

Preparation of Super Paramagnetic Iron Oxide Nanoparticles and Investigation their Magnetic Properties

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Abstract- Super paramagnetic Iron Oxide nanoparticles were prepared by co-precipitation method using NaOH as precipitation agent. Magnetic properties of nanoparticles were measured by a VSM. The crystallite size of particles was calculated by Sherrer formula and magnetic data and compared with the size of nanoparticles which obtained by TEM. The sizes of produced nanoparticles were about 11 nanometer and their saturation magnetizations were 69 emu/gr.

Keywords- Iron oxide, magnetic properties, co-precipitation, ammonia, nanoparticles, super paramagnetic

INTRODUCTION

Iron oxide is known for its low toxicity and biocompatibility. These features make it an ideal element for in vitro diagnostics [1]. So among other technical application such as ferrofluid it used extensively in the field of bio magnetics for a broad range of applications such as drug delivery [2], cell labeling and sorting [3], magnetic resonance imaging and hyperthermia [4]. All these medical applications require that the nanoparticles are super paramagnetic with sizes smaller than 20nm with narrow size distribution to have uniform physical and chemical properties and they should be stable chemically and magnetically. Their reduced size and large surface-to-volume ratio leads to distinct magnetic [5] and electronic [6] properties which are different from those of their bulk counterparts. However, producing iron oxide particles with desired size and acceptable magnetization properties and size distribution without particle aggregation has consistently been a problem and the properties of nanoparticles are strongly dependent on their preparative methods. There are several methods for synthesize these nanoparticles such as Polyol Process [7], sol-gel [8], hydrothermal [9] micro-emulsion techniques [10] and coprecipitation. Among of these methods, co-precipitation is most suitable because it is simple and economic and also the surface of produced nanoparticles can be treated easily with other materials and makes them suitable for medical and technical

applications [11, 12]. In this method by choice of suitable reactant materials, reactant condition and choice suitable route and tools of experiment one can synthesis nanoparticles which their size, size distribution and magnetic properties are desirable.

In synthesize of magnetite nanoparticles by co-precipitation method the Fe^{+2}/Fe^{+3} ratios should remain $\frac{1}{2}$ during the experiment, in order to obtain pure magnetite. The common impurities in this reaction are γ - Fe_2O_3 and α - Fe_2O_3 . The magnetic properties of γ - Fe_2O_3 are similar to the magnetite but α - Fe_2O_3 is a nonmagnetic material and leads to non-desirable magnetic properties of products. The reason of these impurities is deviation of Fe^{+2}/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} [13, 14]. So in this work all stages of experiment were done under nitrogen atmosphere. Experimental investigations show that passing nitrogen gas through the reactant solution has two advantages: 1- prevent of formation of unwanted impurities such as goethite by eliminating oxygen from the reaction medium and 2- leads to smaller sizes of nanoparticles [15].

2. Experimental

2.1 Materials

Ferric chloride ($FeCl_3 \cdot 6H_2O$), ferrous chloride ($FeCl_2 \cdot 4H_2O$), sodium hydroxide (NaOH) were all chemical grade and obtained from Merck.

2.2 Synthesis

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 were added to 120 ml ammonia solution under nitrogen atmosphere and given temperature. Reaction temperature and the concentration of reactants have are shown in table 1. The

solution was stirred 30 min. Black precipitate was decanted by a permanent magnet and washed by distilled water three times and dried in vacuum at 50°C.

Table 1: synthesize condition of magnetic nanoparticles

Reac.Tem. (°C)	[NaOH] (mol/L)	[Fe ⁺² +Fe ⁺³] (mol/L)
90	0.5	0.9

3. Characterization

X-ray powder diffraction (XRD) measurements were carried out with Philips PW3710, using Cu-Kα radiation. Transmission electron microscopy (TEM) investigations have been carried out using a Leo 912 AB transmission electron microscope. Magnetic properties of nanoparticles were measured by VSM technique.

4. Result and discussion

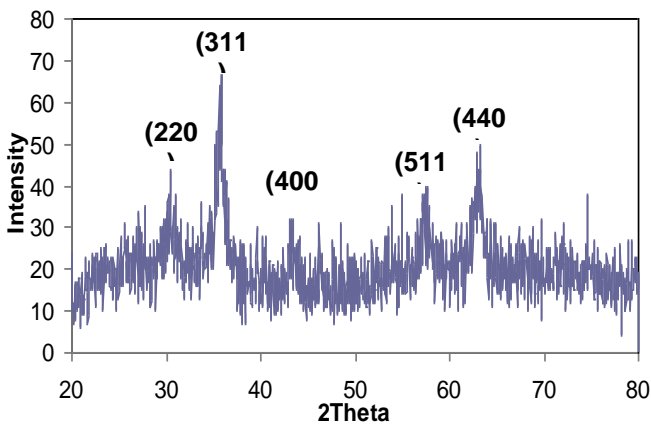


Fig.1: XRD pattern of iron oxide nanoparticles.

The XRD pattern of the precipitate is shown in Fig. 1. Relatively wide peaks are related to the small size of the particles. The pattern of the precipitate 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 the product contain maghemite 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 crystallite size calculated from the FWHM (full width and half maximum) by applying the Debye-Scherrer formula was found to be 11nm. The most intense peak (3 1 1) of the magnetite phase was used for the crystallite size evaluation.

