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Preparation and characterization of SPION functionalized via caffeic acid

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ABSTRACT

Caffeic acid coated superparamagnetic iron oxide nanoparticles (SPION-CFA) was synthesized by reflux method. The structural, spectroscopic and magnetic properties were studied by X-ray diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), and Vibrating sample magnetometer (VSM) techniques. Thermal gravimetric analysis (TG) and Fourier transform infrared spectroscopy (FT-IR) confirmed the presence of CA on the surface of SPION. The theoretical analyzes performed on recorded room temperature VSM spectrum confirmed the formation of superparamagnetic nature of SPION-CFA. The particle size dependent Langevin function was applied to determine the average magnetic particle dimension (D_{mag}) around 11.93 nm. In accordance, the average crystallite and particle sizes were obtained as 11.40 nm and ~12.00 nm from XRD and TEM measurements. The extrapolated specific saturation magnetization (σ_s) is 44.11 emu/g and measured magnetic moment is 1.83 μ_B. These parameters assign small order of magnetization for NPs with respect to bulk Fe_3O_4. Magnetic anisotropy was offered as uniaxial and calculated effective anisotropy constant (K_{eff}) is 34.82×10^4 Erg/g. The size-dependent saturation magnetization suggests the existence of a magnetically inactive layer as 1.035 nm for SPION-CFA.

1. Introduction

Fe_3O_4 spinel magnetic nanoparticles (MNPs) have been extensively studied both for their technological purpose and scientific work. Due to their strong saturation magnetization (M_s) and good biological compatibility, are widely used in different field such as ferrofluids, magnetic records, catalysts, biomedicines, electronic technique, magnetic resonance imaging (MRI), cells separation, tumor hyperthermia, and magnetic field-guided carriers for localizing drugs [1–8]. A large application of Fe_3O_4, have created great scope towards the research field by the scientists. Each day researchers have been trying to develop them in all aspects. Among various methods for producing Fe_3O_4 MNPs, the reflux method is frequently used because of its advantages as low cost, simple equipment, usual raw materials, easy control of the size of the nanoparticles and precise control of the property and chemical composition of the product [9]. To enhance the compatibility between Fe_3O_4 (magnetite) MNPs and tailor the surface properties or functionalization of MNPs, surface modification of Fe_3O_4 NPs is necessary. Many surfactant stablized Fe_3O_4 MNPs have been synthesized to enhance its biological and industrial application, such as perfluoropolyether carboxylic acid [10], such as oleic acid [1], lauric acid [11], citric acid coated Fe_3O_4[12], humic acid [13], and bilayer oleic acid-coated [14] and heptanoic acid [15].

Caffeic acid is a well known natural aromatic compound derived from the phenyl propanoid pathway in plants. Caffeic acid, have attracted an increased attention by the scientists due to their valuable properties, including antioxidant, anticancer, anti-inflammatory, antiviral, antidiabetic and anti-depressive. Due to its pharmaceutical applications there is an established market for caffeic acid production [16–21]. In this study, Caffeic has many functions: (1) it was used as surfactant to prevent the surface oxidation of SPION and (2) to synthesize the smallest nanosized SPION. Some studies have shown that it inhibits carcinogenesis, and other experiments show carcinogenic effects [22].

For the synthesis of spinel nanocompounds, there are many different synthesis routes [23,24]. Each of them has advangates and disadvantages. Among them, thermal decomposition (polyol) is more pronounced one which can be defined as the heating of precursors in a multi-valent high boiling solvents (with the

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reducing property of them). It has many advantages over the other synthesis routes like high polarity solvents are used and well soluble product can be obtained, well crystallized products can be obtained [25].

Outstanding chemical and biological properties of caffeic acid permit modified Fe_3O_4 MNPs. In this study, we stabilized the Fe_3O_4 NPs by caffeic acid as a surfactant to enhance their biocampatibility and chemical properties. From the best of our knowledge, so far there has been no studies done on caffeic acid modified Fe_3O_4 NPs.

2. Experimental

2.1. Chemicals

$FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, caffeic acid ($C_9H_8O_4$, CA) and NaOH were sourced from Merck and were used without further purification.

2.2. Instrumentations

X-ray powder diffraction (XRD) analysis was conducted on a Rigaku Smart Lab operated at 40 kV and 35 mA using Cu Kα radiation ($\lambda = 1.54059$ 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}.

Transmission electron microscopy (TEM) analysis was performed using a FEI Tecnai G2 Sphera microscope. A drop of diluted sample in alcohol was dripped on the TEM grid.

Scanning Electron Microscopy (SEM) analysis was performed, in order to investigate the microstructure of the sample, using FEI XL40 Sirion FEG Digital Scanning Microscope. 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, over the temperature range 30–750 °C under a nitrogen atmosphere.

