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Applying a suitable route for preparation Fe_3O_4 nanoparticles by Ammonia and investigation of their physical and different magnetic properties

ABSTRACT

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Iron oxide nanoparticles were synthesized by coprecipitation method using ammonia as precipitation agent. Most researchers usually add ammonia into the iron salt solution but in this work the salt solution drop wise has been added to the ammonia and the new obtained results were compared with those of other researches. Magnetic properties of nanoparticles were measured by VSM. The effect of reaction temperature and concentration of reactants on the size and magnetic properties of nanoparticles were investigated. The size of particles was calculated by Sherrer formula and magnetic data, and then compared with the size of nanoparticles obtained by TEM. The size of produced nanoparticles ranged from 8 to 17 nanometer and their saturation magnetizations were between 65.5 to 72.5 emu/gr. It was found that increasing reaction temperature increases saturation magnetization of nanoparticles, but variation of concentration of ammonia did not change the saturation magnetization. Saturation magnetization observed here were more than the values reported by others.

Keywords: Magnetite; Magnetic properties; Coprecipitation; Ammonia; Nanoparticles; Superparamagnetism.

INTRODUCTION

Magnetite nanocrystals have attracted much interest recently because of their interesting magnetic and electric properties which are not observed in bulk phases. They are used extensively in the field of biomagnetics for a broad range of applications, such as drug delivery [1], cell labeling and sorting [2], magnetic resonance imaging, sensing [3,4] as well as therapeutic applications such as AC magnetic field-assisted cancer therapy, i.e. hyperthermia [5,6]. All these technological and medical applications require that the nanoparticles are superparamagnetic with sizes smaller than 20nm with narrow size distribution to have uniform physical and chemical properties and they should be stable chemically and magnetically.

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However, producing magnetite particles with the desired size and acceptable size distribution without particle aggregation has consistently been a problem.

In this paper, after investigation of the results of other researches, we attempted to use simplest and most suitable method for synthesis nanoparticles. There are several methods to synthesize nanoparticles such as Polyol Process [7], sol-gel [8], hydrothermal [9] micro-emulsion techniques [10] and coprecipitation method. Among these methods, coprecipitation is the most suitable one because it is simple and economic, and also the surface of produced nanoparticles by this method can be treated easily with other materials making them suitable for medical application [11, 12]. In this method, by choosing suitable reactant materials, reactant condition and route and tools of experiment one, can synthesize nanoparticles with desirable size, size distribution and magnetic properties are desirable.

There are several parameters that affect the size and magnetic properties of nanoparticles in coprecipitation method. The type of alkali affects the properties of nanoparticles. Some investigators use ammonia and some of them use NaOH aqueous solution as precipitant agent. In this paper ammonia has been used for synthesizing of nanoparticles and their properties have been reported. Also the behavior of these nanoparticles at weak magnetic fields has been compared with those synthesized by NaOH aqueous solution. The way of adding reactants is a factor which can affect properties of nanoparticles. Reviewing literature indicates that most of researchers have added ammonia to the salt solution [13-16] but a different method was followed here i.e. the salt solution was added to the ammonia. The rate of adding of solution also affects the nanoparticles properties. Salt solution can be added to the ammonia very quickly or drop by drop. The former has been investigated by D. Bahadur and others and a weak crystallinity have been reported [17]. So, in this work the salts solution was added to the ammonia drop by drop. It seems that the way of stirring the solution affects the size and magnetic properties of nanoparticles. In this work, a homogenizer with high speed was used for stirring the reaction solution instead of an ordinary stirrer. Finally, reaction temperature and concentration of reactants affect the properties of nanoparticles which investigated here.

