

Optimization of Magnetic Properties in Cobalt Ferrite Nanocrystals

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ABSTRACT

Cobalt ferrite (CoFe_2O_4) possesses excellent chemical stability, good mechanical hardness and a large positive first order crystalline anisotropy constant, which made this ferrite a promising candidate for magneto-optical recording media. In addition to precise control on the composition and structure of CoFe_2O_4 , the success of its practical application will depend on the capability of controlling particle size at the nanoscale. This size-controlled synthesis approach became possible by modifying the oversaturation conditions during ferrite formation in water. Optimum oversaturation was achieved by monitoring of the feeding flow-rate of reactant solutions. XRD and FT-IR analyses confirmed the formation of the ferrite structure after a reaction time as short as five minutes. M-H measurements verified the strong influence of synthesis conditions and crystal size on the magnetic properties of ferrite nanocrystals. The coercivity values increased from 210 Oe up to 1337 Oe under optimum synthesis conditions.

Keywords: cobalt ferrite, high coercivity, nanocrystals, modified coprecipitation route.

1 INTRODUCTION

Magnetic nanoparticles have been the subject of intense research because of their potential applications in high-density magnetic recording, magnetic fluids [1-2], etc. Among the various ferrite materials for magnetic recording applications, cobalt ferrite (CoFe_2O_4) has been widely studied because it possesses excellent chemical stability and good mechanical hardness. In addition to the precise control on the composition and structure of CoFe_2O_4 , the success of its practical application relies on the capability of controlling crystal size within the superparamagnetic and single domain limits. It is known that the crystal size is related to the relative interdependence between the nucleation and growth steps, which in turn can strongly be affected by the solution chemistry and precipitation conditions [3-5].

On the above basis, the present research involves a modified co-precipitation synthesis technique where the growth of cobalt ferrite crystals is controlled to achieve high room-temperature coercivity and moderate magnetization at the nanoscale. This size-controlled synthesis approach became possible by controlling the oversaturation conditions and reaction time during ferrite

formation in aqueous solutions. Optimum oversaturation was achieved by a precise monitoring of the feeding flow-rate of reactant solutions under intensive heating conditions.

2 EXPERIMENTAL

2.1 Materials

All reagents were of analytical grade and were used without further purification. Required weights of cobalt chloride and iron (III) chloride hexahydrate salts were dissolved in distilled water to produce an ionic solution with a mole ratio of 1: 2 (Co: Fe). An aqueous solution with an excess of NaOH was used as the alkaline precipitant agent.

2.2 Synthesis of Cobalt Ferrite Nanocrystals

The ferrite nanocrystals were synthesized by conventional and modified coprecipitation method. In the conventional approach, an aqueous solution of 0.055 M Co(II) and 0.11 M Fe(III) was rapidly contacted with an excess of hydroxide (OH^-) ions. The hydrolysis reaction in the presence of an excess of OH^- ions leads to the formation of a paramagnetic Fe-Co hydroxide, which undergoes dehydration and atomic re-arrangement conducive to a ferrite structure. The reactant solution was mechanically stirred at 500 rpm and intensively heated to accelerate the ferrite formation. The intensive heating helped to reduce the reaction time dramatically. Cobalt ferrite nanocrystals were washed out with distilled water, dried at 80°C for 24 hours and characterized.

In order to enhance the magnetic properties by changing the oversaturation conditions, the conventional coprecipitation route was modified by controlling the flow rate of addition of the metal ions solution to the alkaline one. For this purpose, a micro-peristaltic pump with precise control of flow-rate was used.

2.3 Nanocrystals Characterization

Dried powders were characterized using XRD, FT-IR, HRTEM and SQUID techniques. XRD and FT-IR were used to confirm the formation of the ferrite structure. The average crystallite size of produced powders was estimated by using the Scherrer's equation for the (311) peak. Room-

temperature M-H loops were obtained by using a Quantum Design SQUID unit.

