

Superparamagnetic Cobalt Ferrite Nanoparticles: Effect of Temperature and Base Concentration

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Abstract Cobalt ferrite nanoparticles were coprecipitated in air medium using NH_3 , and the effects of temperature and base concentration on the properties were studied. X-ray diffraction (XRD) technique and Fourier transform infrared spectroscopy were used to investigate the structural properties of the samples. Particle sizes and shapes were determined by a transmission electron microscope (TEM). Magnetic measurements were done using vibrating sample magnetometer at room temperature. The proper reaction temperature was found to be 80 °C for the synthesis of superparamagnetic cobalt ferrite nanoparticles. The effect of base concentration on the properties of the superparamagnetic nanoparticles was investigated under this temperature. The magnetization values of cobalt ferrite nanoparticles increased as the base concentration increased and reached to a value of 32.4 emu/g with zero coercivity. The particle sizes (d_{XRD} , d_{TEM} , and d_{VSM}) of cobalt ferrite nanoparticles were calculated from XRD patterns, TEM images, and magnetic data, respectively. It was observed that the d_{TEM} and d_{VSM} are similar to each other, and the d_{XRD} are bigger than those with the similar trend of increase with the increase of base concentration.

Keywords Coprecipitation · Cobalt ferrite nanoparticles · Superparamagnetism · Reaction temperature · Base concentration

1 Introduction

Magnetic nanoparticles have attracted much interest due to their useful properties in many technological areas, such as magnetic recording [1], magnetic fluids [2], MRI contrast agents [3], hyperthermia treatment [4], and targeted drug delivery [5, 6]. Ferrite nanoparticles (Fe_3O_4 , CoFe_2O_4 , NiFe_2O_4 , ZnFe_2O_4 , etc.) have different applications because of their different properties. Among these ferrites, cobalt ferrite nanoparticles have useful properties such as high magnetocrystalline anisotropy and large magnetostrictive coefficients, for magnetic recording and hyperthermia applications [7]. Besides, cobalt ferrite nanoparticles can show superparamagnetism when the particle size is below a critical value of ~6–8 nm as reported in [7]. Coprecipitation, hydrothermal synthesis, and thermal decomposition are the main synthesis techniques to obtain cobalt ferrite nanoparticles. Among them, coprecipitation is a simple and economical way to obtain superparamagnetic nanoparticles [8, 9]. In this technique, cobalt ferrite nanoparticles are synthesized from a solution containing Co^{+2} and Fe^{+3} ions. The particle sizes and magnetic properties of the nanoparticles can be tailored by changing reaction conditions, such as reaction temperature, base concentration, and annealing temperature. There has been limited number of studies on reaction temperature and base concentration.

Kim et al. [10] coprecipitated cobalt ferrite nanoparticles at different temperatures by using NaOH and investigated the structural and magnetic properties. Zhang et al. [11] synthesized cobalt ferrite nanoparticles by changing NaOH

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concentration. In [12], different concentrations of NaOH were used for the coprecipitation at room temperature.

In this study, the cobalt ferrite nanoparticles were synthesized by coprecipitation using various NH_3 concentrations in air medium after obtaining the proper reaction temperature. And, the properties of the nanoparticles were investigated. It is seen that the synthesized cobalt ferrite nanoparticles are superparamagnetic and a quite high magnetization value of 32.4 emu/g was obtained.