In synthesis of magnetite nanoparticles by coprecipitation method the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratios should remain $\frac{1}{2}$ during the experiment in order to obtain pure magnetite. The common impurities in this reaction are $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$. The magnetic properties of $\gamma\text{-Fe}_2\text{O}_3$ are similar to the magnetite but $\alpha\text{-Fe}_2\text{O}_3$ is a nonmagnetic material and leads to non desirable magnetic properties of products. The reason of these impurities is deviation of $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratios from the mentioned value. Existence of oxygen in the reaction media leads to this deviation which oxidize Fe^{+2} ions to Fe^{+3} [18, 14]. So, in this work, all stages of experiment were done under nitrogen atmosphere. Experimental investigation shows that passing nitrogen gas through the reactant solution has two advantages: 1- preventing existence of oxygen in the reaction medium 2- leading to smaller sizes of nanoparticles [19].

EXPERIMENTAL

Chemicals

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (98%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), Ammonia (97%) were purchased from Merck Co. All these reagents were used without further purification. Distilled water was used in this work.

Instrumentation

X-ray powder diffraction (XRD) analysis was conducted on a Philips X'PERT MPD Diffractometer operated at 40 kV and 35mA using $\text{Cu K}\alpha$ radiation. Magnetic measurements were carried out with a Lake Shore Vibrating Sample Magnetometer (VSM) model 7400. Transmission electron microscopy (TEM) was performed using a Leo 912 AB transmission electron microscope (TEM).

Synthesis of nanoparticles

In a typical procedure, desirable amount of Iron (II) and Iron (III) salts were added to distilled water and a mixture of salt solution were prepared. 12 ml of salt solution drop wise was added to 120 ml ammonia solution under nitrogen atmosphere and given temperature. The solution was stirred mechanically at 10000 rpm by mechanical homogenizer for 30 min. Black precipitate was decanted by a permanent magnet and washed by distilled water three times and dried under vacuum

at 50⁰ c. Reaction temperature and concentration of reactants are listed in Table 1.

Table 1. synthesise condition of magnetic nanoparticles

Sample	Reac.Tem. (°C)	[NH ₄ OH] (mol/L)	[Fe ²⁺ +Fe ³⁺] (mol/L)
1	90	0.5	0.9
2	90	3	0.9
3	60	0.5	0.9
4	60	3	0.9
5	30	3	0.9

RESULTS AND DISCUSSION

XRD Investigation

Phase investigation of the crystallized product was performed by XRD. The patterns of three samples fore example are shown in Figures 1 and 2.

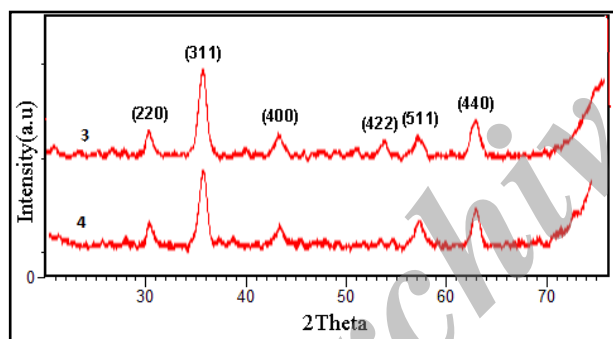


Fig. 1. Effect of concentration of ammonia on the diffraction pattern.

