



SYNTHESIS OF COBALT FERRITE (CoFe₂O₄) NANOPARTICLES BY CO-PRECIPIATION ROUTE

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Cobalt ferrite (CoFe₂O₄) nanoparticles have been synthesized by co-precipitation route in the size range 15-25 nm. The X-ray diffractometer (XRD) and Transmission Electron Microscopy (TEM) analyses of the samples confirmed the formation of single phase cobalt ferrite (CoFe₂O₄) nanoparticles. The size of the particles was studied as a function of annealing temperature and annealing time. It was found that the size of nanoparticles increases linearly with annealing temperature and time due to the coalescence process. Magnetic characterization of samples at room temperature includes DC magnetization hysteresis loops (M-H loops), coercivity (H_C) and saturation magnetization (M_S), confirmed the formation of core shell structure of CoFe₂O₄ nanoparticles. Relatively large coercivity at room temperature compared to micro (bulk) CoFe₂O₄ revealed that Co⁺² ions have large effective anisotropy constant (K_{eff}) and strong magnetocrystalline anisotropy in nano-range. Moderate magnetization was observed due to the inert or canted spin layer at the surface of these nanoparticles which prevents the core spins to align along the field direction.

Keywords : Cobalt Ferrite, Nanoparticles, XRD, TEM, Coercivity and Magnetic nanoparticle

1. Introduction

Cobalt ferrite nanoparticles have many interesting technological, medical and industrial applications. They are used in high frequency applications, recording devices, color imaging, computers and electronic industries. Cobalt ferrite being a well-known hard magnetic material, due to its physical and chemical stability, make it suitable for magnetic recording applications such as audio and videotape and high-density digital recording disks etc. [1, 2]. In the field of medicines, they are used as contrasting agents in magnetic resonance imaging applications (MRI), replacement of radioactive materials used as tracers and delivery of drugs to specific areas of the body [3], where conventional techniques fail for delivery of drugs. The magnetic character of nanoparticles used for recording media depends essentially upon the size, shape and purity. These particles should be single domain, magnetically blocked, having high coercivity, suitable superparamagnetic blocking temperature and moderate magnetization. Various techniques have been used for preparation of nanoparticles. These include; vapor phase reactions [4], evaporation condensation [5], sol-gel processing [6], matrix isolation [7], laser induced vapor phase reaction and aerosol [8] etc.

Generally, it has been observed that control of particle size and its distribution is difficult in nanoparticles prepared by the most of the above methods [2]. In coprecipitation method the control of particle size & its distribution is relatively easy and there is no need of extra mechanical or microwave heat treatments.

The present work deals with synthesis of cobalt ferrite (CoFe₂O₄) nanoparticles by co-precipitation method with heat treatment (annealing) at a temperature ≥ 600 °C. The size and size distribution was controlled by controlling the relative nucleation and growth rates of the particles during the synthesis process. Magnetic characterization of the synthesized samples was also carried out.

2. Experimental

2.1 Chemicals

The chemicals used during synthesis of CoFe₂O₄ were ferric chloride (Fe₃Cl₂.6H₂O) and cobalt chloride (CoCl₂.6H₂O) of HPLC Grade as the starting salts, sodium hydroxide (NaOH) as the precipitating agent, oleic acid and sodium dodecyl sulfate (NaDS) as the surfactant and dispersing medium. All the materials were reagent grade and used without further purification. Double distilled,

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de-ionized water was used as the solvent.

2.2 Synthesis

0.4M solution of ferric chloride ($\text{Fe}_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$) and 0.2M solution of cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) were mixed together in a beaker. 3M solution of sodium hydroxide (NaOH) was then added dropwise to the mixture solution. The reactants were then constantly stirred using a magnetic stirrer until pH more than 12 was achieved. A specified amount of oleic acid (3-4 drops) was added to the solution as the surfactant and coating material [9]. The mixture was then brought to a reaction temperature of 80 °C and stirred for 45 minutes. When the reaction was completed, the mixture was cooled at room temperature and centrifuged @ 2000 rpm for 10 minutes. The precipitate was washed twice with distilled water and dried the synthesized material overnight in static oven at 100 °C. The acquired material was grinded into fine powder. The fine crystalline cobalt ferrite (CoFe_2O_4) was achieved after annealing the grinded material for 6 hours. We synthesized four samples with average sizes of 15 ± 3 , 19 ± 3 , 23 ± 3 and 25 ± 3 nm. Each sample was annealed at different temperature (600, 650, 700 and 750 °C) to get different sizes of CoFe_2O_4 nanoparticles. The size variation and control has been achieved both by the rate of reaction and the annealing conditions [10].

