

SYNTHESIS AND CHARACTERIZATION OF COBALT FERRITE MAGNETIC NANOPARTICLES COATED WITH POLYETHYLENE GLYCOL

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Abstract

Magnetic nanoparticles of cobalt ferrite (CoFe_2O_4) have been synthesized by chemical co-precipitation method with capable of controlling the average particle size of CoFe_2O_4 magnetic nanoparticles. Further, the surface of CoFe_2O_4 nanoparticles was coated with sodium oleate as the primary layer and polyethylene glycol 6000 (PEG-6000) as the second layer. X-ray diffraction (XRD) indicated the sole existence of partially inverse cubic spinel phase of CoFe_2O_4 and the average particle size calculated from XRD of about 29 nm. SEM analysis showed that the surface modification with PEG could increase crystallinity of nanoparticles, decrease the agglomeration and control the shape to more spherical. Fourier transform infrared spectroscopy (FT-IR) analysis indicated existence of two distinct surfactants on the particle surface. In addition, the results of FT-IR indicated that the coated CoFe_2O_4 particles improved with the thermal stability due to the interaction between the CoFe_2O_4 particles and protective layers. Magnetic characterization of CoFe_2O_4 was studied by Electron spin resonance (ESR). The results showed that the existence PEG in the CoFe_2O_4 decrease the spin resonance of conduction electrons.

Keywords: Nanoparticles, Co-precipitation, PolyEthylene Glycol, FT-IR, ESR

1. Introduction

Magnetic nanoparticles have attracted researchers in various fields such as physics, medicine and biology due to their multifunctional properties such as small size, superparamagnetism and low toxicity etc [1-3]. Among this, magnetic nanoparticles of spinel ferrites are of great interest in fundamental science especially for addressing the fundamental relationships between magnetic properties and their crystal chemistry and structure. So, the synthesis and characterization

of spinel metastable nanoferrites have been investigated with a lot of attention [4-6]. Magnetic nanoparticles tend to aggregate due to strong magnetic dipole-dipole attractions between particles. So, modification of the surface of the cobalt ferrite nanoparticles with various biocompatible and biodegradable polymers have been widely investigated [7]. These particles consist of CoFe_2O_4 magnetic cores coated with protective layers. Stability of the coated particles depends on the strength of the bond between core and coating. Normally this coating or nanoshell materials were highly stable and

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dielectric materials such as silica and polymers. They should be water soluble and low toxic in nature.

The importance of targeted drug delivery and targeted drug therapy is to transport a drug directly to the centre of the disease under various conditions and thereby treat it deliberately, with no effects on the body. The greatest therapeutic potential is probably associated with applications involving intelligent particles with a magnetic core to direct the particles to the vicinity of the target and also for temperature-enhanced release of the drug, a recognition layer to which suitable receptors are attached and a therapeutic load adsorbed inside the pores or hosted within internal cavities of the particles. The challenges are formidable, especially those related to the development of suitable recognition layers. Useful recognition moieties attached to the particles must be loaded to a high density while maintaining their desired characteristics. The potential of drug delivery systems based on the use of magnetic nanoparticles stems have significant advantages such as: (i) the ability to target specific locations in the body; (ii) the reduction of the drug quantity needed to attain a particular concentration in the vicinity of the target; and (iii) the reduction of the concentration of the drug at non-target sites minimizing severe side effects. So due to their unique physical properties and ability to function at the cellular and molecular level of biological interactions, cobalt ferrite nanoparticles have been actively investigated as the next generation of targeted drug delivery [8-11]. The structural and magnetic properties of the CoFe₂O₄ and polyethylene glycol (PEG) coated CoFe₂O₄ nanoparticles have been reported in the present study.

2. Experimental

Polyethylene glycol (PEG) has been coated on nanoparticle surfaces to disperse them. Moreover, there is growing interest in attaching PEG conjugate to the surfaces of nanoparticles through chemical bonding. PEG is attached to the nanoparticles surface to prevent the nanoparticles from agglomeration to make them biocompatible [12, 13]. Because PEG is playing

different roles in intracellular uptake of nanoparticles, it is expected that the uptake efficiency will be further improved after the PEG conjugates are attached to nanoparticle surfaces. In this work, cobalt ferrite (CoFe₂O₄) magnetic nanoparticles were prepared using chemical co-precipitation method. The obtained CoFe₂O₄ nanoparticles were coated with an inner layer of sodium oleate and outer layer of polyethylene glycol 6000 (PEG-6000). This product was investigated by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

