

Synthesis of CoFe_2O_4 Magnetic Nanoparticles by Thermal Decomposition

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The amine functionalized CoFe_2O_4 nanoparticles were prepared by thermal decomposition method at reflux temperatures 160 °C and 172 °C. The obtained CoFe_2O_4 nanoparticles at 160 °C reflux temperature show aggregation free poly-dispersed nanoparticles in 4-15 nm range. In an elevated reflux temperature of 172 °C, CoFe_2O_4 show aggregated poly-dispersed nanoparticles in the size range of 20-46 nm. The saturation magnetization value at 300 K exhibited 51 emu/g at reflux temperature of 160 °C. However, the sample synthesized at an elevated temperature of 172 °C has shown a coercive field value of 560 Oe with saturation magnetization of 68 emu/g.

Keywords : CoFe_2O_4 nanoparticles, thermal decomposition, superparamagnetic

1. Introduction

Magnetic materials have the potential to be used for numerous scientific and technological applications, ranging from memory devices [1] and electromagnetic devices [2] to medical diagnostic and drug delivery [3]. Magnetic materials with its energy storage property are said to be hard magnetic materials, which are promising for data storage applications [4]. Also, magnetic nanoparticles with its low loss property are said to be soft magnetic materials, which can be used in biomedical engineering for diagnostics [5] and in microwave engineering as inductor cores [6]. Among various kinds of magnetic nanoparticles, Cobalt ferrite plays extensive interest in the fields of hyperthermia as heat generators [7], as carriers for targeted drug delivery [8] and in microwave engineering as inductor core materials [9]. This is because of its fine tunability of particle size from superparamagnetic to ferromagnetic range and also its chemical (as well magnetic) stability under ambient conditions. In recent days, variety of chemical & physical methods such as sol-gel processing [10], spray drying [11], ball-milling [12], matrix isolation [13], hydrothermal [14], micro-emulsion [15], chemical co-precipitation [16], auto-combustion method [17], sputtering [18], Pulsed laser deposition [19] have been employed for the preparation of well-defined, magnetic nanoparticles with specific

shape and size. Generally, the synthesis of nanoparticles with narrow diameter distribution, high saturation magnetic moment and magnetic stability using non-toxic chemicals has been yet a challenging task. In order to accomplish this, thermal decomposition was used for the formation of homogeneous nanoparticles of cobalt ferrite [20]. Long time heat treatment and hence prolonged evaporation/condensation of solvent allows decomposition of reaction mixture and it results in the reduction of metal ions to form neutral atoms, which initiates nucleation of CoFe_2O_4 particles. The overall reaction parameters relevant to the control of particle size, shape, distribution are reflux time, temperature, the concentration of precursors, reducing agents, and the nature of surfactants serving as the capping agent. However, in particular, the growth of nanoparticles and their aggregation is manipulated by the addition of surfactants and reflux temperature. One of the advantages of this method is that the control of production of ferrite particles, its size and size distribution is relatively easy and there is no need of additional heat treatments and toxic gases. The present work concerns with the influence of reflux temperature on nanoparticles size distribution and its influence on magnetic behavior. Although the nanosized CoFe_2O_4 particles can be obtained by thermal decomposition method, the optimization of parameters for synthesis are still required to control particle size and uniformity. In this paper, we have attempted to study the effects of reflux temperature on particle size and magnetic property of the CoFe_2O_4 nanoparticles.

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2. Experimental Procedure

CoFe₂O₄ nanoparticles were prepared by thermal decomposition of cobalt chloride hexahydrate (CoCl₂·6H₂O) and ferric chloride (FeCl₃) in ethylene glycol (which acts as solvent & reducing agent) in presence of sodium acetate and ethanol amine (surfactants). Briefly, anhydrous FeCl₃ (5.464 g, 25.2 mmol) and CoCl₂·6H₂O (4.608 g, 12.6 mmol) were dissolved in 240 ml ethylene glycol at room temperature and then 4 g of sodium acetate was added to it. The reddish black color solution thus obtained was mechanically stirred for 30 min at 110 °C followed by the addition of 93 ml of ethanol amine. Subsequently, the bath temperature was raised to 160 °C and kept at that temperature for 6 hours. During heat treatment, the entire solution was refluxed using a condenser setup for 6h under high N₂ flow rate. During reflux, fine black colloidal particles appeared in the reaction mixture. Then it was allowed to cool down naturally. After added ethanol, the CoFe₂O₄ colloidal particles were separated from the supernatant solution by using a hard magnet. Further, the obtained products were washed with ethanol for several times and then dried in rotary vacuum for 2 h at 50 °C. In the same manner, the CoFe₂O₄ nanoparticles were synthesized at an elevated reflux temperature of 172 °C. The basic reaction scheme for the formation of CoFe₂O₄ is as follows.