2 Experimental

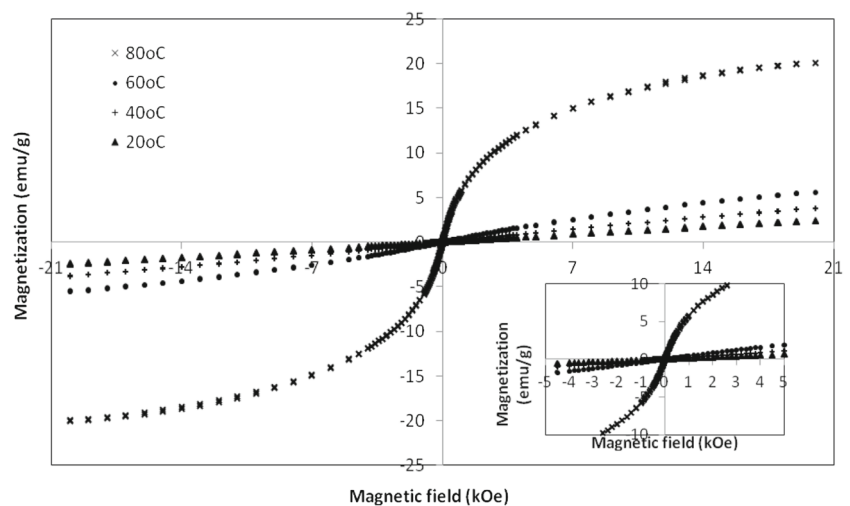
For the co-precipitation, 2.38 g cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Fluka > 98 %) and 5.48 g ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ Sigma Aldrich > 99 %) were used. Ammonium hydroxide (NH_4OH , Merck 25 %) was used for the base source. One hundred milliliters NH_3 solution was added to 100 ml ion salt solution under vigorous stirring. The reaction was performed in air medium for 60 min. After the reaction, the precipitate was washed three times with distilled water and was dried in an oven. The reaction temperature was changed from 20 to 80 °C. And then the base concentration was changed between 0.5 and 9.0 M at a fixed temperature. The crystal structure of the nanoparticles was investigated with X-ray diffractometer (XRD, PANalyticals X'Pert PRO) between 20° and 80° by using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Fourier transform infrared spectroscopy (FT-IR, PerkinElmer) was also used for the structural analysis and the spectrum was recorded at 400–1400 cm^{-1} range using KBr pellets. Particle sizes and shapes were investigated using high-resolution transmission electron microscope (HRTEM, FEI TECNAI G2 F30 model). The physical particle sizes, d_{TEM} , were manually counted and calculated from the TEM images by using Image J programme after taking the TEM pictures

of nanoparticles. Magnetic measurements were done by a vibrating sample magnetometer (VSM, ADE Technologies EV9) at room temperature between -20 and $+20$ kOe with 1 Oe intervals. The magnetization value of the sample at the highest applied field was denoted as M_{max} in whole text.

3 Results and Discussion

It is known that the reaction temperature is a fundamental parameter to synthesize cobalt ferrite (CoFe_2O_4) nanoparticles [10]. Under study, obtaining superparamagnetic CoFe_2O_4 nanoparticles is an important point for the potential applications that require a magnetic switching property [13]. Therefore, using 1.5 M NH_3 , the synthesis was performed at different temperatures (20, 40, 60, and 80 °C) to decide the appropriate reaction temperature. Black precipitate of CoFe_2O_4 was obtained at 80 °C. Magnetic measurements of the samples were performed by vibrating sample magnetometer (VSM) and the magnetization curves are presented in Fig. 1. As seen from the figure, the samples synthesized at 20, 40, and 60 °C show paramagnetic behavior and the sample at 80 °C show superparamagnetic character. The M_{max} values of the samples synthesized at 20, 40, and 60 °C are 2.4, 3.8, and 5.4 emu/g, respectively. The nanoparticles synthesized at 80 °C have higher M_{max} of 19.9 emu/g, and their coercivity, H_c , is zero. In the study [10], CoFe_2O_4 nanoparticles synthesized at 20 °C showed paramagnetic structure with 2.0 emu/g magnetization value at 10 kOe, which is similar to our work. In the same study, the nanoparticles are superparamagnetic with 4.2 emu/g magnetization value at 40 °C and ferrimagnetic (H_c values are 39 and 193 Oe at 60 and 80 °C, respectively) above 40 °C. And, the authors say that there is a considerable change in crystallinity and average particle size between the reaction temperatures 40 and 60 °C.

Fig. 1 Magnetization curves of the samples synthesized at 20, 40, 60 and 80 °C. Inset shows the curves at ± 5 kOe



However, in our study, clear X-ray diffraction (XRD) patterns of the nanoparticles can only be obtained at 80 °C (see below discussion). And, superparamagnetic CoFe₂O₄ nanoparticles can only be obtained at 80 °C. Thus, the reaction temperature was selected as 80 °C and the effect of base concentration was studied accordingly.