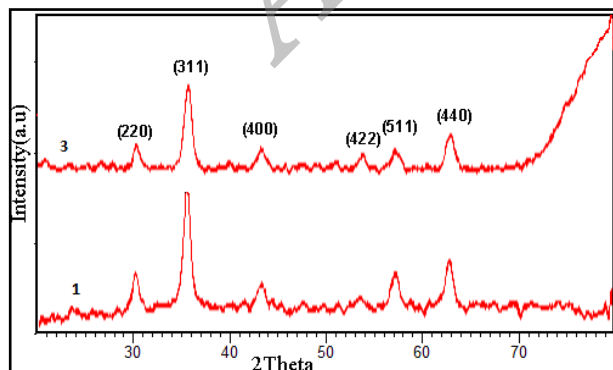


Fig. 2. effect of reaction temperature on the diffraction pattern

The pattern of the samples confirms its major composition of Fe₃O₄ nanocrystal because the position and relative intensity of main peaks match well to those from the JCPDS card (19–0629) for Fe₃O₄ and indicates that the product is iron oxide, Fe₃O₄. The diffraction peaks are broadened owing to small crystallite size. All the observed diffraction peaks could be indexed by the cubic structure of Fe₃O₄ indicating a relative phase purity of iron oxide. However γ -Fe₂O₃, maghemite, has basically the same crystal as magnetite. Thus it is probable that some of the samples contain maghemite as impurity but no other nonmagnetic impurities. But black color of the samples and high saturation magnetization of them tell us that the maghemite impurity is little. Also magnetic properties of maghemite are near the same of the magnetite, then as an overall result the samples do not contain nonmagnetic impurities.

Crystallographic parameters of the samples were calculated by Xpert- plus software version 1.0 and were in agreement with those of magnetite. The peak intensity of sample 1 is more than sample 3 which indicates that the crystallinity of sample 1 is better than sample 3 which can be due to increasing of reaction temperature. The crystallite sizes were calculated from the FWHM (full width and half maximum) applying the Debye-Scherrer formula. The most intense peak (3 1 1) of the magnetite phase was used for the crystallite size evaluation. These values are indicated in Table 2. From this table, one can see that increasing reaction temperature increases the crystallite size of nanoparticles, but changing the concentration of ammonia does not affect them. Also the pattern of samples 3 and 4 in Figure 1 are almost the same. This shows that changing concentration of ammonia does not change the crystallographic properties of nanoparticles.

Table 2. The crystallite size, magnetic size and saturation magnetization of nanoparticles

Sample	Reac.Tem. (°C)	[NH ₄ OH] (mol/L)	D _{XRD} (nm)	D _m (nm)	M _s (emu/gr)
1	90	0.5	17	14	72.5
2	90	3	-	13	72.0
3	60	0.5	13	10	67.0
4	60	3	11	9	67.0
5	30	3	-	8	65.5

Magnetization

Magnetic properties of nanoparticles are affected by their synthesis conditions. Magnetization measurements of iron oxide nanoparticles were performed using VSM technique. Hysteresis curves of the samples at fields of -20000 to 20000 and 300^oK are shown in Figures 3, 4 which indicate the effects of reaction temperature and concentration of ammonia on the hysteresis curve of nanoparticles.

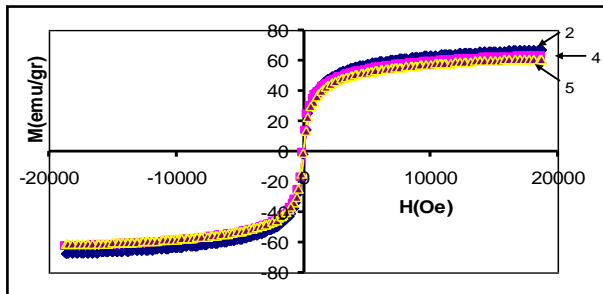


Fig. 3. The effect of reaction temperature on the hysteresis curves of nanoparticles

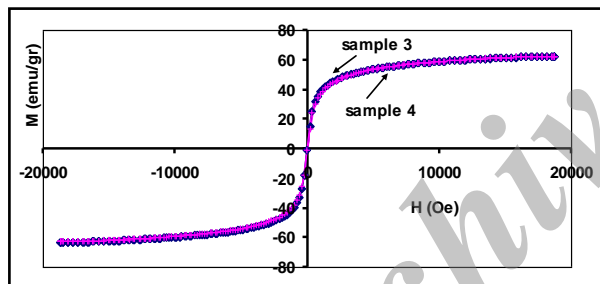


Fig. 4. The effect of concentration of ammonia on the hysteresis curves of nanoparticles

