Chapter 4

Synthesis of Fe₃O₄ Nanoparticles

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Non-aqueous to aqueous phase transfer of oleic acid coated iron oxide nanoparticles for hyperthermia application


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4.1. Introduction

Distinct physico-chemical properties of nanomaterials have made them interesting candidates for their use in various fields in recent years. These properties differ from those in bulk and are strongly influenced by size and shape of the material. Due to the unique optical, electrical, magnetic and catalytic properties of transition metal oxides, they have been of great interest [1]. Among these, magnetite (Fe₃O₄) is an important material and has been mostly studied nanomaterial. Magnetite nanocrystals have been widely used in fields like multiferroics [2], ultrahigh density magnetic storage media [3], ferrofluids [4], in vivo and in-vitro biomedical applications [5, 6]. Due to better biocompatibility, injectability, chemical stability over physiological circumstances and substantial accumulation at the diseased site, magnetite nanocrystals have been widely used for biomedical applications. These magnetic nanoparticles (MNPs) can be used either as a diagnostic tool or in therapeutic applications. Their potential as a contrasting agent makes them suitable for diagnosing cancer in magnetic resonance imaging technique [7], while their heating ability allows them to have therapeutic applications as well which include hyperthermia [8]. These applications are very sensitive to the fundamental properties which are very much dependant on the method of synthesis. In the present chapter, the synthesis of Fe₃O₄ MNPs is discussed in detail.

4.2. Methods for synthesis of Fe₃O₄ MNPs

Several methods are reported in the literature to synthesize Fe₃O₄ MNPs. They can be synthesized using various chemical as well as biological routes. Chemical methods used to synthesize magnetite include co-precipitation, solvothermal method, combustion synthesis, sol-gel method, microwave assisted
synthesis, etc. Biological route involves the use of biological medium for magnetite synthesis, e.g. magnetotactic bacteria.

4.2.1. Chemical methods

Chemistry has played a major role in developing new materials with novel technologically significant properties. The benefit of chemical synthesis is its flexibility in designing and synthesizing new materials that can be refined into the final product. The major advantage that chemical processes offer over other methods is good chemical homogeneity, as it involves mixing at the molecular level. Numerous chemical methods are being used to synthesize magnetic nanostructures for biomedical applications, viz. co-precipitation, microemulsion, sol-gel, thermal decomposition, hydrothermal synthesis, combustion, polyol syntheses [9-12] etc. These methods have been used to synthesize particles with uniform composition and narrow size distribution. However, the most general method for the synthesis of MNPs is the chemical co-precipitation technique of iron salts. Some methods are discussed bellow in brief.

4.2.1.1. Combustion

Solution combustion synthesis makes use of salts, such as nitrates, metal sulfates and carbonates, as oxidants and reducing reagents, fuels such as glycine, sucrose, urea or other water soluble carbohydrates. Nitrate acts as an oxidizer for the fuel during the combustion reaction. The powder can be a pyrolysed product of a single phase, but usually it is a combination of metal oxides and in some cases it needs subsequent heat treatment to form single-phase products, which are usually the results required in this process. Solution combustion synthesis is a method based on the principle that once a reaction is initiated under heating, an exothermic reaction occurs that becomes self-sustaining within a certain time interval,
resulting in a powder as final product. The exothermic reaction begins at the ignition temperature and generates a certain amount of heat that is manifested in the maximum temperature or temperature of combustion. Solution combustion synthesis has the advantage of rapidly producing fine and homogeneous powders. Since it is an exothermic, auto-propagated process and with a high heat release rate, it can be explosive and should be undertaken with extra precautions.