Metal chlorides + Na-acetate + ethylene glycol (ethanol-amine 110 °C) → metal acetate complex + NaCl (160 °C, 6 h reflux) → NH₂ functionalized CoFe₂O₄ + supernatant solution

The nucleation and growth involves the reduction of metal precursors to form metal complexes and their decomposition at 160 °C reflux temperature in an organic solvent under inert atmosphere. Reaction rate in thermal decomposition reaction depends upon various factors such as the concentration of metal precursors, surfactants, reducing agents and temperature [21]. In this work, we were interested to know the optimal temperature to obtain well dispersed, uniform in size and shape of nanoparticles. We synthesized CoFe₂O₄ products at two different reflux temperatures to acquire nanoparticles with diverse physical and magnetic characteristics. It was noticed that the boiling of the reaction mixture commenced slowly at 160 °C and its ultimate boiling temperature was observed to be up to 172 °C. The starting and the ultimate boiling temperatures of the reaction mixture are always inconsistent and are modifiable. These values are solely dependent on constituents of reaction mixture such as ethylene glycol to ethanolamine ratio. Consequently, we were interest-

ed to obtain CoFe₂O₄ products at two different reflux temperatures, namely 160 °C and 172 °C. The crystallographic structure of the CoFe₂O₄ products were studied with a Panalytical X'pert MPD advanced X-ray diffractometer (Cu K α radiation, $\lambda = 1.544 \text{ \AA}$). To obtain specimens for micro structural investigations, 2 μL of the colloidal solutions were dropped onto carbon coated transmission electron microscopy (TEM) Cu grids and then dried. Conventional TEM studies were performed using a Philips CM 100. SQUID magnetometry (Quantum Design MPMS-XL) was used to obtain field dependent magnetization measurements at room temperature condition.

3. Results and Discussion

The diffraction patterns of the samples refluxed at 160 °C and 172 °C are given in Fig. 1. The broadening nature of the diffraction peaks indicates the particles are in nanometric regime. Enhanced broadening of diffraction peaks were seen for the sample obtained at a reflux temperature of 160 °C than that obtained at a reflux temperature of 172 °C. This shows low temperature treatment inhibits the possibility of agglomeration and so reduce particle size. Also, the diffraction patterns obviously show intense peaks along (220), (311), (400), (511) and (440) plane directions. In addition, small peaks

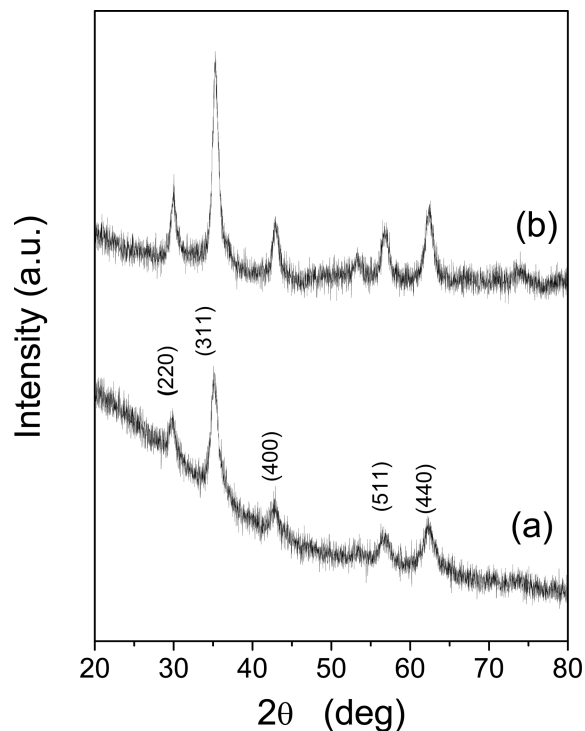


Fig. 1. X-ray diffraction patterns of CoFe₂O₄ nanoparticles prepared at reflux temperatures of (a) 160 °C and (b) 172 °C.

