Synthesis and magnetostructural studies of amine functionalized superparamagnetic iron oxide nanoparticles†

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Superparamagnetic iron oxide nanoparticles are synthesized through co precipitation method by using the new generation base diisopropylamine (DIPA) which electrostatically complexes with iron ions, reduces them and subsequently caps the nanoparticle. Coating of DIPA on the surface of the nanoparticles was confirmed through FTIR and TG-DTA. We investigate the effect of reaction time as well concentration of DIPA on the particle size and magnetic properties of Fe3O4 nanoparticles. Effect of concentration of DIPA on particle size reveals that the nanocrystallite size of Fe3O4 nanoparticles increases to its maximum (the increase is nominally 5.2 nm to 8.5 nm) and then reduces (3.2 nm). Particle size and magnetic properties of the synthesized nanoparticles are also influenced by reaction time; in general as the reaction time increases the particle size increases. The lattice parameter of iron oxide nanoparticles varies from ~8.32 to ~8.39 Å with reaction time. From magnetic measurements, superparamagnetism of the Fe3O4 nanoparticles was confirmed. The results clearly suggest that the magneto-structural properties of Fe3O4 (or any ferrite) can be easily tuned by using DIPA.

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Introduction

Iron oxide magnetic nanoparticles (MNPs) are one of the most accepted multifunctional magnetic materials with diverse applications including high density magnetic storage, catalysis, sensors, environmental remediation and in biomedicine with a platform for high sensitivity bimolecular Magnetic Resonance Imaging (MRI). For these applications iron oxide nanoparticles (NPs) are usually used as a core surrounded by a hydrophilic and biocompatible coating, most usually made up of polymers. But the main limitation concerning the use of conventionally synthesized and polymer functionalized Fe3O4 NPs for biomedical applications is due to the presence of a thick layer that increases the hydrodynamic radii considerably (up to 100 nm), causing damping of the MR signal. This limitation can be overcome by introduction of a cationic surface layer on top of the iron oxide NPs, such as amine (NH2). The amine functionalized iron oxide NP surface is supposed to have very good uptake by cancer cells and provides sharper in vivo and in vitro MRI signals as compared to conventional iron oxide NPs. However along with surface functionalization, the required physicochemical and magnetic properties of iron oxide NPs can be tailored during the synthesis process. The large scale application and tailoring of various physico-chemical properties of iron oxide NPs have prompted the development of several widely used methods including combustion synthesis, micro-emulsion, hydrothermal, reverse micelle, sol gel technique, sonochemical synthesis, citrate precursor technique, microwave plasma, mechanical alloying, co precipitation etc. for the fabrication of stoichiometric and chemically pure spinel ferrite NPs.

Among these synthesis methods, the aqueous co-precipitation route is mostly used method for producing water dispersible MNPs in high yields, since it is cost-effective, less time consuming and easily scalable for industrial as well as pharmaceutical applications. Along with this, for co-precipitation route there is no need of expensive and hazardous solvents, reagents and high temperature or pressure. Ultimately, co-precipitation synthesis in water based system represents a beneficial method and eco friendly synthesis method. Even though co-precipitation technique is most studied and most familiar synthesis method, the control of magnetic properties and crystallinity of NPs synthesized by this route is still needed to be studied thoroughly. Even surprising researchers were working extensively on water based co precipitation synthesis technique, maximum work was carried out with the traditional bases (sodium hydroxide, ammonia, and tetra alkylammonium hydroxides). Pereirra et al. have studied the different bases like NaOH, NH4OH,
isopropanolamine (MIPA), diisopropanolamine (DIPA) etc. and the role played by the bases on the particles’ size, chemical composition, and magnetic properties on Fe₃O₄ NPs. Their results supports that, MIPA and DIPA have an important role on the co-precipitation process since they acted as the base and at the same time as a complexing agent that control the growth of NPs and provides higher surface spin order. Their results shed new light on the design of MNPs with improved properties through the co-precipitation method. Still it is well known that, the reaction conditions may affect the particle properties with which one can customize MNPs for variety of applications.

