magnetometer (VSM). Crystalline phase was identified as Fe_3O_4 and the crystallite sizes were calculated as 19.1 ± 1.1 and 22 ± 1.3 nm for uncalcinated and calcinated products from X-ray line profile fitting. The capping of heptanoic acid around Fe_3O_4 nanoparticles was confirmed by FT-IR spectroscopy, the interaction being via bridging oxygen's of the carboxylate and the nanoparticle surface and also by TG analysis. VSM measurements showed that both samples exhibited typical superparamagnetic behavior at room temperature with different *Ms* values. The ε' decreases with increasing frequency for both composites and permeability has almost same values for all temperatures at higher frequencies. As synthesized and calcinated samples conductivity increase linearly with the temperature.

1. Introduction

Magnetite (Fe_3O_4) is a common magnetic iron oxide that has a cubic inverse spinel structure with fcc close packed oxygen anions and Fe cations occupying interstitial tetrahedral and octahedral sites. Magnetite unit cell can be represented with the formula $(Fe_8^{3+})_A[Fe_{40/3}^{3+}Fe_{8/3}^{2+}]_BO_{32}$, where A and B indicate tetrahedral and octahedral positioning, respectively. The electrons can hop between Fe^{2+} and Fe^{3+} ions in the octahedral sites at room temperature, rendering magnetite an important class of half-metallic materials [1,2]. Due to its strong magnetic and semiconducting properties, magnetite (Fe_3O_4) is one of the preferred well known filler materials, which is combined with polymers/nanocomposites to be used as magnetic recording media, and in medical applications [3–7]. Therefore, magnetite has the potential for providing the desired magnetic and electrical properties to the final composite.

Magnetic polymer nanocomposites represent an important class of functional materials, in which the magnetic nanoparticles are embedded in polymer matrix. These nanocomposites hold immense potential for the new fields of applications such as drug targeting, electromagnetic devices and industrial automatization besides electromagnetic interference suppression [8–10]. The coating of long-chain polymer molecules on ferrite particles serves as protective layer that prevents agglomeration of the particles and minimizes the direct exposure of the ferrite surface to the biological environment [11–17]. These nanocomposites hold immense potential for the new fields of applications such as drug targeting, electromagnetic devices and industrial automatization besides electromagnetic interference suppression [10]. Petcharoen and Sirivat [18] used both oleic acid and hexanoic acid to coat Fe_3O_4 NPs, they also studied the effect of chain length of organic acid on the magnetism and conductivity of the resultants nanocomposites. Ünal et al. [19] studied on the synthesis, conductivity and dielectric characterization of salicylic acid-Fe_3O_4 nanocomposite and ac and dc conductivity measurements revealed semiconductor conduction characteristics, and various trends were observed, as a function of frequency and temperature, revealing different mechanisms dominating based on the temperature dependent reorganization of the nanocomposite. Niasari et al. [20] used the octanoic acid to prevent the agglomeration for the synthesis of $NiFe_2O_4$ NPs with small crystallite size.

The fatty acid found naturally in the animal fats containing the carboxylic group can be used as the coating agent for the magnetite. The heptanoic acid was selected to study the effect on the chain length of coating agent. The purpose of this work is the preparation of magnetite nanoparticles by via Reflux method. The chemical, morphological, thermal, electrical conductivity magnetic properties the synthesized and calcinated magnetite nanoparticles were investigated. To the best of our knowledge, this is the first

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report on its synthesis, electrical transport property (electronic/dielectric) and magnetic characterization.

2. Experimental

2.1. Chemicals and instrumentations

All of the chemical reagents ($FeCl_2{\cdot}4H_2O$, heptanoic acid ($C_7H_{14}O_2$), NaOH were of analytical grade and were used without further purification. Double distilled, deionized water was used as a solvent. All experiments were done under the protection of argon gas.

X-ray powder diffraction (XRD) analysis was conducted on a Rigaku Smart Lab operated at 40 kV and 35 mA using Cu K_α radiation (λ = 1.54059 Å).

Fourier transform infrared (FT-IR) spectra of the samples were recorded with a Perkin Elmer BX FT-IR infrared spectrometer in the range 4000–400 cm^{-1}.

Scanning electron microscopy (SEM) analysis was performed, in order to investigate microstructure of samples, using Field Emission Gun JEOL 6335F. Samples were coated with gold at 10 mA for 2 min prior to SEM analysis.

The thermal stability was determined by thermogravimetric analysis (TGA, Perkin Elmer Instruments model, STA 6000). The TGA thermograms were recorded for 5 mg of powder sample at a heating rate of 10 °C/min in the temperature range 30–750 °C under nitrogen atmosphere.

VSM measurements were performed by using a vibrating sample magnetometer (LDJ Electronics Inc., Model 9600) and magnetization measurements were carried out in an external field up to 15 kOe at room temperature.