along (111), (422) and (533) planes were also noticed. All these reflections confirm the inverse spinel structure of CoFe_2O_4 with face centered cubic unit cell [22]. The lattice parameter (a) was calculated by using the relation, $a = d(h^2 + k^2 + l^2)^{1/2}$, where d is the interplanar spacing and h, k, l are Miller indices [23]. The calculated value of lattice constant 'a' from (400) reflection was 8.396 Å. This value is nearer to the reported value of that of CoFe_2O_4 ($a = 8.391$ Å) (22-1086). The mean crystal size (D_{hkl}) was estimated from the line broadening of XRD pattern using Debye-Scherrer formula $D_{(hkl)} = (k \times \lambda) / (\beta \times \cos \theta)$ where k is a shape factor (0.94 for spheres), λ is X-ray wavelength (1.541 Å), β is the corrected width of the XRD peak at half height and θ is the corrected reference peak width at angle θ [22]. The evaluated mean diameters of the particles were around 5 and 13 nm for the samples obtained at reflux temperatures of 160 °C and 172 °C, respectively.

At high reflux temperature, the enhanced evaporation/condensation rate of reaction mixture causes increased reduction rate of metal ions, which aids rapid nucleation and growth of cobalt ferrite particles. However, at low reflux temperature, the slow evaporation/condensation rate of reaction mixture causes decreased reduction rate of metal ions and it results in small sized particles.

TEM was used to investigate the length scale and shape of the nanoparticles synthesized at different reflux temperatures. The TEM photographs are shown in Fig. 2. The low magnification of TEM photographs (Fig. 2(a) and (c)) of the samples obtained at 160 °C and 172 °C shows well dispersed and aggregated nanoparticles, respectively. The high magnification image (Fig. 2(b)) of the sample refluxed at 160 °C assures well dispersed, spherical nanoparticles with narrow distribution of size. The average value of CoFe_2O_4 nanoparticles size varies in the range of 4-15 nm. The high resolution image clearly shows the amine functionalized CoFe_2O_4 nanoparticles. The CoFe_2O_4 nanoparticles are seen as dark hue due to its high electron density. It is also noticed that amine functionalization surrounding the nanoparticles is obviously perceptible for larger nanoparticles. The amine functionalization surrounding nanoparticles appear as grey hue due to its low electron density. The thickness of amine functionalization was approximately about 4 nm. In the high resolution image (Fig. 2(d)) of sample refluxed at 172 °C, the nanoparticles were aggregated together to form larger particles due to the rapid evaporation/condensation rate aided nucleation & growth mechanism. The high magnification image assures nanoparticles with different sizes due to the aggregation of particles. The average particle size varies in the range of 20-46 nm. In this case, thickness of amine function-

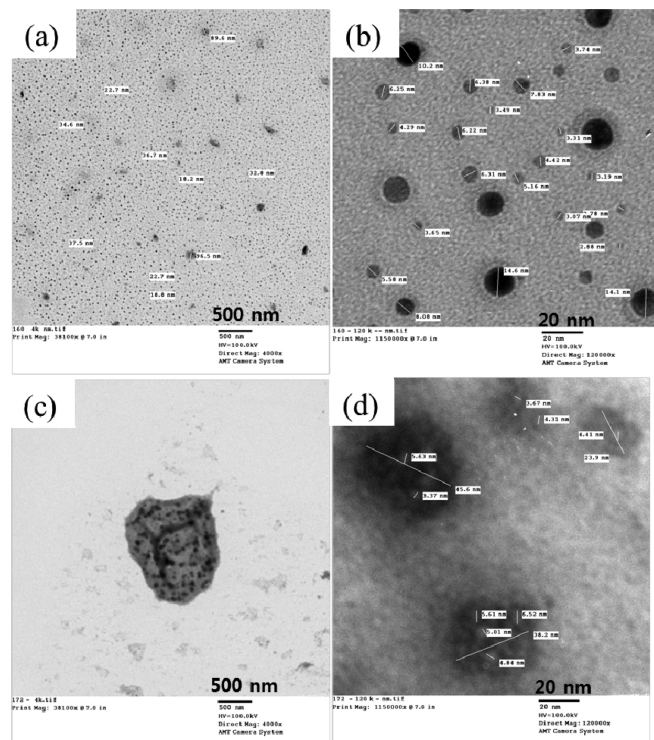


Fig. 2. Low and high resolution TEM images of CoFe_2O_4 nanoparticles prepared at reflux temperatures of 160 °C (a, b) and 172 °C (c, d), respectively.

alization is approximately about 8 nm. For both the samples, it is identified from TEM photographs that the average crystallite size is 4-5 nm, which tend to aggregate and grow into different sizes based on reflux temperature and time. This indicates that in thermal decomposition method, reflux temperature and time plays a key role in controlling particle size by means of agglomeration of crystallites. It is also noted that the average particle sizes obtained from X-ray line broadening technique matches well with the sizes of smaller nanoparticles measured using TEM observation for the samples obtained at 160 °C and 172 °C. One understanding from TEM observation is that our samples have wide range of particle size distribution. The smallest particles are dominant for the sample refluxed at 160 °C, whereas larger particles are dominant for the sample obtained at an elevated reflux temperature of 172 °C.