In this context in the present investigation, we adopted a new approach to describe and predict the impact of the main synthesis parameters in co-precipitation method on the properties of synthesized MNPs. We chose reaction time and concentration of alkaline media (DIPA) as a parameters of interest. All syntheses were carried out in a well defined and controlled reaction setup. Magnetic properties of synthesized MNPs were measured by a superconducting quantum interference device (SQUID) and crystallographic and chemical properties by TGA, XRD, FTIR and TEM etc.

**Experimental**

**Materials and reagents**

Ferrous chloride tetrahydrate (≥99%), ferric chloride hexahydrate (≥99%), bis[2-hydroxypropyl]-amine (DIPA, ≥98%), were purchase by Sigma Aldrich. Hydrochloric acid (analytical grade) was by Panreac and was used for the synthesis purpose. Double distilled water used throughout the experiments. All reagents were used without further purification.

**Synthesis**

MNPs were prepared by the aqueous co-precipitation method under alkaline conditions using DIPA as the base. In which, 20 mmol of FeCl₂·6H₂O and 10 mmol of FeCl₃·4H₂O were dissolved in 25 cm³ of deoxygenated 0.5 M HCl solution. This solution was quickly added to 250 cm³ of a deoxygenated 3.0 M solution of DIPA (pH 11–12) at room temperature with vigorous mechanical stirring. A black precipitate was formed immediately and stirring was continued for 2 h. The precipitate was magnetically separated, washed with deoxygenated water several times. After washing obtained precipitate was dried at room temperature.

Particles were prepared at different reaction times of 1/2, 1 and 2 h. The other parameters such as reagent concentrations, reaction temperature and the stirrer speed (1200 RPM) were kept constant. Particles are also prepared with different alkali concentration of 3.0, 5.0, 7.0 M. We denoted the prepared samples as N31/2, N31, N32, N51/2, N51, N52, N71/2, N71, N72 for 3.0, 5.0, 7.0 M concentration with 1/2, 1 and 2 h reaction time respectively. In this nomenclature, ‘N’ stands for nanoparticles, first numeric is for normality while second numeric is for reaction time in hours.

**Physico-chemical characterization**

Structure and phase of as synthesized Fe₃O₄ NPs was studied by XRD (miniflex 600) with Cu-Kα radiation (λ = 1.5404 Å) in the 2θ range from 20 to 80°. The patterns were evaluated by PANalytical X’pert high score software and compared with standard JCPDS (card no. 19-0629). Presence of the magnetic core and ligands on the surface of MNPs was confirmed by FTIR spectroscopy (Perkin Elmer spectrometer model no. 783, USA). The particle size of Fe₃O₄ NPs was measured with TEM (Philips CM 200 model, operating voltage 20–200 kV, resolution 2.4 Å).

Magnetic properties of dried MNPs were studied using commercial Quantum Design superconducting quantum interference device (SQUID) magnetometer. The isothermal magnetization (M) versus applied magnetic field (H) at an applied field of ±15 kOe at room temperature and ZFC-FC measurements were performed over the temperature range 5–370 K with constant field 100 Oe.

**Results and discussion**

**Reaction mechanism**

In the synthesis of NPs/nanomaterials, the crystal structure, shape, size and size distribution are mainly controlled by crystallization process (nucleation and growth). A theoretical approach to understand the mechanism of crystal formation provides a greater control over the size, shape and composition of nanocrystals which helps to tune the above mentioned properties by varying the crystallization conditions.

In co-precipitation technique, new phase is formed when the temperature of the solute decreases below phase formation point and the concentration of solute in a solvent exceed its equilibrium solubility or supersaturated. Such supersaturated solutions have high Gibbs free energy and the overall energy of the system would be reduced by segregating solute from the solution. This reduction of Gibbs free energy is the driving force for both nucleation and growth. The Gibbs free energy per unit volume of the solid phase (ΔGₛ) is dependent on the concentration of the solute and is given as,

\[
\Delta G_v = -kT \Omega \ln(C/C_0) = -kT \Omega (1 + \sigma)
\]

where, C and C₀ are the concentrations of the solute and the equilibrium concentration or solubility respectively, σ is the supersaturation (defined by (C – C₀)/C₀) and Ω is the atomic volume. If σ is zero, ΔGᵥ would be zero means there is no nucleation would occur without supersaturation. When the concentration of solute exceeds than the equilibrium concentration (C > C₀), the ΔGᵥ becomes negative and nucleation occurs spontaneously. After nucleation the newly formed nucleus is stable only when its radius exceeds a critical size, r* which is given by,

\[
r^* = -2\gamma/\Delta G_v
\]
and continues to grow bigger. At the critical size \( r = r^* \), \( d\Delta G/\, dr = 0 \), critical energy, \( \Delta G^* \), is defined by,

\[
\Delta G^* = 16\pi \gamma /3(\Delta G_v)^2
\]