3 RESULTS AND DISCUSSION

3.1 XRD Analyses

XRD analyses confirmed the formation of the ferrite structure for a reaction time as short as five minutes. Under non-controlled flow-rate conditions, i.e. conventional coprecipitation approach, the average crystallite size varied from 12 nm to 14 nm as the reaction time was increased from 5 to 180 minutes, respectively (Figure 1 and Table 1). Although minor, the increase in average crystallite size for longer reaction times could be attributed to crystal growth, favored by Oswald-ripening process. The ferrite lattice parameter was estimated at 8.38 Å, which is in good agreement with the bulk value of 8.377 Å.

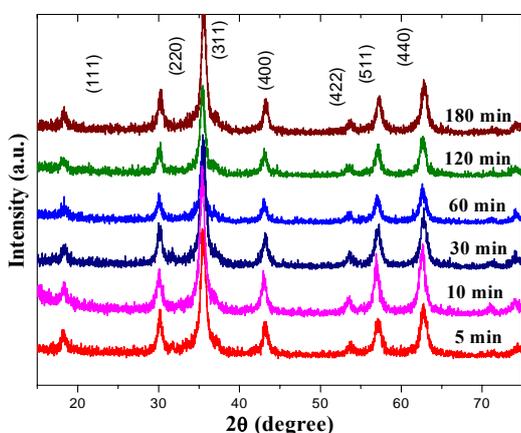


Figure 1: XRD patterns for CoFe_2O_4 powders synthesized at different reaction times with no control of flow-rate.

Reaction Time (min)	a (± 0.02 Å)	t (nm)
5	8.38	12
10	8.39	12
30	8.37	13
60	8.40	15
120	8.43	13
180	8.37	14

Table 1: Lattice parameter, 'a', and average crystallite size, 't', for CoFe_2O_4 synthesized at different reaction times.

Figure 2 shows the XRD patterns for the ferrites produced at different flow-rates of reactants additions and 60 minutes of reaction. As seen, the crystallinity of the ferrite products was very sensitive to the variation in flow-rate. Broad and noisy XRD peaks were observed for the sample synthesized at 1 mL/min. This peak broadening suggests a poor development of the ferrite structure and was

attributed to the extremely low saturation conditions established at that particular flow-rate. Well-defined and sharp peaks of the ferrite structure were observed for the solids synthesized at flow-rates above 1 mL/min.

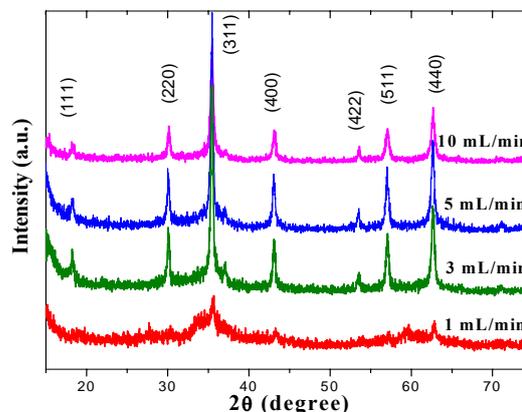


Figure 2: XRD patterns for CoFe_2O_4 powders synthesized at different flow rates. The reaction time was 60 minutes.

Table 2 summarizes the corresponding estimations of the lattice parameter and average crystallite size for the ferrite powders produced at different flow-rates. It is clear that crystal growth was promoted by controlling the flow-rate of the addition of reactants. The establishment of suitable heterogeneous nucleation conditions, where earlier nuclei should have acted as pre-existent seeds, could have promoted crystal growth. Average crystallite size varied from 31 nm to 24 nm for flow-rates between 1 mL/min and 10 mL/min, respectively. These sizes are almost 2.5 times larger than the average crystallite size obtained with no control of the flow-rate. The lattice parameter values are consistent with that of bulk Co-ferrite.

Flow Rate (mL/min)	a (± 0.02 Å)	t (nm)
1	8.334	31
3	8.39	23
5	8.39	21
10	8.38	24

Table 2: Lattice parameter and average crystallite size for CoFe_2O_4 nanoparticles synthesized at different flow rates of the addition of reactants.

3.2 FT-IR Measurements

FT-IR spectra for CoFe_2O_4 produced at different flow-rate of addition of reactants are shown in Figure 3. The band at 540 cm^{-1} can be assigned to the M-O tetrahedral bond in the ferrite structure. The poor development of the ferrite structure in the sample produced at a flow-rate of 1 mL/min is evidenced by the broadening of the ferrite band.