2.3 Characterization

Physical characterization (size determination) of the particles was performed by X-ray diffractometer (model JDX-11 of Joel Company Ltd., Japan) and Transmission Electron Microscope (Model 120 kV, Philips, 400). For nano-size determination, Debye Scherrer formula was used by comparing the strongest peak in the XRD pattern. Magnetic characterization of CoFe_2O_4 nanoparticles was performed at room temperature by using vibrating sample magnetometer (VSM, model BHV-50 of Riken Denish Company Ltd., Japan) with maximum applied field upto 6 kOe. The coercivity and saturation magnetization for one of the representative samples (25 nm) of CoFe_2O_4 were calculated and have been discussed in the subsequent section.

3. Results and Discussion

Figure 1 shows the X-ray diffraction pattern of the prepared CoFe_2O_4 . The XRD pattern was compared with standard PDF Card for CoFe_2O_4 showing that the final product was cobalt ferrite with inverse spinel structure. No extra peaks were present in the XRD pattern. It was confirmed that

the sample prepared was cobalt ferrite of pure phase with no impurities. Figure 2 shows the TEM image of CoFe_2O_4 particles annealed at 700 °C for 6 hours. In the figure, it is seen that some particles are spherical in shape and a few are elliptical. Some agglomerated particles are also observed in the image. It was found that agglomeration increases linearly with annealing temperature. The size of the particles was measured both from XRD pattern using Scherrer formula and TEM image using standard bar (20 nm) given in the image. Both the results were found in good agreement with each other.

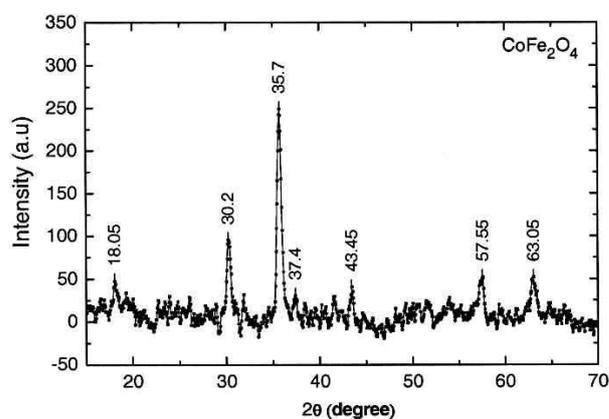


Figure 1. X-ray diffraction pattern of CoFe_2O_4 nanoparticles prepared by co precipitation route, after annealing at 700 °C for 6 hrs with average crystallite size of about 23 nm.

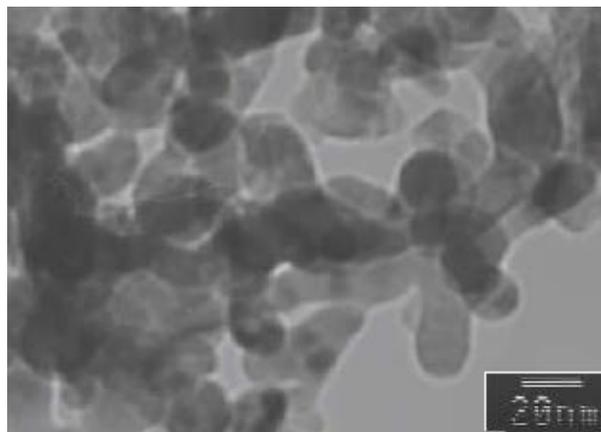


Figure 2. TEM micrograph of CoFe_2O_4 nanoparticles synthesized after annealing at 700°C for 6 hrs

Figure 3 shows the variation of particle size with annealing temperature at constant annealing time (6 hrs). It is clear from the figure that particle size increases linearly with annealing temperature. This increase in size of the particles was due to the coalescence process in these particles at high

temperature that results in increasing the average size of the particles [11]. Figure 4 shows the dependence of particle size on annealing time at constant annealing temperature (600 °C). This indicates that longer annealing time enhances the coalescence process which in turn increases the particle size. Thus it was observed that particle size can be controlled by varying the annealing temperature and time. Smaller and uniformly distributed particles were obtained if the nucleation rate was higher than the growth rate. High pH values i.e. >12 of the reaction was maintained for high yield. The advantage of this method (co-precipitation) over the other methods like sol-gel, chemical vapor deposition, vapor phase reactions etc is that the control of production of ferrite particles, and its size & size distribution is relatively easy and there is no need of extra mechanical or microwave heat treatments.

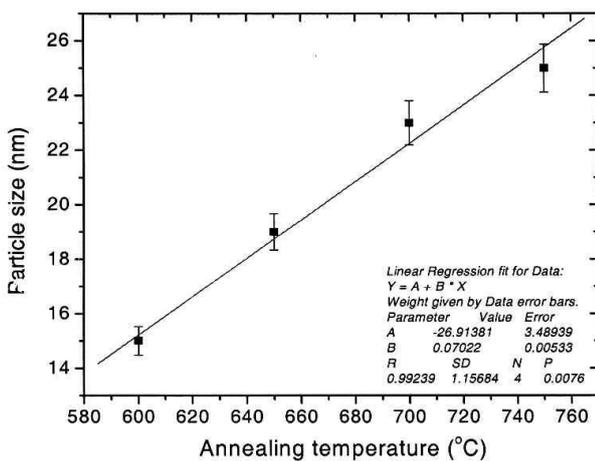


Figure 3. Particle size (nm) as a function of annealing temperature (°C) for CoFe₂O₄ nanoparticles at annealing time of 6 hrs.