\( \Delta G^* \) is the energy barrier for that a nucleation process must overcome. The critical size represents the limit how small NPs can be synthesized by nucleation from supersaturated solution. If the concentration of solute increases as a function of time, no nucleation would occur even above equilibrium solubility. When the supersaturation reaches to a certain value above the solubility the nucleation occurs, which corresponds to the energy barrier for the formation of nuclei (Fig. 1) (eq. \( \Delta G^* \)). However, the growth of the particles can continue through nuclear addition until the concentration of precipitated species reaches to an equilibrium concentration.\(^{18}\)

When the critical size \( r^* \) is smaller than the particle size of synthesized particles \( r \) (\( r > r^* \)) the smaller particles grow more rapidly than the larger ones because smaller particles have more free energy driving force compared to larger ones and this is the stage where nearly monodisperse size distribution can be obtained by stopping the reaction. Whereas, the increase in critical nuclei size \( (r^*) \) due to decrease in supersaturation ratio there is occurrence of ripening process.\(^{19}\) After the growth phase the terms agglomeration and aging are used to describe features of the changes in the solid particles. Tendency of smaller particles in a liquid suspension to coalesce into larger aggregates is nothing but agglomeration. The other variety of processes that changes a precipitate after its formation covers under the title aging. For example: Ostwald ripening. \( i.e. \) the tendency of larger crystals to cultivate at the expense of smaller crystals when the crystals formed after nucleation. Another crucial process which transforms with aging is initial nucleation of a metastable solid phase, which can be well understood with the example of amorphous solid particles that crystallize with time of a hydrated crystalline solid that converts to a more stable material.\(^{20}\)

Basically, co-precipitation process consists of a condensation reaction in which cations present in the solution bond together through oxygenated bridges, such as OH or O₂. It begins by the initiation of monomer species, such as M–OH, whose concentration increases rapidly with the base addition. Then, the precipitated hydroxide converts to the oxide by replacement of the hydroxide bridges by oxygen bonds. In the present investigation, the co precipitation carried with alkanolamines, in which Fe₃O₄ NPs nucleated by simultaneous hydrolysis and dehydration of a mixture of divalent and trivalent iron salt solution. The ratio of concentration of Fe³⁺ and Fe²⁺ salts were kept constant and salt solutions were prepared in acidic matrix so as to avoid formation of iron hydroxides before initiation of reaction. In acidic medium (at pH 3), the first phase of Fe³⁺ to precipitate in hydrolysis is ferrihydrite. The magnetite forms after addition of alkanolamine (base) on increasing pH, the divalent Fe²⁺ integrate in to the ferrihydrite and forms an intermediate complex material of Fe²⁺-ferrihydrite and later compensates as inverse spinel structured magnetite. The overall chemical reaction can be expressed as,

\[
2\text{Fe}^{3+} + \text{Fe}^{2+} + 8\text{OH}^- = \text{FeO}_2\cdot\text{Fe}_2\text{O}_3 + 4\text{H}_2\text{O}
\]

The basicity of the alkanolamines is lower as compared to the old generation bases (NaOH, NH₄OH etc.) which help to reduce particle size of the NPs.