This fact is in good agreement with XRD results, which suggested a poor crystallinity in this particular sample. On the other hand, the enhanced intensity of the M-O band with rising flow-rates suggests the further enhancement in the crystallinity of the product.

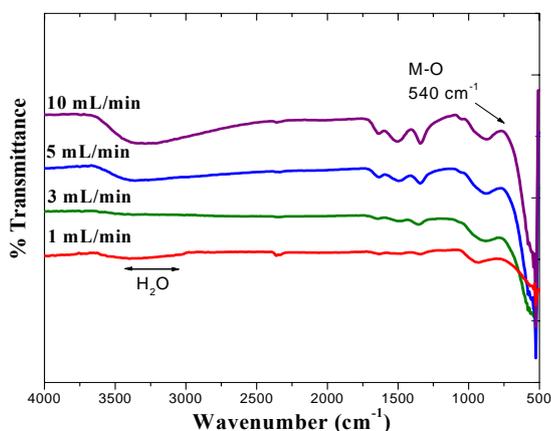


Figure 3: FT-IR spectra for CoFe_2O_4 samples produced at different flow-rate of addition of reactants.

3.3 HRTEM Observations

HRTEM images of ferrite samples produced at 10 mL/min and reaction times of 5 minutes and 60 minutes are given in Figure 4. Particles were polydisperse; however, the promotion of crystal growth by prolonging the reaction time was evidenced. The size distribution was not determined because of the aggregation of the particles.

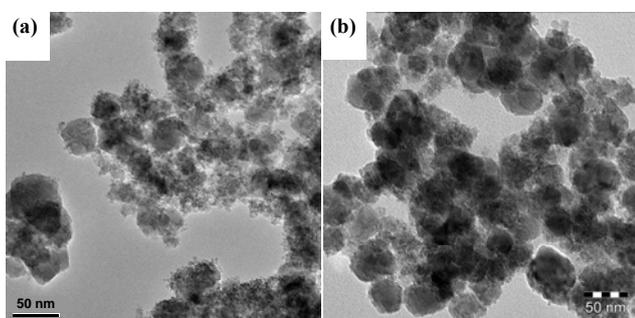


Figure 4: HRTEM pictures for CoFe_2O_4 nanoparticles produced after 5 minutes (a), and 60 minutes (b) of reaction. The flow-rate was 10 mL/min.

3.4 SQUID Measurements

Room-temperature M-H measurements confirmed the influence of crystal size on the magnetic properties of ferrite nanocrystals. As Figures 5-a and 5-b show, the coercivity showed a rising trend from 237 Oe up to 460 Oe when the reaction time was prolonged from 5 minutes to 60 minutes. A longer reaction time caused the coercivity to drop to 348 Oe. The corresponding maximum

magnetization values did not exhibited a clear trend and ranged between 43 emu/g and 62 emu/g. The presence of superparamagnetic particles is suggested by the lack of saturation of the M-H profile, even for an applied field as high as 5T. Although a long enough reaction time could have favored crystal growth, the variability in the superparamagnetic fraction in the powders could explain both, the low coercivity and magnetization values. Table 3 summarized obtained results.