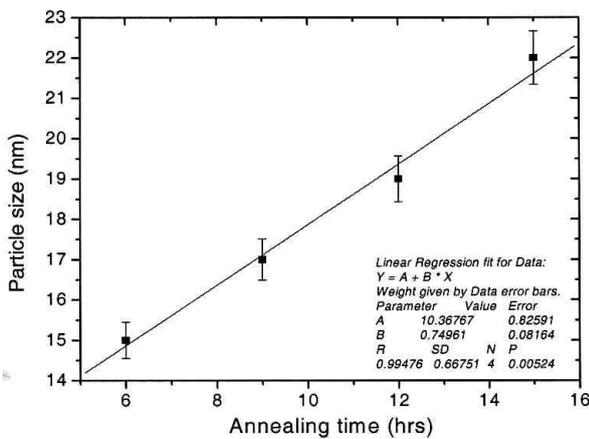


Figure 4. Particle size as a function of annealing time (hrs) for CoFe₂O₄ nanoparticles prepared at 600 °C annealing temperature

Figure 5 shows the magnetization (hysteresis) loop of cobalt ferrite nanoparticles at room temperature. The figure revealed that cobalt ferrite (CF) has a coercivity of ~1080 Oe and saturation magnetization of ~68 emu/gm. The value of coercivity in CF nanoparticles was found much higher than its micro (bulk) coercivity value (> 750 Oe) and its saturation magnetization was smaller than its micro value (~ 80.8 emu/gm) [12, 13]. The high coercivity in cobalt ferrite nanoparticles is due to the cobalt ions that have high magnetocrystalline anisotropy at small sizes that increases the effective anisotropy constant of cobalt ferrite which in turn increases the coercivity of nanoparticles (according to the relation $H_c = 2K_{eff}/M_s$) [10, 12, 14]. The second explanation for the increased coercivity in case of nanoparticles is the increase of effective anisotropy constant (K_{eff}) due to the contribution of surface anisotropy constant (K_s) (according to the relation $K_{eff} = K_{bulk} + (6/d)K_s$) that plays more important role in case of nanoparticles due to the pronounced surface to volume ratio of atoms [15]. The decrease in saturation magnetization in CF nanoparticles is due to inert or dead layer [5, 9] around the nanoparticles at the surface (shell) that prevents the core ferrimagnetic spins to align along the field direction.

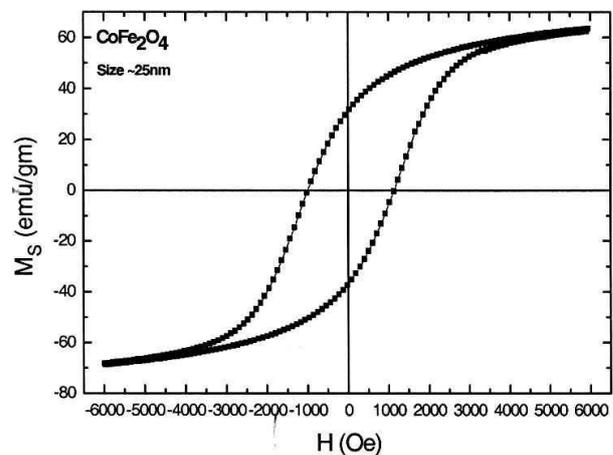


Figure 5. Hysteresis loop for 25 nm CoFe₂O₄ nanoparticles at room temperature at maximum applied field upto 6 kOe.

As a result the saturation magnetization in case of nanoparticles decreases. Another explanation for the smaller magnetization in nanoparticles is the canted spins or spin glass like layer [16, 17] at the surface of nanoparticles that arises due to the larger fraction of surface to volume atoms in small particles. These canted spins can cause the reduction of saturation magnetization in these

nanoparticles. Due to these canted spins at the surface (shell) of nanoparticles, no true saturation in these particles is achieved even at very high applied field. This effect alongwith core/shell structure in cobalt ferrite has been discussed in detail elsewhere [14, 18].

4. Conclusion

CoFe₂O₄ nanoparticles in the size range 15-25 nm have been synthesized by coprecipitation method. The size of the nanoparticles appeared to increase linearly with annealing temperature and time most probably due to coalescence that increases linearly with annealing temperature and time. The particle size and its distribution were controlled by controlling the nucleation and growth rates of the reaction. The very high coercivity in CF was due to the pronounced contribution of surface anisotropy constant (K_{surf}) towards the effective anisotropy constant (K_{eff}) in cobalt ferrite nanoparticles. The smaller value of M_s is attributed to either due to the inert or dead layer at the surface of nanoparticles or due to the greater fraction of surface spins in these particles that tend to be in a canted or spin glass like state with reduced net magnetic moment in these particles.

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