The crystallographic structure and phase purity of Fe₃O₄ NPs were investigated by powder XRD. Fig. 2 shows the XRD patterns of all the synthesized NPs. All of the NPs exhibited a typical spinel ferrite diffractogram, confirming the expected cubic spinel structure (Fd₃m).\(^{21,22}\) The average crystallite size \( D_c \) was calculated using the Scherrer formula,

\[
D_c = \frac{K \lambda}{\beta \cos \theta}
\]

where, \( \beta \) is the peak width at half-maximum (FWHM), \( K \) is the so-called shape factor which is 0.9 for spherical particles, \( \lambda \) is

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Fig. 1  Synthesis of iron oxide nanoparticles by co precipitation method.
the wavelength, \( \theta \) is the Bragg diffraction angle. The average crystallite sizes of the NPs are calculated from the most intense peak (311) using the said equation. The calculated crystallite size for all samples was below \( \approx 10 \) nm (Table 1).

In the present investigation it is found that, as the concentration of the alkaline media DIPA increases from 3 M to 5 M, there is initial increase in the crystallite size from \( \approx 5 \) nm to \( \approx 8 \) nm. When further increase in the concentration of DIPA to 7 M there is broadening of the XRD peaks leads to decrease in crystallite size to \( \approx 1 \) nm. These results are in well accordance with the Mullin,\(^{23}\) where he summarizes that, as the concentration of reacting substances in solution increases, \( i.e. \), as the initial supersaturation is increased, the mean size of the precipitate particle increases to a maximum and then decreases. This phenomenon is based on the Weimann law of precipitation, which can be formulated as “With progressively increasing concentration of the reacting solutions, the mean magnitude of the individual crystals of the precipitates will pass through maximum”.\(^{24}\) From this one can conclude that there is direct relation between core size and amine concentration as, core size of NPs travels through maxima with increase in concentration of DIPA.

The crystallite size of the NPs is also influenced by the reaction time. It was found that, the average crystallite size increases from 4.1 nm to 5 nm, 6.8 nm to 7.8 nm and 1.3 nm to 2.8 nm for 3 M, 5 M and 7 M as the reaction time increases from 1/2 h to 2 h (as shown in Fig. 3). This increase in crystallite size with increasing reaction time can directly correlate with the Lifshitz–Slyozov–Wagner (LSW) model for coarsening.\(^{14}\) According to the simple thermodynamic considerations of Gibbs-Thomson effect,\(^{25}\) coarsening is striving by the dependence of the solubility of a solid phase on the particle size. Suppose, that the particles are spherical, and then the solubility “\( C_r \)” of particles of radius \( r \) is,

\[
C_r = C_a \exp\left(\frac{2\gamma V_m}{rRT}\right)
\]

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Table 1 Effect of concentration of DIPA and reaction time on structural properties such as crystallite size observed from XRD (\( D_c \)), X-ray density (\( D_X \)), lattice constant (\( a \)), unit cell volume (\( V \)), particle size by TEM (\( D_{TEM} \)), magnetic particle size (\( D_m \)) by and on magnetic properties as saturation magnetization (\( M_s \)), and blocking temperature (\( T_B \)) of Fe3O4 NPs

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>( D_X ) (g cm(^{-3}))</th>
<th>( a ) (Å)</th>
<th>( V ) (nm(^3))</th>
<th>( D_c ) (nm)</th>
<th>( D_{TEM} ) (nm)</th>
<th>( D_m ) (nm)</th>
<th>( M_s ) (emu g(^{-1}))</th>
<th>( T_B ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N31/2</td>
<td>5.35</td>
<td>8.32</td>
<td>0.57</td>
<td>4.12</td>
<td>5.21</td>
<td>2.42</td>
<td>34.33</td>
<td>100.05</td>
</tr>
<tr>
<td>N31</td>
<td>5.28</td>
<td>8.35</td>
<td>0.58</td>
<td>4.86</td>
<td>6.33</td>
<td>2.36</td>
<td>37.28</td>
<td>130.00</td>
</tr>
<tr>
<td>N32</td>
<td>5.20</td>
<td>8.39</td>
<td>0.59</td>
<td>5.06</td>
<td>7.08</td>
<td>2.78</td>
<td>44.24</td>
<td>140.04</td>
</tr>
<tr>
<td>N51/2</td>
<td>5.34</td>
<td>8.32</td>
<td>0.57</td>
<td>6.86</td>
<td>8.52</td>
<td>3.32</td>
<td>44.16</td>
<td>135.00</td>
</tr>
<tr>
<td>N51</td>
<td>5.27</td>
<td>8.36</td>
<td>0.58</td>
<td>7.57</td>
<td>10.14</td>
<td>3.59</td>
<td>60.52</td>
<td>145.04</td>
</tr>
<tr>
<td>N52</td>
<td>5.21</td>
<td>8.39</td>
<td>0.59</td>
<td>7.88</td>
<td>10.14</td>
<td>3.59</td>
<td>60.52</td>
<td>145.04</td>
</tr>
<tr>
<td>N71/2</td>
<td>5.33</td>
<td>8.32</td>
<td>0.57</td>
<td>1.32</td>
<td>1.99</td>
<td>1.28</td>
<td>11.81</td>
<td>75.00</td>
</tr>
<tr>
<td>N71</td>
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<td>8.34</td>
<td>0.58</td>
<td>1.55</td>
<td>2.98</td>
<td>1.49</td>
<td>13.35</td>
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</tr>
<tr>
<td>N72</td>
<td>5.22</td>
<td>8.39</td>
<td>0.59</td>
<td>2.81</td>
<td>3.22</td>
<td>2.09</td>
<td>21.67</td>
<td>79.99</td>
</tr>
</tbody>
</table>