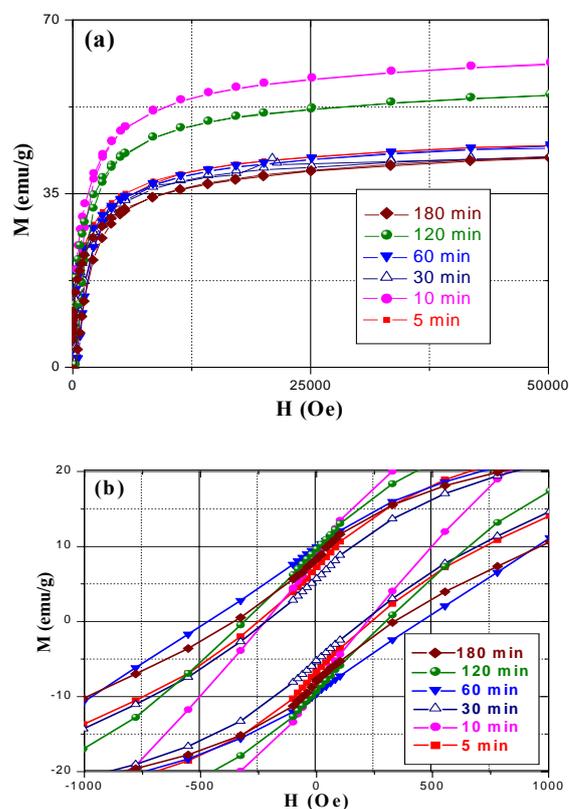


Figure 5: M-H plots (a) and loops (b) at 300K for CoFe_2O_4 synthesized at different reaction times with no control of flow-rate.

Reaction Time (min)	H_c (Oe)	M_{\max} (emu/g)
5	237	45
10	225	62
30	210	43
60	460	45
120	304	55
180	348	43

Table 3: Coercivity and magnetization for ferrite nanocrystals synthesized at different reaction times.

The coercivity was increased dramatically under controlled flow-rate conditions (Figure 6). This parameter increased from 237 Oe, (no control on flow rate), up to 1337 Oe for 10 mL/min, after 5 minutes of reaction. The corresponding maximum magnetization was 53 emu/g.

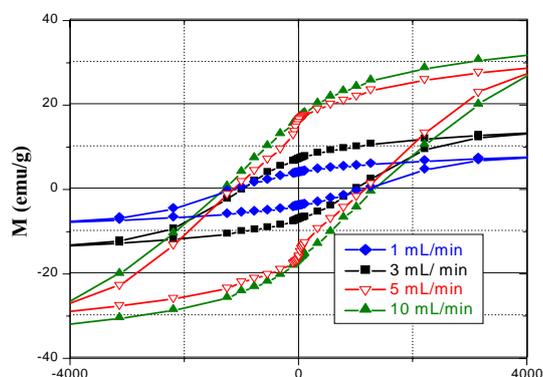


Figure 6: M-H loops at 300K for CoFe_2O_4 synthesized at different flow-rates. The reaction time was 5 minutes.

The exact values of coercivity and magnetization for those nanocrystals produced at different flow rates are listed in the following table. Based on information available from XRD and HRTEM analyses, the drastic enhancement in coercivity can be attributed to the promotion of crystal growth within the single domain region.

Flow Rate (mL/min)	H_c (Oe)	M_{\max} (emu/g)
1	1148	15
3	1000	22
5	1150	42
10	1337	53

Table 4: Coercivity and magnetization values corresponding to the ferrite nanocrystals synthesized at different flow rates. The reaction time was 5 minutes.

3.5 Experimental Design

A factorial design 2^3 was accomplished in order to determine which parameters are significant in the synthesis of the cobalt ferrite nanocrystals. The reaction time, the flow-rate of addition of reactants and the NaOH solution concentration were the parameters selected for the experimental design. It is important to notice that these experiments were accomplished under more intensive heating conditions than those described in the previous sections. Furthermore, the high (+) and low (-) levels of the evaluated parameters were selected based on the trends observed in the previous experiments.

Table 5 shows the parameters studied, their levels and the possible combinations between them. In this case, the dependent variable was the coercivity. In order to observe the wide range of coercivity that can be obtained just varying the parameters as suggested by the statistical design, the lowest and the highest coercivity values were selected and presented in figure 7. Coercivity values between 870 Oe (combination 'ab') and 4626 Oe (combination 'a') were achieved.

Combinations	A B C Design	A: Reaction Time (min)	B: Flow Rate (mL/min)	C: NaOH (M)	H_c (Oe)
1	- - -	5	0.85	0.34	4518
a	+ - -	180	0.85	0.34	4626
b	- + -	5	20	0.34	871
ab	+ + -	180	20	0.34	870
c	- - +	5	0.85	0.54	2877
ac	+ - +	180	0.85	0.54	3448
bc	- + +	5	20	0.54	922
abc	+ + +	180	20	0.54	1007

Table 5: Experimental design parameters, possible combinations and its corresponding response (coercivity) for the nanocrystals produced.