The field dependent magnetization curves measured at room temperature for the CoFe_2O_4 nanoparticles prepared at different reflux temperatures as shown in Fig. 3. By using Arrott plot analysis, the values of magnetic moment (M) in low magnetic field region can be clarified for distinction of the superparamagnetic and ferromagnetic phase due to the remanence magnetic moment at zero magnetic field. In the Arrott plot, the intercept of a linear

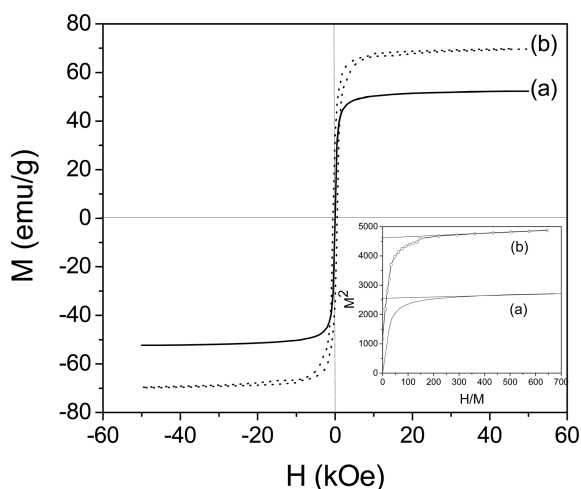


Fig. 3. Magnetization curves of CoFe_2O_4 nanoparticles prepared at reflux temperatures of (a) 160°C and (b) 172°C . Inset shows the Arrot plot analysis.

M^2 versus H/M plot, extrapolated to H/M from high magnetic fields, corresponds to the square of saturation magnetic moment (M_s^2) [24]. The measured values of saturation magnetization (M_s) was about 51 and 68 emu/g for the products obtained at reflux temperature of 160°C and 172°C , respectively. These values are less than the corresponding saturation magnetization value of its bulk counterpart [25]. The decrease in saturation magnetization value could be attributed to a decrease in particle size due to surface capsulation by ethanolamine and also due to the structural distortion in the surface layer of nanoparticles. The smaller particles with structural distortion in the nanoparticle surface compared to its bulk form in which it could reduce the number of moments contributing for magnetic moment. Also, it is obvious that a significant difference in magnetization curves were noticed for the samples prepared at two different temperatures. The product obtained at a reflux temperature of 160°C shows approximately zero coercive field and remanence magnetization, which are characteristics of superparamagnetic behavior. The observation of zero remanence magnetization and coercive field values at room temperature ensures minimal or no magneto static exchange interactions when the external magnetic field is switched off. It means that thermal energy can triumph over anisotropy energy barrier of single particle and the net magnetization of nanoparticles in the absence of an external field is become zero. This assures that there are no magnetic exchange interactions amongst nanoparticles and each nanoparticle acts as single magnetic domain when the applied magnetic field attain zero. Such that, there is no agglomeration of CoFe_2O_4 nanoparticles prepared at a reflux

temperature of 160°C . Contrarily, a hysteresis loop exhibited wider for CoFe_2O_4 nanoparticles prepared at reflux temperature of 172°C than that of 160°C . Improved saturation magnetization of 78 emu/g with a coercive field of 560 Oe. These results show that the reflux temperature plays an important role in controlling size distribution and aggregation of CoFe_2O_4 nanoparticles, which will significantly, influences the magnetic properties such as permeability and coercivity of the products.

4. Conclusion

The study demonstrates that reflux temperature was found to affect particle size, morphology (agglomeration) and so magnetic property. The diameter of the CoFe_2O_4 particles prepared at 160°C varied in the range 4-15 nm. On the contrary, the product prepared at 172°C was highly aggregated with an average size of 20-46 nm. Furthermore, the magnetic studies provide an excellent superparamagnetic nanoparticulate system for the product prepared at 160°C . To obtain the superparamagnetic CoFe_2O_4 nanoparticles, the evaporation/condensation rate of reaction mixture should be controlled within their boiling temperature for reduction rate of metal ions for regulation of particle size and their distribution in thermal decomposition method.

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