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Effect of fatty acid chain length and concentration on the structural properties of the coated $CoFe_2O_4$ nanoparticles

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ABSTRACT

The present study investigates the effect of various synthesis parameters including chain length of fatty acids, concentration ratio of precursor to fatty acid, reaction temperature and aging time on the structural as well as magnetic properties of the $CoFe_2O_4$ nanoparticles. The synthesis of nanoparticles was achieved successfully in aqueous solution by the conventional Co-precipitation technique using Fe^{3+} and Co^{2+} ions by the addition of a strong base NaOH. Herein, the Oleic acid and Lauric acid was used as the stabilizing agent during the nucleation stage of the nanoparticles. The structural as well as morphological properties were characterized by XRD, FTIR and FESEM techniques and the magnetic intensity was investigated by vibrational sample magnetometer (VSM). The XRD analysis of the coated nanoparticles confirmed that the cubic spinel phase of the $CoFe_2O_4$ nanoparticles were retained after coating and the crystallite size reduced as the concentration of fatty acid increased. FESEM analysis revealed that the synthesized nanoparticles were of spherical shape and the extent of nanoparticle aggregation reduced gradually as the ratio of precursor to oleic acid was decreased from 4 to 1. Further, the hysteresis loop confirmed the ferromagnetic nature of the coated nanoparticles with high coercivity.

Introduction

Transition metal oxide ferrite nanoparticles such as cobalt ferrite ($CoFe_2O_4$), manganese ferrite ($MnFe_2O_4$), nickel ferrite ($NiFe_2O_4$) and zinc ferrite ($ZnFe_2O_4$) exhibit some unique physical and chemical properties which are significantly different from the bulk materials due to their extremely small size and high surface area. Among the various ferrite nanoparticles, inverse spinel ferrites such as $CoFe_2O_4$ possess excellent chemical stability, high coercivity, moderate saturation magnetization and high crystalline anisotropy. These properties make it a promising agent for drug delivery [1], magnetic resonance imaging (MRI) [2], hyperthermia treatment [3], catalysis [4] and water treatment [5]. Along with the uniformity in the composition and structure, the crystallite size of the nanoparticles should be restricted within the super paramagnetic and single domain scale in order to meet all this applications. Moreover, the critical size of the nanoparticles should be limited in the size range of 30–50 nm in order to achieve the single domain particles. The structure and crystallite size of the nanoparticles are related to the relative interdependence between the nucleation and growth stage, which in turn depends on the various reaction conditions.

Synthesis technique plays an important role in controlling the size and shape of the nanoparticles. A variety of techniques such as co-precipitation [6], thermal decomposition [7], hydrothermal [8], sonochemical [9] and microemulsion [10] have been reported so far for the synthesis of $CoFe_2O_4$ nanoparticles. However, co-precipitation proved to be the most convenient and versatile method because of its simplicity and low reaction temperature.

Ferrite nanoparticles have high surface energy due to their high surface to volume ratio so they tend to aggregate in order to compensate for the effect of surface energy. Also the bare ferrite nanoparticles have high chemical activity and are easily oxidized in air which results in loss of magnetism as well as stability in the proper solvent. Coating of nanoparticles with several organic molecules such as surfactant not only provides a barrier for the particle aggregation but also enhances their further functionalization properties. Naturally available long chain fatty acids such as oleic acid proved to be an effective coating agent for the $CoFe_2O_4$ nanoparticles since there exists a strong chelating bidentate bonding interaction between –COO– group and Fe atom [11]. Ayappan et al. [12] have reported the effect of dielectric constant of the

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solution on the particle size and the saturation magnetization of the $CoFe_2O_4$ nanoparticles coated with oleic acid. The average particle size increases from 10 ± 1 nm to 16 ± 1 nm as the dielectric constant of the solvent is increased from 47 to 80. Paneerselvam et al. [13] have studied the high temperature stability of oleic acid capped $CoFe_2O_4$ nanoparticles. The study shows the decomposition of oleic acid coated $CoFe_2O_4$ nanoparticles into α-Fe and CoO under annealing at 800 °C. Mirabet et al. [14] have reported the high temperature thermal decomposition technique for the synthesis of $CoFe_2O_4$ nanoparticles using olyelamine as stabilizer and solvent. Ligand exchange reaction has also been carried out in order to produce dispersions of the synthesized nanoparticles in polar media. Recently Sirivat et al. [15] have investigated the effect of various fatty acids on the morphology and the magnetic intensity of the Fe_3O_4 nanoparticles. The magnetite nanoparticles were successfully controlled in the size range of 30–50 nm and the surface modification enhances their stability in various solvents.

It may be envisaged that along with various reaction conditions the length of fatty acid hydrophobic chain also plays an important role in controlling the size and interfacial properties of the ferrite nanoparticles. However, the detail investigation on the effect of length of hydrophobic chain on the physiochemical properties of the $CoFe_2O_4$ nanoparticles was not reported in previous literatures. The present study aims at systematic study on the effects of some synthesis variables such as concentration ratio of precursor to fatty acids, reaction temperature, aging time and length of fatty acid chain on the synthesis of $CoFe_2O_4$ nanoparticles. Co-precipitation method was adopted for the synthesis of $CoFe_2O_4$. Different long chain fatty acids namely, oleic acid and lauric acid were used as coating agent in order to examine the effect of chain length on the size and interfacial properties of the coated ferrite nanoparticles.