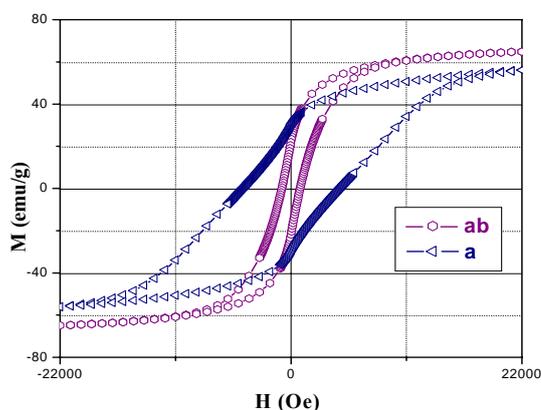


Figure 7: M-H loops at 300K for CoFe_2O_4 synthesized at different flow-rates (0.85 mL/min, combination 'a', or 20 mL/min, combination 'ab'). The corresponding reaction time and NaOH concentration were 180 minutes and 0.34M, respectively.

An analysis of variance (ANOVA) and an 'F-test' were undertaken to determine which parameters are more significant to the variation in coercivity. The variance of the experimental error was calculated evaluating three replicates in the central point of the design. The F distribution for three grades of liberty at a level of confidence of 95% and 99% are 10.1 and 34.1, respectively. Accordingly, factor 'B' (flow rate of the reactants addition)

is significant at a level of confidence of 99% whereas factor 'C' (NaOH concentration) become significant at a level of confidence of 95%. The interaction 'BC' was also found to be significant at a 95% level. The statistical analysis also suggested that reaction time is not a significant parameter.

3.6 Acidic Treatment

The sample prepared at the conditions suggested by the experimental design (combination 'a'), which exhibited coercivity of 4626 Oe, was submitted to an acid washing under room temperature conditions. Accordingly, fixed amounts of cobalt ferrite nanocrystals were contacted with nitric acid solutions 20% v/v for 30 minutes. After washing and drying, the powders were analyzed by VSM. As figure 8 shows, the coercivity for the acid-treated powder was as high as 5840 Oe. To the best of our knowledge, this is the first report of single domain cobalt ferrite nanocrystals exhibiting such a high coercivity. The increase in coercivity can be attributed to the dissolution of superparamagnetic nanoparticles and/or the poorly crystallized fraction in the product.

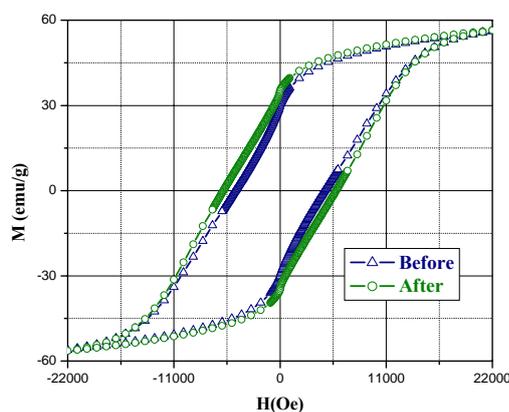


Figure 8: M-H loops at 300K for CoFe_2O_4 nanocrystals before and after acid treatment.

4 CONCLUDING REMARKS

A suitable control of CoFe_2O_4 nanocrystals size has been accomplished through a precise control of the oversaturation conditions during the ferrite formation in aqueous phase. Optimum oversaturation was attained by monitoring the flow-rate of the addition of reactants, which should have also promoted heterogeneous nucleation and hence, crystal growth. The average crystallite size in ferrite powders synthesized under flow-rate controlled conditions was around 24nm, which is almost twice the size obtained when the flow-rate was not controlled. The favorable effect on crystal growth was reflected in the enhancement of the coercivity values for ferrite nanocrystals produced at different flow-rates. The coercivity values were increased from 237 Oe, with no control of flow-rate, up to 1337 Oe,

when the flow-rate of the addition of reactants was kept constant at 10 mL/min. The reaction time was as short as five minutes. The selection of the optimum synthesis conditions and suitable treatment under acidic conditions permitted an increment in coercivity up to 5840 Oe. Obtained results suggest the viability in optimizing magnetic properties of cobalt ferrite nanocrystals by restricting crystal growth within the single domain region.

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