In order to investigate the effect of base concentration on the properties of CoFe₂O₄ nanoparticles, base concentration was changed from 0.5 to 9.0 M. The initial base concentrations and the measurements of CoFe₂O₄ nanoparticles are presented in Table 1. The XRD patterns of the samples S1, S3, S7, and S8 were selected and given in Fig. 2. It is observed in Fig. 2a that sample S1 shows amorphous-like structure with no XRD peaks which may be caused by the small particles size of the nanoparticles. In the patterns of S3, S7, and S8, however, the (311), (400), (511), (440), and (533) peaks were observed at $2\theta \approx 35, 44, 57, 62,$ and 74° , respectively. The observed peaks are the characteristic peaks of CoFe₂O₄ according to the JCPDS 22-1086 card. The mean crystal sizes, d_{XRD} , were calculated from (311) peak in the patterns using Scherrer’s equation [14], and the results were summarized in Table 1. The d_{XRD} were 7.3, 7.1, 9.9, and 14.9 nm for S3, S6, S7, and S8, respectively. The particle sizes obtained from XRD patterns increases with increasing base concentration.

For further information about the structure of the samples, Fourier transform infrared spectroscopy (FT-IR) analysis was done and the spectra of some samples are shown in the 1400–400 cm⁻¹ region in Fig. 3. For all samples, the transmittance peak is observed at about 590 cm⁻¹. The peak in the spectrum of S1 is very weak, and its intensity is higher for the other samples. The peaks in the range of 500–600 cm⁻¹ indicate the intrinsic stretching vibration of M–O bond, where M corresponds to the metal ion at the tetrahedral site [15]. Thus the peak observed in the spectrum implies the formation of CoFe₂O₄ [15–17]. The

final pH of the solutions after coprecipitation is between 8.6 and 11.1. These pH values are suitable for the precipitation process since a complete precipitation takes place at the pHs between 8 and 14 as indicated in [18]. It can be deterred from the structural analysis that base concentrations from 1.0 to 9.0 M are suitable to obtain CoFe₂O₄ nanoparticles.

TEM images were obtained to investigate the particle size and shape of the samples. TEM images are given in Fig 4. The physical particle sizes, d_{TEM} , of CoFe₂O₄ nanoparticles were also determined by TEM analysis and given in Table 1. The d_{TEM} are $2.4 \pm 1.0, 5.3 \pm 1.2, 6.3 \pm 1.5, 5.8 \pm 1.8,$ and 7.5 ± 1.5 nm for samples S1, S3, S6, S7, and S8, respectively. The d_{TEM} increases as the base concentration increases from 0.5 to 6.0 M, and then it decreases at 8.0 M and increases again at 9.0 M. By looking at the XRD pattern, FTIR spectrum, and TEM image of S1, it can be said that at the lowest base concentration particle formation is on the first stage and the growth process is not completed. The calculated d_{XRD} values are bigger than d_{TEM} values; however, the similar trend of increase with increasing base concentration is observed.

Magnetization curves of the nanoparticles synthesized with various base concentrations are presented in Fig. 5. All samples except for S8 are superparamagnetic with zero coercivity. A large amount of increase in the M_{max} from 7.2 to 16.3 emu/g is observed as the base concentration increases from 0.5 to 1.0 M. And, the M_{max} continues to show smaller steps of increase from 16.3 to 32.4 emu/g with increasing base concentration from 1.0 to 6.0 M. This is followed by a little decrease to 28.7 emu/g when the sample was synthesized at 8.0 M, and a slight increase to 31.9 emu/g with a little H_c value (4 Oe) is observed at 9.0 M. In [8], superparamagnetic CoFe₂O₄ nanoparticles have magnetization of 4.2 emu/g at 10 kOe applied field and the other samples with higher magnetization values (36 and

Table 1 Synthesis conditions and magnetic properties of CoFe₂O₄ nanoparticles

Sample	Base concentration (M)	Particle sizes			Magnetic properties	
		d_{TEM} (nm ± Δnm)	d_{XRD} (nm)	d_{VSM} (nm ± Δnm)	M_{max} (emu/g)	H_c (Oe)
S1	0.5	2.4 ± 1.0	–	2.9 ± 0.3	7.2	–
S2	1.0	–	–	4.2 ± 0.2	16.3	–
S3	1.5	5.3 ± 1.2	7.3	5.1 ± 0.5	21.3	–
S4	3.0	–	–	5.3 ± 0.4	25.7	–
S5	4.5	–	–	5.5 ± 0.5	31.2	–
S6	6.0	6.3 ± 1.5	7.1	5.7 ± 0.6	32.4	–
S7	8.0	5.8 ± 1.8	9.9	5.6 ± 0.6	28.7	–
S8	9.0	7.5 ± 1.5	14.9	–	31.9	4