Combustion synthesis is a low temperature synthesis technique that offers a unique mechanism via a highly exothermic redox reaction to produce oxides. The combustion reaction itself acts as a power-house instead of using high temperature furnaces during post-annealing procedures for prolonged time. These features make combustion synthesis an attractive method for the manufacture of technologically useful materials at lower costs compared to conventional ceramic processes. In combustion synthesis, the exothermicity of the redox (reduction-oxidation or electron transfer) chemical reaction is used to produce useful materials such as advanced catalysts, ceramics, alloys, composites, intermetallics and nanomaterials. A combustion reaction can be influenced by various processing parameters such as C/H ratio (type of fuel), the fuel to oxidizer ratio (F/O), the water content of the precursor mixture and the ignition temperature. The powder characteristics such as nature of agglomeration, surface area, crystallite size and size distribution are primarily governed by enthalpy or flame temperature generated during combustion which itself is dependent on nature of the fuel and F/O ratio [13]. By varying the F/O ratio, the particles with desired properties can be synthesized [14]. In fact, the reaction mechanism of the combustion is very complex. In general, a good combustion synthesis does not react violently, produces non-toxic gases and acts as a complexant for metal cations. The rapid generation of a large volume of gases during combustion dissipates the heat from the process and limits the temperature rise, reducing the possibility of premature
sintering between the primary particles. The generation of gases also helps limit interparticle contact, resulting in a more powdery product.

4.2.1.2. Microemulsion

A microemulsion is defined as a thermodynamically stable isotropic dispersion of two immiscible liquids, as an interfacial film of surface-active molecules stabilizes the microdomain of either or both liquids. In water-in-oil microemulsion, fine microdroplets of the aqueous phase are trapped within assemblies of surfactant molecules dispersed in a continuous oil phase. These microdroplets will continuously collide, coalesce and break again [15]. Conceptually, when reactants A and B are dissolved in two identical water-in-oil microemulsions, they will form an AB precipitate on mixing. The growth of these particles in microemulsions can be conceptualized as a progress of interdroplet exchange and nuclei aggregation [16-18]. The finely dispersed precipitate so produced can be extracted from the surfactants. Water-in-oil microemulsions have been shown to be a simple and versatile method to prepare nanosized particles [19-24] and with the favorable characteristics that could make this method useful for both in vivo and in vitro applications.

4.2.1.3. Hydrothermal synthesis

Hydrothermal syntheses of ultrafine Fe₃O₄ MNPs have been reported in the literature. These reactions are performed in aqueous media in reactors or autoclaves where the pressure can be higher than 2000 psi and the temperature can be above 200°C. There are two main routes for the formation of ferrites via hydrothermal conditions: hydrolysis and neutralization or oxidation of mixed metal hydroxides. These two reactions are very similar, except that ferrous salts are used in the first method. In this method, the reaction conditions, such as solvent, time and temperature usually have vital effects on the products [25]. Indeed, it was observed that the particle size of Fe₃O₄ powders increased with a
prolonged reaction time and higher water content resulted in the precipitation of larger \( \text{Fe}_3\text{O}_4 \) particles. In the hydrothermal process, the particle size in crystallization is controlled mainly through the rate processes of nucleation and grain growth, which compete for the species. Their rates depend upon the reaction temperature, with other conditions held constant.

### 4.2.2. Biological methods

The physico-chemical methods have been used successfully to produce NPs of inorganic material. However, these are expensive and involve the use of toxic chemicals. In addition, it is difficult to produce mono size dimension of NPs. Therefore, the development of clean, non-toxic, monodiameter dispersity and ecofriendly methods are in demand. The usage of toxic chemicals used in the physical and chemical synthesis of NPs is a factor which limits its biomedical applications. Hence, methods for the synthesis of NPs that are reliable, nontoxic and eco-friendly are of vital importance. Furthermore, the synthesis of NPs of different sizes, shapes, compositions and controlled dispersity is an important aspect of nanotechnology to develop new cost effective procedures. Biosynthesis method of NPs synthesis can fulfil all these necessities and thus it has been emerged as a promising field of research. Biosynthesis of NPs is obtained by two tracks such as intracellular and extracellular [26] and manufactured NPs are employed in several areas including health and planet care. Magnetotactic bacteria synthesize intracellular MNPs composed of single domain nano-crystals. These crystals are chemically homogeneous and possess a definite morphology and are enclosed by protein embedded lipid bilayer, known as magnetosome [27]. Marine \textit{Magnetotactic bacterium} MV-1 isolated from sulfide-rich sediments of an estuarine salt marsh is used for bioreduction of nitrous oxide and ferric quinate to iron-rich magnetosome in presence of anaerobic condition [28, 29].
4.3. Experimental

4.3.1. Single precipitation method

Fe$_3$O$_4$ NPs were prepared by single precipitation method. Coprecipitation method is more simplified and made cost-effective in this work. The precursor used for the synthesis of Fe$_3$O$_4$ was ferrous chloride (FeCl$_2$) only. No data is available on synthesis of Fe$_3$O$_4$ NPs using FeCl$_2$ as the sole precursor. The present type of synthesis procedure in absence of any oxidant is not reported in earlier literature.