Experimental

Materials

The reagents used in the experiment, ferric nitrate nona hydrate ($Fe(NO_3)_3{\cdot}9H_2O$), oleic acid ($C_{18}H_{34}O_2$) and lauric acid ($C_{12}H_{24}O_2$) were purchased from Loba Chemie Ltd., India. Cobalt nitrate hexa hydrate ($Co(NO_3)_2{\cdot}6H_2O$), ethanol (C_2H_5OH) and sodium hydroxide (NaOH) were procured from Merck Ltd., India. All chemicals were of analytical grade and used without further purification. Deionised water was used for the reaction. In order to avoid any precipitation of iron oxy-hydroxides prior to synthesis, the solution of Fe (III) and Co (II) were made by dissolving the required amount of metal salts in 0.01 M HCl solution.

Preparation of $CoFe_2O_4$ nanoparticles

The synthesis of $CoFe_2O_4$ nanoparticles was carried out by co-precipitation of Fe (III) and Co (II) in an aqueous solution of NaOH. An aqueous solution of Co $(NO_3)_2{\cdot}6H_2O$ (0.25 M, 25 ml) and Fe $(NO_3)_3{\cdot}9H_2O$ (0.5 M, 25 ml) were mixed at a molar ratio of 1:2 under continuous stirring in a round bottom flask. The initial pH of the solution was maintained at 1.8, which was heated to various desired temperatures (27 °C, 60 °C and 80 °C). 25 ml of 3 M NaOH solution was prepared and added drop wise to the aqueous salt solution under continuous stirring using a magnetic stirrer (Ikon Instruments, India). The reaction mixture was continuously stirred and NaOH solution was added till pH level reached at around 11. The mixture turned into a dark brown precipitate indicating the completion of reaction and formation of ferrite nanoparticles. After a digestion time of 60 min, a specified amount of oleic acid or lauric acid at various concentration ratio (precursor:fatty acid) as 1:1, 2:1 and 4:1) was added as the coating agent and the solution was maintained at the desired temperature under continuous water reflux for various aging time (2 h, 6 h and 8 h). The solution was then cooled to room temperature (27 °C). Thereafter the resulting precipitates were washed with deionised water to remove impurities followed by washing using ethanol to eliminate excess fatty acids from nanoparticles. The precipitate was then dried at 105 °C for 8 h. The product was then grinded into fine powder and then calcined at a temperature of 600 °C for 6 h. The final product was characterized for the evaluation of various structural as well as magnetic properties.

Characterization of the $CoFe_2O_4$ nanoparticles

The nanoparticle so obtained was characterized by X-ray diffraction (XRD), Fourier transform infrared spectrometry (FTIR), field emission scanning electron microscopy (FESEM) and vibrating sample magnetometer (VSM) analysis for the evaluation of various properties. The $CoFe_2O_4$ nanoparticles were characterized for the presence of various functional groups by the FTIR (Make: Perkin Elmer, USA, Model: LR 64912C). FTIR analysis was performed with the KBr-supported technique in the range of 450–4000 cm^{-1} with a scanning rate of 40 and a resolution of 4 cm^{-1}. A wide angle X-ray diffractometer (Bruker D8) was used to study the crystallite structure of the nanoparticles. Scanning was done from high angle 2θ value between 20° and 75° at a speed of 0.5 s/° in continuous mode at an increment of 0.05. XRD patterns were obtained using radiation (Cu Kα = 0.154 nm). The X-ray source was operated at 40 kV and 20 mA. The mean crystallite size of the crystals is determined by the Scherrer equation [16]. FESEM (Zeiss LSM 510 Meta) was used to examine the morphological structure and to measure the average particle size. The analysis was done by LEO 1430 vp at 5 kV at magnification of 240KX. The magnetic properties of the synthesized nanoparticles were investigated by the vibrating sample magnetometer (VSM; Lakeshore 7410). The hysteresis loops were measured under a magnetic field strength of 15,000 Gauss at room temperature. The data were taken with 80 points/loop with a scan speed 10 s/point.

Results and discussion

FTIR analysis

The FTIR spectra of the $CoFe_2O_4$ nanoparticles synthesized at 80 °C, pH 11, for 2 h aging time with different concentration ratio of precursor to oleic acid are shown in Fig. 1. The high frequency bands in the range of 594 cm^{-1} corresponds to the vibration of Fe–O bonds. The strong peaks at 1403 cm^{-1} and 1504 cm^{-1} are due to the symmetric and asymmetric stretching vibration of the carboxyl group (–COO–) and the bands at 2852 cm^{-1} and 2953 cm^{-1}

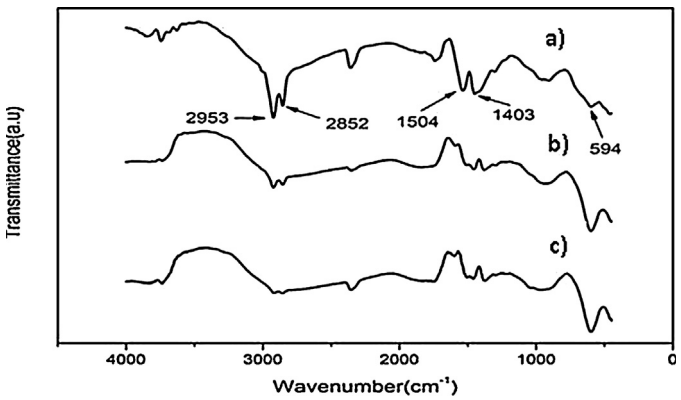

Fig. 1. FTIR spectra of the oleic acid coated $CoFe_2O_4$ samples synthesized at different ratio of precursor:oleic acid. (a) 1:1, (b) 2:1 and (c) 4:1.