Fig. 2 XRD patterns of Fe3O4 NPs at room temperature.

Fig. 3 Variation of crystallite size as a function of reaction time for 3, 5 and 7 M concentrations.
where $C_\infty$ is the solubility at a flat surface, $T$ is the temperature, $\gamma$ the surface energy, $R$ the molar gas constant and $V_m$ is the molar volume. For the case where \( \frac{2\gamma V_m}{RT} \) is less than 1, then the exponential term in eqn (5) can be linearized and considering the growth is determined by diffusion of the solute from the smaller particles to the larger particles, the subsequent rate law is obtained,

$$\bar{r}^3 - \bar{r}_0^3 = \frac{8\gamma C_\infty D V_m^2}{9RT} t = At \quad (7)$$

where $\bar{r}$ is the average particle radius at time $t$ and $\bar{r}_0$ is the average particle radius at time zero. This model provides a quantitative treatment of the time dependence of the particle size and size distribution.\(^\text{26}\)

Lattice constants were calculated to be $\sim 8.32$ Å for the 1/2 h reaction time samples N31/2, N51/2 and N71/2 which are attributed to the formation of maghemite. As the reaction time increases to 1 h, there is slight change in lattice constant which is about 8.35 Å (considering single phase) which is intermediate between those of maghemite ($a = 8.346$ Å, JCPDS # 39-1346) and magnetite ($a = 8.391$ Å JCPDS #19-0629) for all concentration 3, 5 and 7 M. This intermediate value of lattice parameter may be due to the presence of large surface energy of particles and the formation of maghemite at the interface of particles because Fe$^{2+}$ ions are more sensitive to oxidation, so ultimately surface ferrous ions can get oxidized to ferric ions which leads to the formation of maghemite. Although all samples prepared at 1/2 and 1 h reaction time for both 3 and 5 M concentration contains characteristic peaks of magnetite, there may be presence of small amount of maghemite (Fe$_2$O$_3$) especially at the surface of the particles which is difficult to detect from XRD. These results reveal the presence of both types of iron oxides. Whereas, the lattice parameter determined for all samples having reaction time 2 h in all concentration was found to be 8.39 Å, which is in good agreement with the standard value of magnetite 8.39 Å (Table 1). From these observations one can conclude that, along with concentration the reaction time also plays a pivotal role in the formation of iron oxide NPs.

FT-IR analysis was performed to confirm the formation of iron oxide NPs and to get information about the positions of the ions in the crystal through vibrational modes. Generally in magnetite, all Fe$^{2+}$ ions occupy octahedral interstices and half of the Fe$^{3+}$ ions occupy the tetrahedral interstices and remaining half of the Fe$^{3+}$ in octahedral sites. Normal and inverse spinels have four IR bands representing the two fundamentals absorption bands, the first IR fundamental band was due to tetrahedral and second due to octahedral complexes.