2g FeCl$_2$.4H$_2$O was dissolved in 50 mL 1M HCl by heating upto 70 ºC. 50 mL 3M NaOH (or anhtdrous ammonia) was added to it at 60ºC drop by drop with constant stirring. A black precipitate was formed which was nothing but Fe$_3$O$_4$ NPs. Oxygen required to complete the reaction probably comes from air as the procedure was carried out in open environment. The precipitate was allowed to settle down by applying external magnetic field. The precipitate was then separated, washed with distilled water till the neutral pH is achieved. The precipitate was then dried at RT and used for further studies.

3 FeCl$_2$.4H$_2$O + 6 NaOH + $\frac{1}{2}$ O$_2$ $\rightarrow$ Fe$_3$O$_4$ + 6 NaCl + 15 H$_2$O ............ (4.1)

4.3.2. Coprecipitation method

Conventional coprecipitation method uses mixture of FeCl$_2$ and FeCl$_3$ for MNPs synthesis [30-33]. The co-precipitation technique is being mostly used chemical synthesis method for MNPs synthesis. FeCl$_3$ and FeCl$_2$ were used as precursors for the reaction in 2:1 proportions. In this process the salt solution of the required metallic elements is reduced by NaOH (or ammonia) solution. The reactants when mixed at temperature of 90ºC. After the mixing the reaction is continued for 40 min. The reaction taking place is shown as follows:

2 Fe$^{3+}$ + Fe$^{2+}$ + 8 OH$^-$ $\rightarrow$ Fe$_3$O$_4$ + 4 H$_2$O .................. (4.2)
4.4. Results and Discussion

4.4.1. Structural and morphological characterization of Fe$_3$O$_4$ MNPs

Fig. 4.1 (a) and (b) show the powder XRD patterns for Fe$_3$O$_4$ MNPs prepared by single precipitation using NaOH and ammonia respectively. The main characteristic peaks were obtained with the (hkl) values of (220), (311), (400), (422) and (511). These were then matched with the JCPDS file number 82-1533, which corresponds to Fe$_3$O$_4$ phase. Both the NPs show inverse spinel structure. The crystallite sizes of NPs were calculated from FWHM of the most intense peaks using the Debye-Scherrer formula. The crystallite sizes obtained were 20 nm and 22 nm for Fe$_3$O$_4$ MNPs prepared by single precipitation using (a) NaOH and (b) ammonia respectively. Fig. 4.2 (a) and (b) show the powder XRD patterns for Fe$_3$O$_4$ MNPs prepared by coprecipitation using NaOH and ammonia respectively. The crystallite sizes obtained were 23 nm and 22 nm for Fe$_3$O$_4$ MNPs prepared by coprecipitation using (a) NaOH and (b) ammonia respectively.

![XRD patterns](image)

**Fig. 4.1:** XRD patterns obtained from Fe$_3$O$_4$ MNPs prepared by single precipitation using (a) NaOH and (b) ammonia.
Fig. 4.2: XRD patterns obtained from Fe$_3$O$_4$ MNPs prepared by coprecipitation using (a) NaOH and (b) ammonia.

The Selected Area Electron Diffraction (SAED) patterns for MNPs prepared by single precipitation using (a) NaOH and (b) ammonia are shown in Fig. 4.3 and those of MNPs prepared by coprecipitation using (a) NaOH and (b) ammonia are shown in Fig. 4.4. They show bright ring patterns indicating polycrystalline nature of the MNPs, as indicated by XRD patterns. The ring pattern corresponds to (220), (311), (400), (422) and (511) planes which can be clearly seen in XRD results.
Fig. 4.3: SAED patterns of Fe₃O₄ MNPs prepared by single precipitation using (a) NaOH and (b) ammonia.