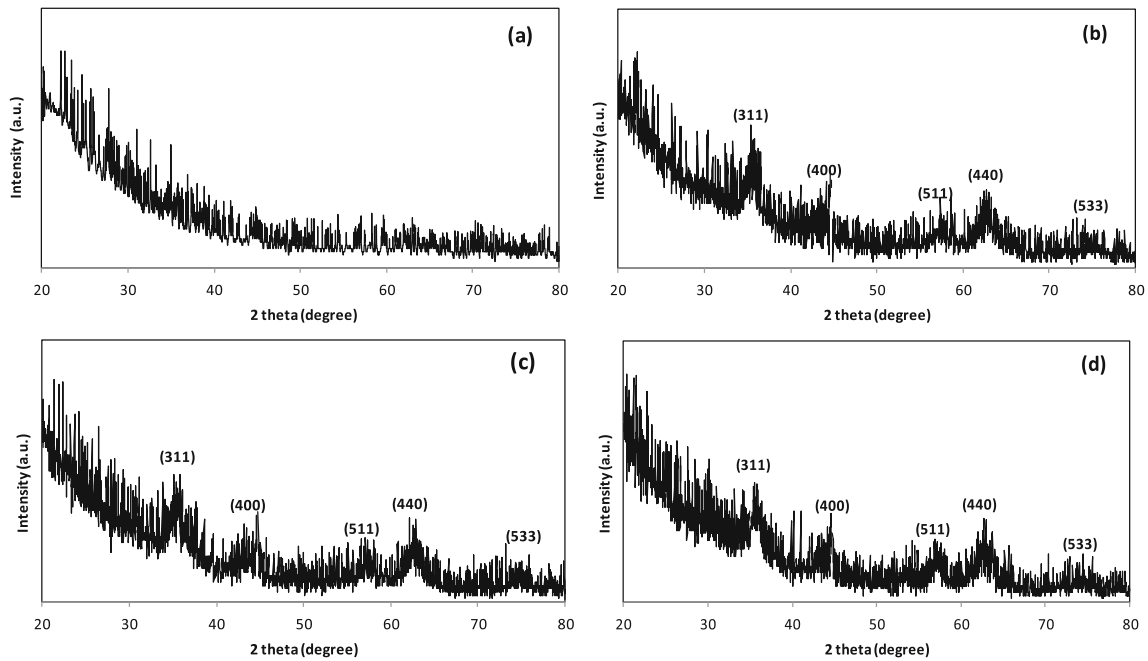


Fig. 2 The XRD patterns of the samples **a** S1, **b** S3, **c** S7, and **d** S8

58.3 emu/g) show H_c (39 and 193 Oe). Jovanovic et al. [19] synthesized CoFe_2O_4 nanoparticles by coprecipitation, and

they found the magnetization value as 3.2 emu/g and H_c as 3.9 Oe. In another study [11], all samples show H_c values as high as 5628 Oe and the sample with maximum magnetization (36.24 emu/g) has H_c of 673 Oe. Also in [16], as-synthesized CoFe_2O_4 nanoparticles show high values of H_c (2100 Oe) and saturation magnetization (43 emu/g). Oleic acid-coated CoFe_2O_4 nanoparticles were studied in [20], and they showed H_c values higher than 200 Oe. Under study, the main point is to obtain superparamagnetic CoFe_2O_4 nanoparticles with high M_{max} values. The obtained M_{max} values are close to that of CoFe_2O_4 nanoparticles with ferrimagnetic character [11–20]. More importantly, the M_{max} values of our nanoparticles are quite higher than the values obtained for superparamagnetic CoFe_2O_4 nanoparticles [10].