Vibration of iron ions in tetrahedral positions was attributed to the high frequency band and low frequency band was attributed to the vibration of iron ions in octahedral positions.\(^\text{27}\) The room temperature FT-IR spectra of the as prepared samples are shown in Fig. 4. The spectra were recorded in the range from 400 cm$^{-1}$ up to 4000 cm$^{-1}$. According to Waldron,\(^\text{28}\) the band appeared at 350–450 cm$^{-1}$ ($v_2$) is attributed to the stretching vibration of Fe$^{3+}$–O$^{2-}$ in the octahedral complexes and at 500–600 cm$^{-1}$ ($v_1$) to that of bending vibrations in tetrahedral complexes.

![FT-IR spectra of Fe$_3$O$_4$ NPs.](image-url)
From Fig. 4 it is observed that, the FTIR spectra of the Fe₃O₄ NPs exhibits two strong bands one is around 589 cm⁻¹ and other one is around 449 cm⁻¹ assigned to Fe–O stretching vibrations in the tetrahedral and octahedral complexes respectively. Whereas, the stretching vibration of 589 cm⁻¹ is found with the shoulder around 630 cm⁻¹ due to the slight oxidation of the NPs surface. Along with this, various stretching vibrations 650–800 cm⁻¹ and at around 3300–3500 cm⁻¹ were detected for all samples. In which vibrational bands around 3414 cm⁻¹, 1615 cm⁻¹ and 877 cm⁻¹ are attributed to the N–H stretch, N–H bend and N–H wag respectively. While different vibrational bands observed in the range of 1440–1070 cm⁻¹ are corresponds to the C–N stretch and C–C–N bending. All these stretching vibrations are attributed to fingerprint of vibrational modes of DIPA, indicating their adsorption on the surface of the NPs.

The absorption of DIPA on the surface of synthesized Fe₃O₄ NPs are well demonstrated by the TG-DTA. TG-DTA is one of the extremely valuable characterization techniques for thermal characterization of NPs which provides quantitative evidence on the structure of the NPs coating, also allows us to determine the bonding strength of the ligands to the NPs surface and its thermal stability. Typically, ligands that are bound more strongly desorbs at higher temperatures. Fig. 5 shows the typical TG-DTA of the N32 sample. From TG-DTA curves it is observed that, there are three major weight loss processes. First step is in between ~30–120 °C, in which there is presence of small endothermic peak below 110 °C accompanied with (3.85%) weight loss, which corresponds to the volatilization of the organic content and to the evaporation of the residual water content. The second and major weight loss process occurs from ~120 to 375 °C with simultaneous exothermic peak at ~270 °C which is attributed to the breakdown of DIPA from the surface of the Fe₃O₄ NPs. This temperature is much higher than the pure DIPA (83 °C, bp). Consequently, temperature shift could be owing to multilayered adsorption of DIPA on the surface of Fe₃O₄ NPs which requires higher temperature for the vaporization of bound DIPA. Third process is in the range ~375–565 °C at which ~5% weight loss occurs with simultaneous exothermic peak at ~494 °C corresponding to complete decomposition of carbonaceous matter. The strong desorption temperature compared to DIPA is indicative of an increased bonding strength to the NPs surface. This deduction concludes that, there is adsorption of DIPA on the surface of synthesized Fe₃O₄ nanoparticle.

TEM pictures were obtained for all Fe₃O₄ NPs synthesized at different concentrations and reaction time as described in the Experimental section to observe the shape and size of the NPs.
Fig. 6 show three representative images for N3, N5 and N7 at 1/2, 1 and 2 h samples respectively. All TEM images show roughly Gaussian-shaped particle size distribution. From TEM pictures it is revealed that, all NPs are nearly spherical in nature, well distributed and slightly in aggregated form. This agglomeration is an indication of exchange of interaction between particles or the high reactivity of the synthesized particles. Histograms of the average diameters were generated from TEM images with the help of ImageJ software. The corresponding distribution histograms are shown in Fig. 6. All distributions are unimodal and slightly asymmetrical, with a skewed shape toward the larger areas, characteristic of a lognormal distribution. The average particle size of the NPs is 5.2 nm, 8.5 and 3.2 nm for N31/2, N51 and N72 samples respectively which is in well agreement with the particle diameters obtained from XRD data.