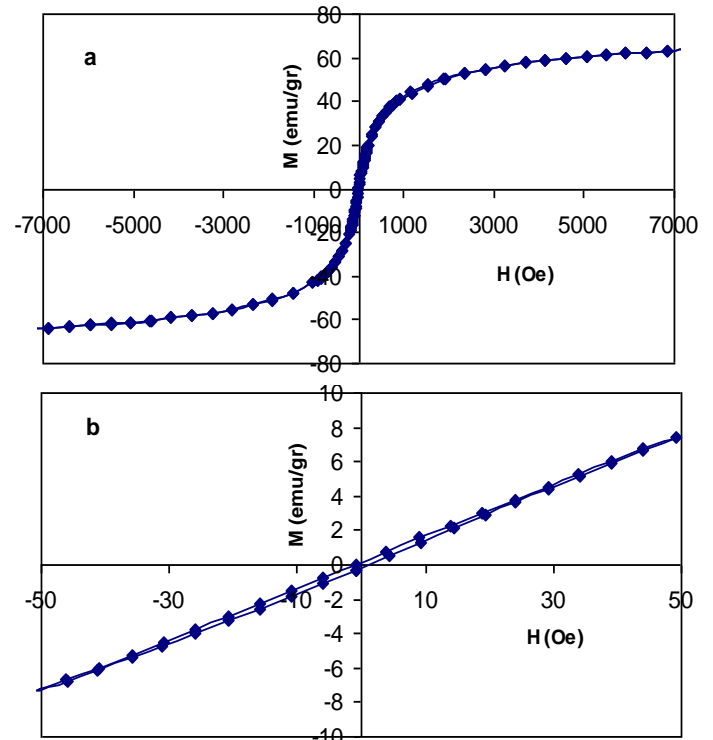


Fig. 2: Magnetization curves of nanoparticles at high (a) and low (b) fields.

Magnetization measurements of iron oxide nanoparticles were performed using VSM technique and hysteresis curves of the samples at fields of -7000 to 7000 and -50 to 50 Oersted at 300⁰K are shown in Fig. 2. Magnetic size of nanoparticles were calculated by the following formula [16]

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

This relation which 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 [17]. Saturation magnetization, M_s , calculated from extrapolation of the plot of M vs. $1/H$. saturation magnetization and magnetic size of particles were found to be 69 emu/gr and 10 nm respectively.

The value of saturation magnetization is smaller than the bulk sample. The reason of this can be due to nonmagnetic layer on the surface of nanoparticles [18].

Fig. 2a indicates that the samples did not reach saturation magnetization at the fields of 7000 Oersted which is in agreement with the result reported by others [19,20]. Fig. 2b

shows that prepared nanoparticles here do not have remanent and coercive field. The absence of saturation magnetization at high field of 7kOe 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 (13nm for magnetite), 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 and thus hysteresis diminishes and coercive field is zero which is characteristic feature of superparamagnetism regime [21]. 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.

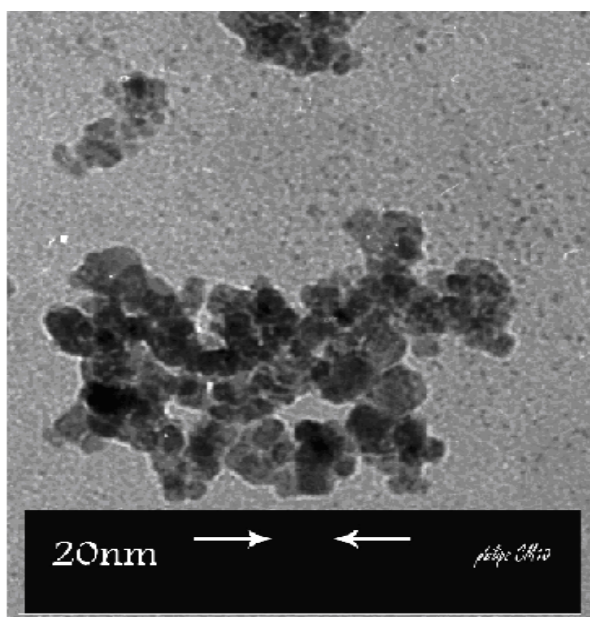


Fig. 3: TEM image of nanoparticles

Fig. 3 shows the TEM image of nanoparticles. The particles are almost not spherical and their mean size are 10-13 nanometer which are in agreement with XRD and magnetization results and indicates that most of nanoparticles are single crystal and single domain [15]. According to the TEM images, the agglomeration is occurred in the iron oxide Nano powders. The agglomeration is due to the van der Waals force between particles.

CONCLUSION

Superparamagnetic Iron Oxide nanoparticles were prepared by coprecipitation method. Particle sizes which calculated from magnetic data were in good agreement with those

obtained from X-ray analysis and TEM micrographs. However magnetic size was a little smaller than TEM and XRD size. The reason of this is due to magnetic dead layer on the surface of nanoparticles which does not contribute to the magnetic properties, but it does add to the overall mass of the particle.

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