The electrical conductivity of the product was studied in the temperature range 20–120 °C with a heating rate of 10 °C/s. The sample was used in the form of circular pellets of 13 mm diameter and 3 mm thickness. The pellets were sandwiched between the gold electrodes and the conductivities were measured using Novocontrol dielectric impedance analyzer in the frequency range 1 Hz–3 MHz, respectively. The temperature (between −100 and 250 °C) was controlled with a Novocool Cryosystem.

2.2. Procedure

A 2 g $FeCl_2{\cdot}4H_2O$ was dissolved in 25 ml of heptanoic acid via magnetic stirrer under Ar gas and pH was adjusted to 11 with 2 M NaOH. Then final solution was refluxed at 160 °C for 4 h under Ar. The black-brown solid product was obtained and washed with distilled water/ethanol, then dried at 80 °C for 2 h (uncalcinated). Finally, precursor was calcined at 600 °C for 3 h (calcinated) (Scheme 1). Alkalization reaction of ferrous ions has been extensively studied by Refait and Olowe [21–23] and they proposed the following reactions for the mechanism of formation of Fe_3O_4:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad \text{(I)}$$

$$3Fe(OH)_2 + 1/2O_2 \rightarrow Fe(OH)_2 + 2FeOOH + H_2O \quad \text{(II)}$$

$$Fe(OH)_2 + 2FeOOH \rightarrow Fe_3O_4 + 2H_2O \quad \text{(III)}$$

Thus, in the synthesis with ferrous ions alone, as in our case, Fe_3O_4 is formed as a result of the dehydration reaction of ferrous hydroxide and ferric oxyhydroxide (reaction (III)) in which the latter compound is produced by the partial oxidation of ferrous hydroxide by O_2 dissolved in air (reaction (II)). This is the mechanism controlling the transformation of iron hydroxide phases to the final phase of magnetite.

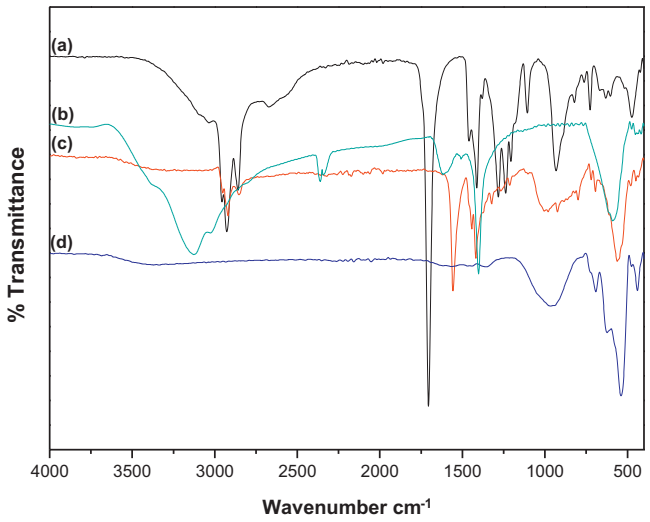
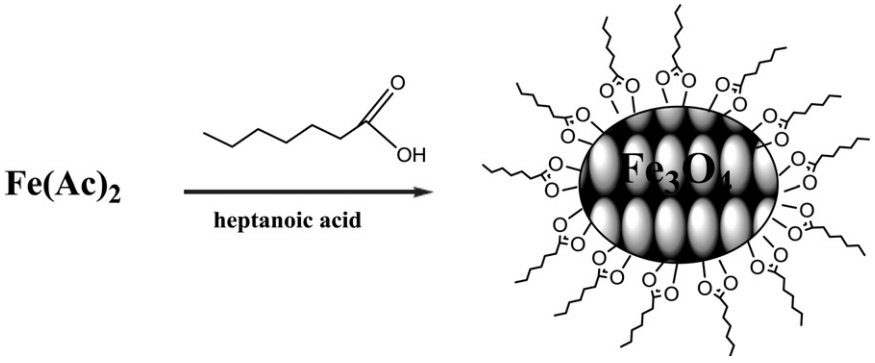


Fig. 1. FT-IR spectra of (a) pure heptanoic acid, (b) uncoated Fe_3O_4 NPs and (c) Heptanoic acid@Fe_3O_4 nanocomposite, (a) uncalcinated and (b) calcined form.

3. Results and discussion

3.1. FT-IR analysis

Fig. 1 shows the typical FT-IR spectrum of uncoated Fe_3O_4 NPs, Heptanoic acid@Fe_3O_4 nanocomposite before and after calcination, heptanoic acid and suggested linkage of heptanoic acid to iron oxide surface. In the spectrum for heptanoic acid presented in Fig. 2c, two sharp bands at 2927 and 2860 cm^{-1} were attributed to



Scheme 1. Schematic representation of synthesis of Heptanoic acid@Fe_3O_4 nanocomposite before calcination.