In the co-precipitation method, an aqueous solution of 0.1 M cobalt chloride and aqueous solution of 0.2 M ferric chloride was prepared with Fe-to-Co mole ratio of 2:1. An aqueous solution of 0.8 M sodium hydroxide was used as the precipitant agent. The desired amount of aqueous solution of cobalt chloride and ferric chloride were taken and subjected to stirring using a magnetic stirrer for half an hour. Under stirring, the aqueous solution of sodium hydroxide was added drop wise to the mixed solution until a pH = 11.5 was reached. The liquid precipitate was then brought to reaction temperature of 80°C and stirred for 1 h. The product was then cooled to room temperature. The precipitates were filtered and washed several times with deionised water. Finally, the precipitated powders were dried overnight using an oven at 80°C in order to remove excess water. The resulting material was annealed 800°C for 5 h [14].

The polyethylene glycol solution with suitable concentration was prepared by dissolving PEG-6000 powder in distilled water. The mixture of water and cobalt ferrite nanoparticles was vigorously stirred for 15 minutes and then a solution 10 ml sodium oleate was added to the mixture with slow agitation. After stirring for 30 minutes, the mixture was centrifugated 6000 rpm to obtain the stable ferrofluid [15].

The surface morphology of as prepared powder and coated powder were observed by the Carl Zeiss MA15/ EVO 18 scanning electron microscope (SEM). The binding of sodium oleate and polyethylene glycol to the cobalt ferrite nanoparticles was confirmed by Perkin Elmer/

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Spectrum RX I model Fourier transform infrared spectrometer (FTIR) with the range of 4000 cm⁻¹ to 400 cm⁻¹. X-ray diffraction pattern of the prepared nanoparticles was recorded by Bruker D8 diffractometer using CuK α radiation ($\lambda = 0.15406\text{nm}$) with the accelerating voltage of 40 kV and current of 30 mA. Diffraction data were recorded in the range of $10^\circ < 2\theta < 90^\circ$ with a step size of 0.06° and the rate of $0.5^\circ \text{ min}^{-1}$. The X-band electron spin resonance (ESR) of cobalt ferrite nanoparticles studied using JEOL Model JES FA 200 type ESR spectrometer. The measurements were done at 9.3GHz with modulation frequency 100KHz. The readings were recorded in the range of 0 to 800mT with sweep time of 2 minutes with a power of 0.9mW.

3. Result and discussion

3.1 Powder X-ray Diffraction

The XRD pattern of the prepared sample was shown in Figure 1. All the detectable peak could be indexed with the standard reference data (JCPDS: 22-1086). It was clearly seen that the reflection peaks became sharper indicating the enhancement of crystallinity. The lattice parameter such as the values of d, the distance between adjacent planes in the Miller indices

(hkl) was calculated from the Bragg equation ($\lambda = 2d \sin\theta$) and the particle size of the CoFe₂O₄ was determined by the X-ray line broadening method using the Debye-Scherrer equation:

$$D = K \lambda / \beta_D \cos\theta \tag{1}$$

Where D is the particle size in nanometers, λ is the wavelength of the radiation (1.54056 \AA for CuK α radiation), K is a constant equal to 0.9, β_D is the peak width at half-maximum intensity and θ is the peak position. The Density of metal ferrite nanoparticles is calculated by the following formula

$$D = n M / N a^3 \tag{2}$$

Where 'n' is the number of atoms in a unit cell, 'M' is the molecular weight in gram/mol, 'N' is the Avogadro number (6.023×10^{23}), 'a' is the lattice constant (\AA). Particle sizes, indexing values, d-spacing, lattice parameter (a) and density of metal ferrite magnetic nanoparticles were reported in Table 1. The peaks (220) and (311) reveal the formation of spinel phase in metal ferrite nanoparticles. The constant density results are indicating the strong structure formation of metal ferrite nanoparticles.