Fig. 4.4: SAED patterns of Fe₃O₄ MNPs prepared by coprecipitation using (a) NaOH and (b) ammonia.

The EDAX spectra were used for a quantitative elemental analysis of MNPs, which are shown in Fig. 4.5 and Fig. 4.6. The corresponding peaks in all the MNPs were due to Fe and O only. All the spectra did not show any additional impurity peak implying purity of the samples.
**Fig. 4.5:** EDAX spectra of Fe$_3$O$_4$ MNPs prepared by single precipitation using (a) NaOH and (b) ammonia.

**Fig. 4.6:** EDAX spectra of Fe$_3$O$_4$ MNPs prepared by coprecipitation using (a) NaOH and (b) ammonia.

SEM images of Fe$_3$O$_4$ MNPs prepared by single precipitation using (a) ammonia and (b) NaOH are shown in Fig. 4.7 while those of prepared by coprecipitation using (a) ammonia and (b) NaOH are shown in Fig. 4.8. The bare particles showed a high degree of agglomeration due to dipole – dipole interaction. All the MNPs were spherical in shape. It was observed that MNPs prepared using
NaOH showed less degree of agglomeration as compared to bare MNPs prepared using ammonia in both the synthesis methods.

**Fig. 4.7**: SEM images of Fe₃O₄ MNPs prepared by single precipitation using (a) ammonia and (b) NaOH.

**Fig. 4.8**: SEM images of Fe₃O₄ MNPs prepared by coprecipitation using (a) ammonia and (b) NaOH.

The size and shapes of the MNPs were observed using TEM. The TEM images MNPs are shown in Fig. 4.9 and Fig. 4.10 ((a) for NaOH and (b) for ammonia) for single and coprecipitation respectively. Fe₃O₄ MNPs prepared via single precipitation using ammonia were highly agglomerated with particle size 16.5 ± 4.3 nm while MNPs prepared via single precipitation using NaOH were well dispersed with particle size 22.8 ± 5.1 nm.
**Fig. 4.9:** TEM images of Fe$_3$O$_4$ MNPs prepared by single precipitation using (a) ammonia and (b) NaOH.

**Fig. 4.10:** TEM images of Fe$_3$O$_4$ MNPs prepared by coprecipitation using (a) ammonia and (b) NaOH.

Fe$_3$O$_4$ MNPs prepared via coprecipitation using ammonia were highly agglomerated with particle size 21.4 ± 3.9 nm while MNPs prepared via coprecipitation using NaOH were well dispersed with particle size 24.8 ± 4.1 nm. Bare MNPs have strong magnetic dipole-dipole interaction and hence are attracted...
strongly and form big clusters causing bigger particle size. These results are comparable with the XRD results.

4.4.2. Magnetic characterization of Fe\textsubscript{3}O\textsubscript{4} MNPs

The attractive or repulsive forces between magnetic materials can be described in terms of magnetic dipoles—tiny bar magnets with opposite poles. Materials can thus be classified into diamagnetic, paramagnetic, ferromagnetic, ferrimagnetic and antiferromagnetic according to the arrangement of their magnetic dipoles in the absence and presence of an external magnetic field. If a material does not have magnetic dipoles in the absence of an external field and has weak induced dipoles in the presence of a field, the material is referred to as diamagnetic. The magnetization of a diamagnet responds in the opposite direction to the external field. If a material has randomly oriented dipoles that can be aligned in an external field, it is paramagnetic. The magnetization of a paramagnet responds in the same direction as the external field. The magnetic interactions derived from the above two types of materials are very weak. For a ferromagnetic material, the magnetic dipoles always exist in the absence and presence of an external field and exhibit long-range order. Macroscopically, such a material displays a permanent magnetic moment. The difference in the source of the net magnetic moment can also be used to distinguish ferromagnetism from both ferrimagnetism and antiferromagnetism. In a ferromagnetic material there are always weaker magnetic dipoles aligned antiparallel to the adjacent, stronger dipoles in the absence of an external magnetic field. For an antiferromagnetic material, the adjacent dipoles are antiparallel in the absence of an external field and cancel each other. In general, magnetic materials are refereed to those characterized by either ferro or ferrimagnetic features [34].
**Table 4.1:** The Saturation Magnetization ($M_s$), Coercivity ($C_e$) and Remenance ($M_r$) values calculated from the $M$-$H$ loops for Fe$_3$O$_4$ MNPs prepared by single precipitation using NaOH and ammonia.