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

2.3. Synthesis of SPION

For the typically synthesis of SPION-CFA, 10 ml 0.4 M solution of iron chloride ($FeCl_3 \cdot 6H_2O$) and 10 ml 0.2 M solution of iron chloride ($FeCl_2 \cdot 4H_2O$) were mixed in distilled water. Distilled water was used as the solvent in order to avoid the production of impurities in the final product. A specified amount of caffeic acid was added to the solution as a surfactant and coating material. A 1.5 M solution of sodium hydroxide (NaOH) was prepared and slowly added to the salt solution dropwise. The pH of the solution was constantly monitored as the NaOH solution was added. The reactants were constantly stirred using a magnetic stirrer until a pH level of 7–8 was reached. The liquid precipitate was then brought to a reaction temperature of 80 °C and stirred for 5 h. The product was then cooled to room temperature. To get particles free from sodium and chlorine compounds, the precipitate was washed twice with distilled water and then with ethanol to remove the excess surfactant from the solution. The obtained products were dried at 80 °C for 3 h.

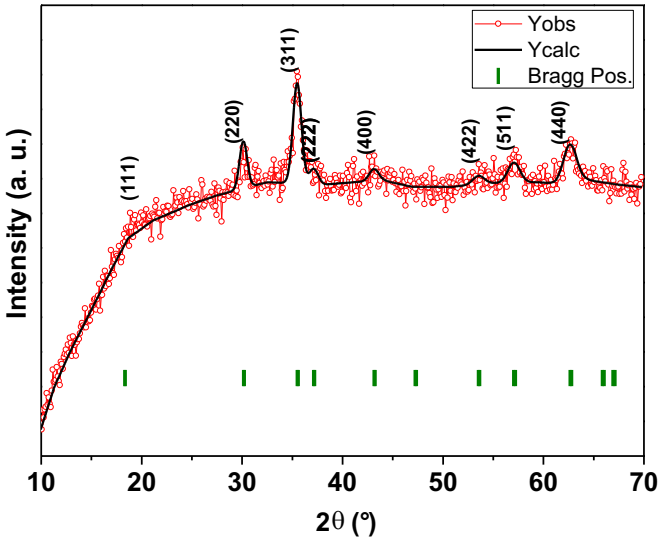

Fig. 1. XRD powder pattern and profile matching of SPION-CFA.

3. Results and discussion

3.1. XRD analysis

The XRD powder pattern of SPION-CFA is presented in Fig. 1. As it can be clearly seen from the Fig. 1, The Rietveld analysis was used for the phase analysis of the product by using the following observed hkl values ((111), (220), (311), (222), (400), (422), (511), (440)). The similar peaks were found for SPION-CFA (Lattice parameter: $a_o = 8.383124$ Å (Fd-3m space group), which reveals that caffeic acid coating does not result in the phase change of bare Fe_3O_4. All of the observed diffraction peaks are indexed by the cubic structure of Fe_3O_4 (JCPDS no. 19-629). The diffraction peaks are broadened owing to very small crystallite size of the product. The calculated average crystallite size (By Scherrer equation), D_{XRD}, is 11.4 nm indicating the nanocrystalline structure of the as-prepared ferrite product.

3.2. FT-IR analysis

FT-IR spectra of both pure CA and SPION-CFA are presented in Fig. 2a and b respectively. A large and intense band at 3450 cm^{-1}

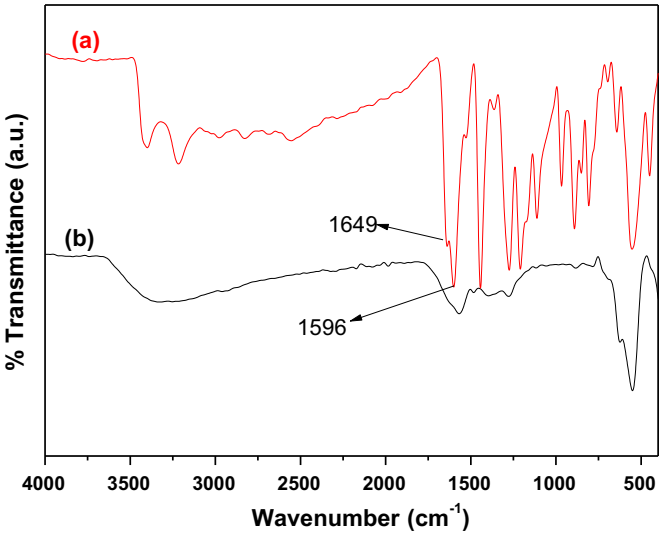

Fig. 2. FT-IR spectra of (a) pristine CA and (b) SPION-CFA.