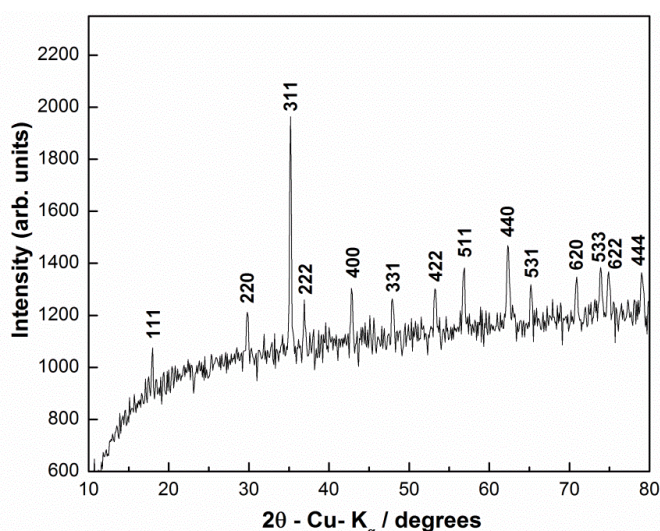


Figure 1. Powder X-ray Profile of cobalt ferrite nanoparticles

3.2. SEM analysis

Scanning electron microscope image (SEM) of CoFe₂O₄ (a) and PEG coated CoFe₂O₄ (b)

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were shown in Figure 2. According to the SEM the agglomeration is very strong in the CoFe₂O₄ nanoparticles. This agglomeration is due to the Van der Waals force between the particles. After the surface coating, there is a decrease in the agglomeration. SEM confirms the successful

coating of PEG which was immobilized on the surface of the CoFe₂O₄ nanoparticles. A coarse surface was obtained after the coating reveals the surface modification. This coarse surface may increase the surface strength of the nanoparticles.

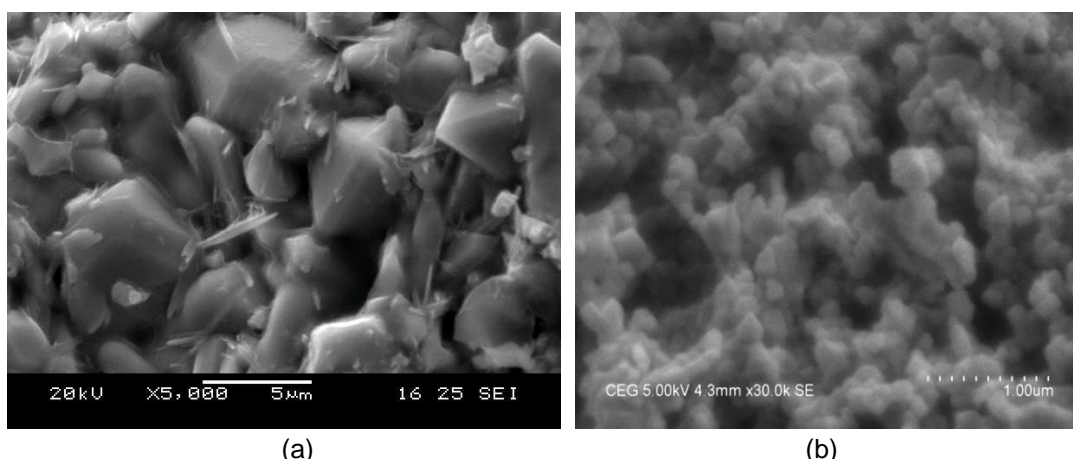


Figure 2 The SEM images of CoFe₂O₄ nanoparticles (a) CoFe₂O₄ (b) coated CoFe₂O₄

3.3. FTIR analysis

Figure 3 shows the FTIR spectrum of bare CoFe₂O₄ nanoparticles (a) and PEG coated

CoFe₂O₄ nanoparticles (b). Infrared studies were carried out in order to ascertain the purity and nature of the cobalt ferrite nanoparticles.