<table>
<thead>
<tr>
<th>Property</th>
<th>NaOH</th>
<th>Ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100K</td>
<td>300K</td>
</tr>
<tr>
<td>$M_s$ (emu/g)</td>
<td>55.74</td>
<td>51.65</td>
</tr>
<tr>
<td>$M_r$ (emu/g)</td>
<td>159.13</td>
<td>16.89</td>
</tr>
<tr>
<td>$C_e$ (Oe)</td>
<td>14.25</td>
<td>2.24</td>
</tr>
</tbody>
</table>

**Table 4.2:** The Saturation Magnetization ($M_s$), Coercivity ($C_e$) and Remenance ($M_r$) values calculated from the $M$-$H$ loops for Fe$_3$O$_4$ MNPs prepared by coprecipitation using NaOH and ammonia.

<table>
<thead>
<tr>
<th>Property</th>
<th>NaOH</th>
<th>Ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100K</td>
<td>300K</td>
</tr>
<tr>
<td>$M_s$ (emu/g)</td>
<td>55.44</td>
<td>50.57</td>
</tr>
<tr>
<td>$M_r$ (emu/g)</td>
<td>159.53</td>
<td>13.51</td>
</tr>
<tr>
<td>$C_e$ (Oe)</td>
<td>13.86</td>
<td>1.97</td>
</tr>
</tbody>
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**Fig. 4.11:** $M-H$ loops of Fe$_3$O$_4$ MNPs prepared by single precipitation using (a) NaOH and (b) ammonia at 100 and 300 K.

**Fig. 4.12:** $M-H$ loops of Fe$_3$O$_4$ MNPs prepared by coprecipitation using (a) NaOH and (b) ammonia at 100 and 300 K.

Generally Fe$_3$O$_4$ NPs show superparamagnetic behavior below size less than 20nm which is characterized by zero coercivity and zero remanence [35-38]. Fig 4.11 shows MH curve of Fe$_3$O$_4$ NPs prepared by single precipitation method using NaOH and ammonia at 300K. Fig 4.12 shows MH curve of Fe$_3$O$_4$ NPs prepared by coprecipitation method using NaOH and ammonia at 300K. The graph
clearly shows superparamagnetic nature of the NPs at 300K as coercivity and remanence values are very negligible. Saturation magnetization (Ms) values for NPs were observed to be 51.65 emu/g and 50.84 emu/g at 300K shown in Table 4.2 (for NaOH and ammonia respectively) for single precipitation as well as 50.57 emu/g and 50.65 emu/g at 300K (for NaOH and ammonia respectively) for coprecipitation which are small compared to that of theoretical value of bulk Fe$_3$O$_4$ (Ms= 92 emu/g). Saturation magnetization has been reported to decrease as the particles size of magnetite decreases below 30 or 20 nm, due to finite size effect [39].

4.6. Conclusions

The study confirmed that the pure phase Fe$_3$O$_4$ MNPs can be synthesized using single precipitation method, with FeCl$_2$ as the sole source for MNPs synthesis and without using any oxidant. Single precipitation is a simpler and cost effective alternative for co-precipitation technique. Method for synthesis as well as the alkali used to obtain Fe$_3$O$_4$ affects the properties of MNPs. The particle size 22.8 ± 5.1 nm and 23.5 ± 4.3 nm were obtained for single precipitation method, respectively for NaOH and ammonia, while 21.4 ± 3.9 and 24.8 ± 4.1 nm were obtained for coprecipitation method, respectively for NaOH and ammonia. These particle sizes are suitable for their application in biomedical field. Synthesized MNPs were superparamagnetic in nature with zero coercivity and remanence values. However saturation magnetization of MNPs obtained from NaOH usage was higher than that of MNPs obtained from ammonia reduction. Additionally, the prior showed less degree of agglomeration than the later which will facilitate to improve their colloidal stability. Hence, owing to desirable properties of the MNPs synthesized with single precipitation method using NaOH, they are used for the further proposed work.
REFERENCES