Figures 3 and 4 show that magnetization of nanoparticles increased by increasing reaction temperature but not affected by changing the concentration of ammonia. Magnetic sizes of nanoparticles were calculated by the following formula [20].

$$D_m = \left(\frac{18K_B T \chi_{in}}{\pi \rho M_0^2} \right)^{\frac{1}{3}} \quad (1)$$

This relation derived from Langevin formula at weak fields approximation, is written at

cgs units where χ_{in} is the initial magnetic susceptibility, $\chi_{in} = (dM/dH)_{H \rightarrow 0}$, ρ is the density of Fe₃O₄ (5.26g/cm³) and $M_0 = 93 \text{ emu/gr}$ is the saturation magnetization of bulk Fe₃O₄ [22]. Saturation magnetization, M_s , calculated from extrapolation of the plot of M vs. $1/H$. The results are shown in Table 2. The values of saturation magnetization are smaller than the bulk samples. The reason of this can be due to nonmagnetic layer on the surface of nanoparticles [19, 22].

Figure 3 and 4 indicate that the samples did not reach saturation magnetization at the fields of 2 tesla which is in agreement with the result reported by others [22-26]. The absence of saturation magnetization at high field of 20kOe and the absence of hysteresis, coercivity and remanent magnetization at room temperature indicate that the nanoparticles exhibit a superparamagnetic behavior. When the size of magnetic nanoparticles reduces below a critical value, the $K_B T$ term is greater than the energy barrier which is caused by magnetic anisotropy. Thus, the thermal energy is able to reorient the domains/particles and thus hysteresis diminishes and coercive field is zero which is characteristic feature of superparamagnetism regime [24].

Moreover, the magnetic size of the nanoparticles determined from the magnetic data is a little smaller than the physical size determined from XRD and TEM (coming at the next section) techniques. The reason is for the magnetically dead layer on the surface of nanoparticles. This layer does not contribute to the magnetic properties, but it does add to the overall mass of the particle.

According to Table 2, the samples derived at high reaction temperature exhibit higher saturation magnetization, which is in agreement with the results reported by others [26], but changing the concentration of ammonia did not affect saturation magnetization. Increasing saturation magnetization is in agreement with increasing of crystallite size and improving of crystallinity. The values of saturation magnetization in this work are more than those reported by others [13-15]. In coprecipitation method, the factor which governs on the size of nanoparticles is the ratio of nucleation rate to growth rate. If nucleation rate is faster than growth rate, the size of particles will be smaller. Since ammonia is a weak base,

increasing its concentration in this study does not affect the rate of nucleation and as the consequence; the size of particles does not increase.

We also synthesized five samples by NaOH as precipitant agent while the other parameters were the same as those synthesized by ammonia (their XRD pattern dose not shown here). Their magnetic behavior at weak fields is compared in Figure 5. Although two samples are shown in the Figure 5, all samples showed the same behavior.

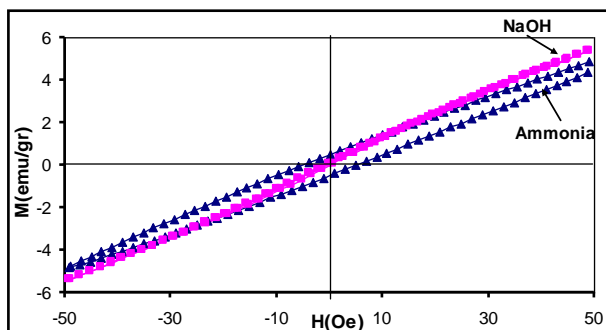


Fig. 5. Comparing magnetic behavior of nanoparticles synthesized by ammonia and NaOH at weak fields.

As one see from Figure 5, the samples synthesized by ammonia show small coercivity and remanent magnetization but both of these quantities are zero for the samples prepared by NaOH. Also, as shown in Table 3, magnetization at a given field for the former samples is more than latter ones which is in agreement with relative size of nanoparticles. But the notable thing is that, as one see from this table, saturation magnetization of sample C synthesized by NaOH is much more than the one synthesized by ammonia. We should have more investigation to explain this behavior.