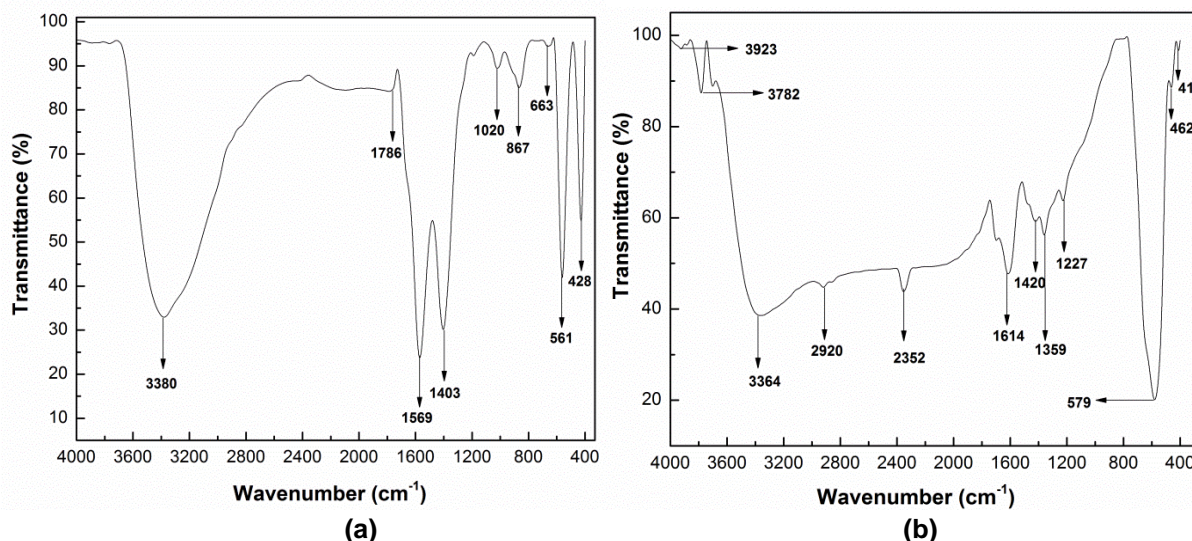


Figure 3. FTIR Spectra of CoFe₂O₄ nanoparticles (a) CoFe₂O₄ (b) coated CoFe₂O₄

The FTIR spectra of CoFe₂O₄ showed transmittance at 579cm⁻¹ relates to Fe-O bond. The transmittance at 462 and 411cm⁻¹

determines in the metal oxide bond (Co-O) in the nanoparticles. The peak observed at 3782cm⁻¹ are assigned to OH group and 3364cm⁻¹ confirms

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the OH stretching and deformation in the bare CoFe₂O₄ nanoparticles. The IR spectra for the coated sample show peak at 3380 cm⁻¹ which is attributed to the O-H stretching vibrations while at 1403cm⁻¹ to the symmetric C-H stretching

vibrations. The peak at 1020cm⁻¹ may be attributed to C-O-C stretching of ether. The strong peaks observed at 561 and 428cm⁻¹ in the coated CoFe₂O₄ confirms the metal oxide bands in spinel structure.

Table 1: Geometric parameters of CoFe₂O₄ nanoparticles

| Peak | Θ (plane) | a (Å°) | d _{hkl} (Å°) | Particle size (D) (Å°) | Density (g/cc) |
|------|-----------------|-----------|--------------------------|---------------------------|-------------------|
| 1 | 9 (111) | 8.53 | 4.847 | 33.51 | 5.02 |
| 2 | 14.9 (220) | 8.47 | 2.968 | 32.84 | 5.13 |
| 3 | 17.585 (311) | 8.46 | 2.531 | 30.81 | 5.14 |
| 4 | 18.45 (222) | 8.43 | 2.424 | 29.82 | 5.2 |
| 5 | 21.4 (400) | 8.44 | 2.099 | 29.33 | 5.18 |
| 6 | 23.965 (331) | 8.23 | 1.926 | 28.41 | 5.58 |
| 7 | 26.595 (422) | 8.43 | 1.713 | 28.56 | 5.2 |
| 8 | 28.45 (511) | 8.4 | 1.615 | 27.29 | 5.26 |
| 9 | 31.17 (440) | 8.42 | 1.483 | 28.92 | 5.22 |
| 10 | 32.585 (531) | 8.46 | 1.419 | 27.65 | 5.14 |
| 11 | 35.45 (620) | 8.4 | 1.3273 | 27.79 | 5.26 |
| 12 | 36.95 (533) | 8.4 | 1.2798 | 26.36 | 5.26 |
| 13 | 37.45 (622) | 8.4 | 1.2652 | 26.99 | 5.26 |
| 14 | 39.5 (444) | 8.4 | 1.2114 | 27.77 | 5.26 |

3.4. ESR studies

The X-band ESR spectrum of cobalt ferrite nanoparticles at room temperature was shown in Figure 4. This spectrum reveals the high spin-

spin relaxation nature due to its high line- width. This ESR line-shape is usually encountered in metals when the itinerant electrons relax their spin state [16-17]. So, the peaks below 30mT (Figure 4.) can be associated with temperature

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independent Pauli spin-susceptibility of itinerant electrons. This would confirm that this peaks definitely are not from local spins which strongly exhibit a Curie spin-susceptibility against temperature. But in the Figure 5, this conduction

electron peaks totally disappear due to the PEG coating. So, the conduction electrons presence in the CoFe₂O₄ nanoparticles leads to form the bond between the protective layers and the particle surface.