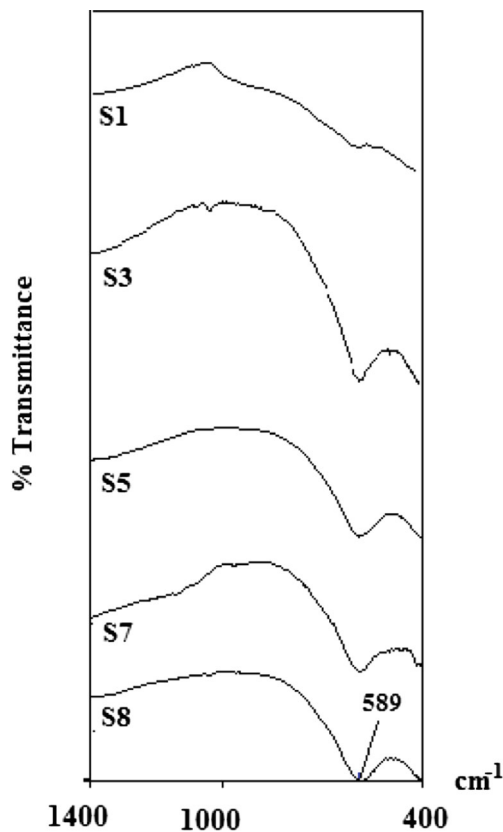
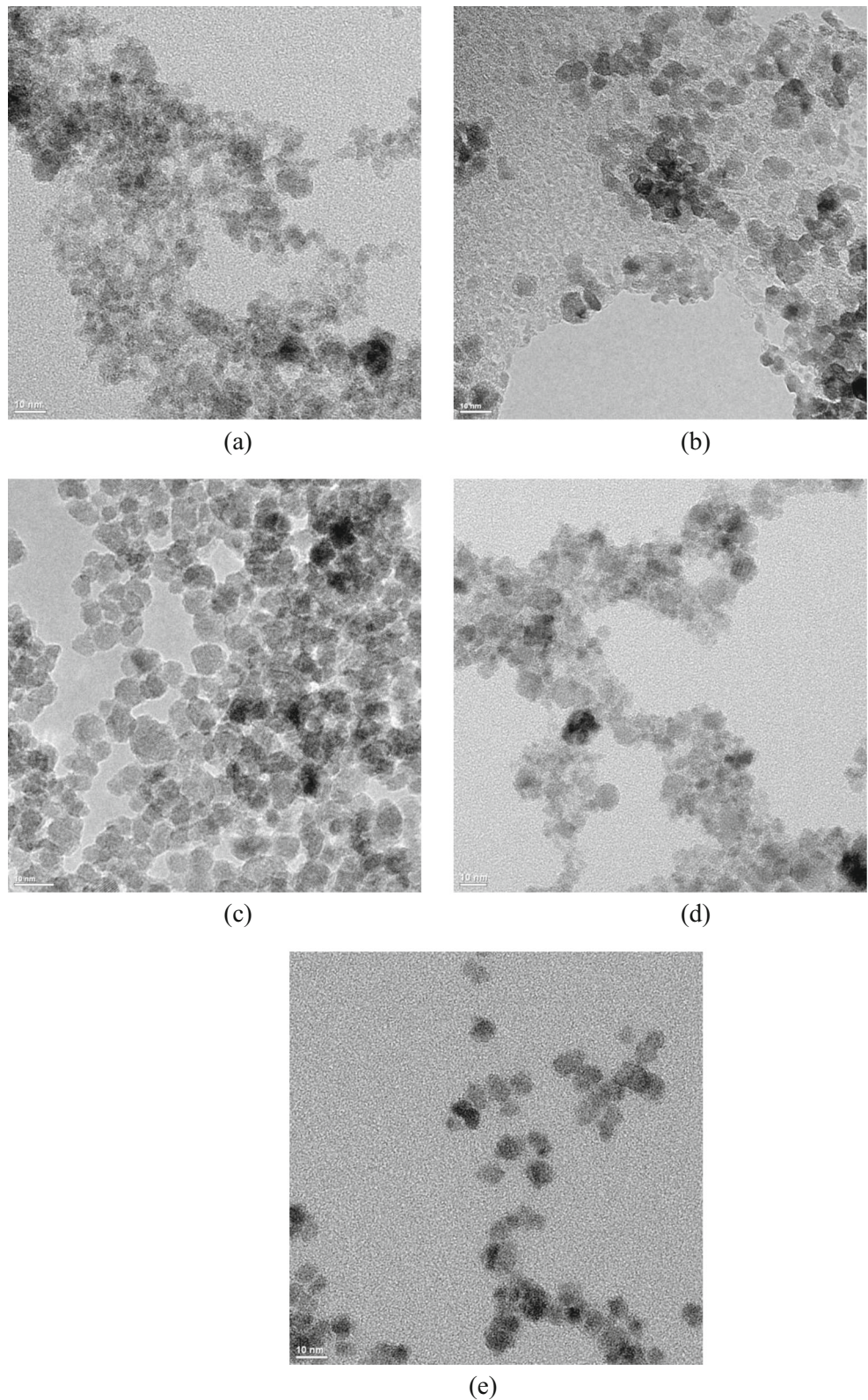