Table 3. Comparing of size and saturation magnetization of nanoparticles synthesized by NaOH and ammonia

sample	[OH ⁻] (mol/L)	Reac.Tem (°C)	M _s (emu/gr)		D _{XRD} (nm)	
			NaOH	NH ₄ OH	NaOH	NH ₄ OH
A	3	60	61.0	67.0	8	11
B	0.5	60	67.0	67.0	9	13
C	0.5	90	82.0	72.0	10	17

TEM investigation

Average particle size and morphology of nanoparticles were detected using a Leo 912 AB transmission electron microscope (TEM). Figure 6 shows the TEM images of samples 1 and 4. The particles are almost spherical and their mean size is 15 and 10 nanometer respectively which is in agreement with XRD and magnetization results and indicates that nanoparticles are single crystal and single domain [22].

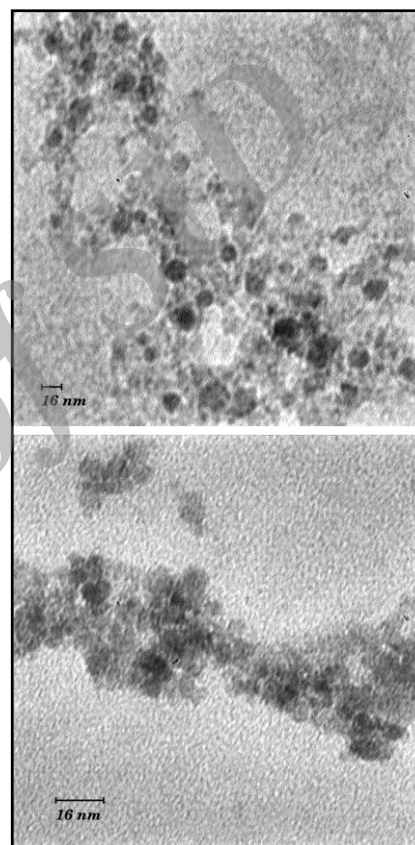


Fig. 6. TEM image of sample 1; reaction temperature: 90°C and concentration of ammonia: 0.5 mol/L (Left) and TEM image of sample 4; reaction temperature: 60°C and concentration of ammonia: 3 mol/L (Right)

According to the TEM images, the agglomeration occurred in the iron oxide nanopowders. The agglomeration is due to van der Waals force between particles. Also TEM images show that the synthesized iron oxide nanopowders are nearly mono dispersed particles. Monodispersity of particles might be duo to stirring method here, the mechanical homogenizer with high speed.

CONCLUSIONS

Superparamagnetic Iron Oxide nanoparticles were prepared by coprecipitation method using a mechanical homogenizer for stirring the solution. Particle size calculated from magnetic data was in good agreement with those obtained from X-ray analysis and TEM micrographs. It was found that increasing reaction temperature increases saturation magnetization of nanoparticles which was in agreement with improvement of crystallite structure of samples caused by increasing reaction temperature but changing concentration of ammonia does not affect the size and saturation magnetization of nanoparticles. The reason for this might be the fact that ammonia is a weak base and increasing its concentration in this work, which salt solution was added to the ammonia drop wise, does not affect nucleation and growth rate. Magnetic saturation of nanoparticles synthesized here were more than those reported by the other studies which used to add ammonia to salt solutions. Synthesized nanoparticles can easily be coated by tetra methyl ammonium hydroxide, citric acid, oleic acid and other surfactants. These coated nanoparticles can be dispersed in the water or other hydrocarbon carriers such as kerosene and make ion stable or surfactant stable ferrofluids respectively. Magnetic behavior of samples synthesized by ammonia differed from those synthesized by NaOH, and explanation of this notable behavior needs more investigation.

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