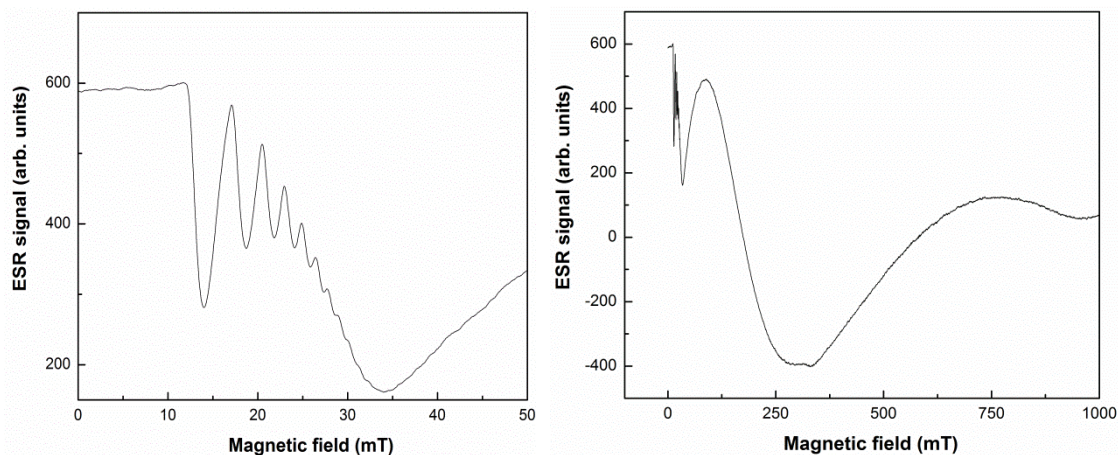


Figure 4. Electron spin resonance spectrum (ESR) of (a) CoFe₂O₄ (b) conduction electrons peaks from graph

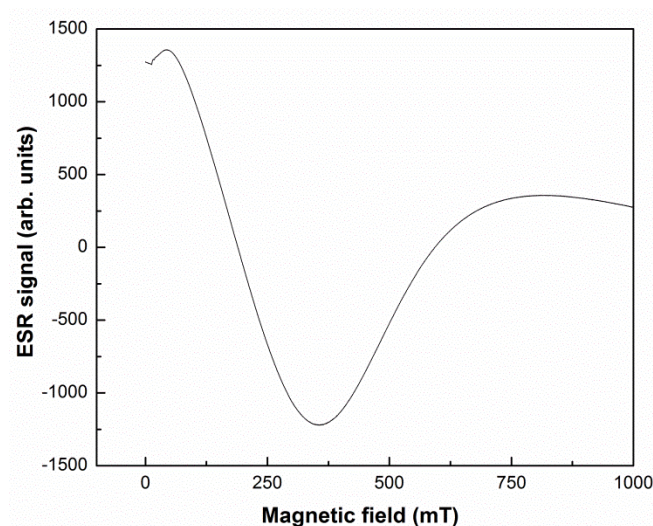


Figure 5. Electron spin resonance spectrum (ESR) of PEG coated CoFe₂O₄

4. Conclusion

The cubic spinel phase of CoFe₂O₄ was prepared by coprecipitation method, the average size of the CoFe₂O₄ nanoparticles is about 29 nm. SEM results confirm the CoFe₂O₄ particles formation. PEG coated surface analysis confirms the fine coating through some coarse structure

and decrease in agglomeration of CoFe₂O₄ nanoparticles. The measurements of FTIR could indicate through the strong transmission peaks that the CoFe₂O₄ nanoparticles were successfully coated by sodium oleate and PEG. From the ESR results, conduction electrons from CoFe₂O₄ nanoparticles play an important role in the bond

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formation between the protective layers and nanoparticles surface. Investigation of the specific surface of hybrid material crystalline phases and morphology of the final compound proved that the obtaining PEG coated CoFe₂O₄

nanoparticles is the hybrid system. The final product presents interesting potential application in biomedicine, due to the fact that shows features of magnetic nanoparticles.

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