Fig. 3 The FTIR spectra of CoFe_2O_4 nanoparticles

The mean magnetic sizes, d_{MAG} , were calculated according to the equation in [21] and listed in Table 1. Magnetic size increases from 2.9 ± 0.3 to 4.2 ± 0.2 nm as the base concentration increases from 0.5 to 1.0 M and then slightly increases and stays almost constant as the base concentration keeps increasing, see Table 1. The d_{VSM} and d_{TEM} values are close to each other, and d_{XRD} values are larger than those. It might be inappropriate to directly correlate the d_{XRD} values and properties of the samples since the XRD patterns showed high noises. However, the similar trend of change is observed on the d_{XRD} , d_{TEM} , and d_{VSM} and hence the corresponding properties. Besides, the d_{TEM} was taken into consideration to further explain the properties of the nanoparticles. The d_{TEM} of superparamagnetic CoFe_2O_4 nanoparticles are between 2.4 ± 1.0 and 6.3 ± 1.5 nm, and the size of the nanoparticles showing coercivity is $7.5 \pm$

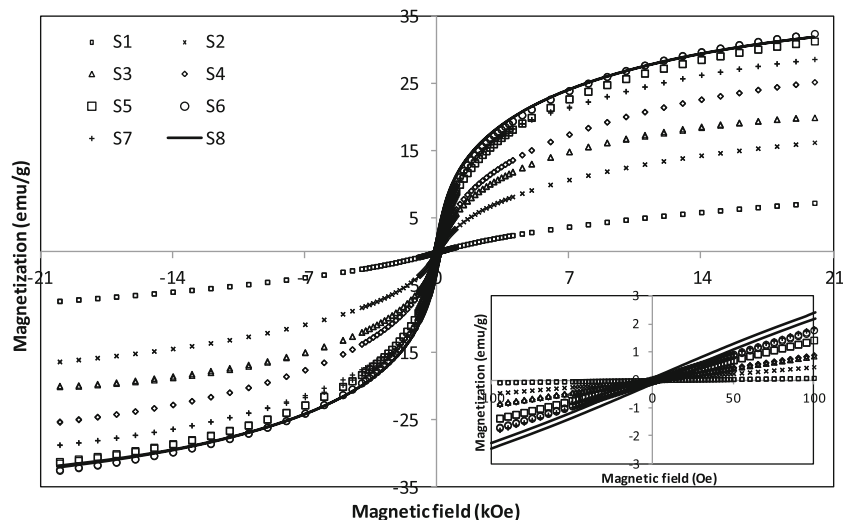
Fig. 4 TEM images of CoFe_2O_4 nanoparticles **a** S1, **b** S3, **c** S6, **d** S7, and **e** S8. (Scale bars show 10 nm)



1.5 nm. These values are in good agreement with the study [7], saying that the superparamagnetic particle size limit of CoFe_2O_4 nanoparticles is $\sim 6\text{--}8$ nm.

A study using different NaOH concentrations showed that the size of CoFe_2O_4 nanoparticles with coercivities increases as the base concentration increases; however, the

Fig. 5 Magnetization curves of the samples S1–S8. *Inset* shows the curves at ± 100 Oe



saturation magnetization slightly changes [22]. In our study, the M_{\max} of the superparamagnetic CoFe_2O_4 nanoparticles increases from 7.2 to 32.4 emu/g with increasing the d_{TEM} from 2.4 ± 1.0 and 6.3 ± 1.5 nm. Due to the increase of surface to volume atomic ratio for small particles, the surface canting of magnetic moments increases and magnetization value decreases as stated in [23, 24]. Therefore, the M_{\max} is lower for the small nanoparticles and increases as the particle size increases from 2.4 ± 1.0 to 6.3 ± 1.5 nm with the increase of base concentration. For the sample S7, the M_{\max} slightly decreases with a correlation of particle size.

4 Conclusions

Cobalt ferrite nanoparticles were synthesized in air medium using NH_3 as base source. Their characterizations were made according to the reaction temperature and base concentration. In order to comprehensively investigate the structure of the synthesized samples, X-ray diffraction and Fourier transform infrared spectroscopy were performed. It was observed that the superparamagnetic cobalt ferrite nanoparticles can only be synthesized at 80°C . At this temperature, the effect of base concentration on the properties of the nanoparticles was investigated. It is seen that the particle sizes and corresponding magnetization values can be altered by the change of the base concentration. Results showed that cobalt ferrite nanoparticles, which are synthesized using base concentrations between 0.5 and 8.0 M, are superparamagnetic, and the maximum magnetization value among these nanoparticles is 32.4 emu/g.

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