**Magnetic properties**

Fig. 7 shows the room temperature hysteresis magnetization of dried samples obtained by SQUID with an applied magnetic field ±15 K.Oe. All samples exhibited superparamagnetic behavior, demonstrating that the thermal energy overcomes the anisotropy energy barrier of a single particle and also the
where $M$ is the domain magnetization of the bulk Fe$_3$O$_4$ (88 emu g$^{-1}$), $D_m$ is the magnetic diameter, $\chi_i$ is the initial magnetic susceptibility $\chi_i \sim (dM/dH) H \rightarrow 0$, and $\epsilon$ is the volume fraction of magnetic oxide. Here $\epsilon$ is defined as 1, and $H_0$ is obtained from the experimental data at a high external field where $M$ versus $1/H$ is linear with an intercept on the $M$-axis of $1/H_0$. The results of the calculations using only the magnetite phase were listed in table. From Table 1 it was observed that, magnetic particle sizes were showed the same trend (as like $D_{XRD}$ and $D_{TEM}$) i.e. increasing with reaction time, firstly increasing and then decreasing trend with increase in concentration of alkaline media. The size estimations made from magnetic data are slightly lower than the sizes obtained from TEM; this may have come from the magnetically dead surface layer as reported in ref. 35 and 36.

To study the effect of reaction time and concentration on magnetic properties of synthesized NPs from measurements of the blocking temperature for FC and ZFC processes is an interesting research topic. Zero-field-cooled (ZFC) magnetizations were measured by cooling sample in a zero magnetic field and then increasing the temperature in a static field of 100 Oe, while field-cooled (FC) curves were obtained by cooling the samples in the same static field. Typically in ZFC curve, magnetization increases with temperature and reaches to the maximum at a temperature $T_m$, thus it indicates that the magnetic moment of each particle is blocked along its easy magnetization direction at temperature $T$, which depends on different physical properties of the particle as particle volume, anisotropy and orientation.

Magnetization as a function of temperature in the applied field of 100 Oe was performed between 5 K and 350 K. From the FC and ZFC curves in Fig. 7d–f, we can observe its irreversibility, typical of the blocking process in superparamagnetic NPs. Furthermore, above the blocking temperature, the magnetization decreases as the temperature increases. From the behavior of the ZFC and FC curves, it is possible to conclude that these curves are almost overlapped above the blocking temperature, $T_m$, indicating the presence of the small-sized particles. Also it was observed that, all samples exhibit $T_m$ at lower temperature i.e. below 200 K (listed in Table 1) and was influenced by the particle size. It is found that, the ZFC-FC magnetization curves start to diverge near to the $T_m$ estimated with the ZFC curve. This is due to the relatively narrow size and shape distribution of the sample. It was also observed that $T_m$ increases with increase in particle size of the NPs, because the distance between the particles is not enough to reduce the dipolar interactions.

Indeed, for the iron oxide NPs, according to the Neel Model transition from the blocked to the superparamagnetic regime occurs at different temperatures for different particle sizes. In the present investigation for all synthesized NPs, the ZFC and FC curves also join together at about $T_m$, suggesting that magnetic aggregation is almost not present, in agreement with the individual particle coating and the pseudomorph-assembly. Magnetization ZFC curve coincides with that of FC above 150 K. This irreversible behavior is a characteristic of superparamagnetism.37

**Conclusion**

This study demonstrates that, high-yield, one pot synthesis of surface modified Fe$_3$O$_4$ NPs accomplished by the co precipitation method. Most interesting result is the effect of concentration of DIPA and reaction time on structural and magnetic properties of precipitated particles. As the concentration of DIPA increases from 3 M to 5 M the particle size initially increases reaches to its maximum $\sim$8.4 nm to $\sim$7.5 nm and then decreases up to $\sim$1.3 nm for 7 M concentration. The reaction time required to complete the growth of Fe$_3$O$_4$ NPs is found to be above 1/2 h. Improved magnetic properties of Fe$_3$O$_4$ NPs are found as compared to the reported in literature. From this study one can conclude that the use of DIPA is a potentially very interesting easy route to obtain desirable size and magnetic properties of Fe$_3$O$_4$ NPs by choosing appropriate parameters.
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