CHAPTER - 3

PLA OF IRON IN
AQUEOUS MEDIA
Section-3.1: PLA of Iron in Water

3.1.1 Introduction

Recently, synthesis of magnetic nanomaterials have been a field of intense study, due to the novel mesoscopic properties shown by particles of quantum dimensions located in the transition region between atoms and bulk solids. Due to quantum size effect and large surface to volume ratio, magnetic NPs significantly change magnetic property and show superparamagnetic character. Based on their unique mesoscopic physical, chemical, thermal, and mechanical properties, superparamagnetic NPs offer a high potential for several biomedical applications. Superparamagnetic NPs have many applications such as drug delivery, magnetic resonance imaging (MRI), hyperthermia and tissue repair [1-2].

Iron and its oxide [commonly including hematite ($\alpha$-Fe$_2$O$_3$), maghemite ($\gamma$-Fe$_2$O$_3$), and magnetite (Fe$_3$O$_4$)] NPs have received considerable attention due to its applications in magnetic, electric, electronic, pigmental, catalyst and biomedical purposes [3-6]. The report of synthesis and properties of Wüstite (FeO) NPs are very rare, because it is usually formed at high temperature or high pressure and stable only above 560 °C [7-9]. Recently, Liu et al. [10] have reported synthesis of FeO NPs using PLA, but they have not studied magnetic, optical bandgap and thermal properties. The Nanosized FeO particles have gained great potential for catalysis and gas sensor applications [11-13]. In the present study, we have successfully synthesized FeO NPs using PLA, in double distilled water (DDW) and studied optical, magnetic and thermal properties.

3.1.2 Material Synthesis and Characterization

The experimental procedure and arrangement for the laser ablation of metal target in aqueous environment have been described earlier in Chapter-2. A High purity (Spec pure, Johnson Matthey) iron slice was emerged in 20 ml of DDW. Different pulse energy
(30, 40, 50 and 60 mJ) of laser has been employed for ablation to synthesize FeO NPs. Obtained colloidal suspension of NPs after ablation was separated, dried and used for further characterization.

XRD pattern of as synthesized FeO sample was recorded by CuK\textsubscript{α} radiation of Rigaku, Japan (Model: Ultima-III) using X-ray wavelength $\lambda = 1.5406$ Å. UV-visible absorption spectra of as synthesized colloidal solution of NPs were recorded using Perkin Elmer Lambda 35. Photoluminescence spectrum was recorded by xenon lamp using 280 nm as excitation wavelength. IR spectroscopy was performed using Thermo Scientific ATR- FTIR spectrometer. TEM images were recorded using TEM (model number FEI Tecni G2F30STWIN). A drop of colloidal solution of NPs was placed on the copper grid and dried at 60° C before imaging the particle shape and size. Magnetic measurement has been carried out by a VSM (Lakeshore, USA) at different temperature.

3.1.3 Results and Discussion

(A) X-ray Diffraction

The smoothed and background corrected XRD pattern of FeO NPs synthesized at 40 mJ, is shown in Fig. 3.1.1. Peak positions at $2\theta = 34.56^\circ, 36.20^\circ, 42.05^\circ, 44.30^\circ, 60.98^\circ, 72.72^\circ$, and $76.52^\circ$ correspond to the FeO phase with plane [002], [111], [200], [101], [220], [311], and [222] respectively. The system is FCC with lattice parameters, $a = 4.294$, (JCPDF No. 751550, 491447). The peak situated at $50.56^\circ, 55.60^\circ$ and $67.27^\circ$, indicate the formation of metallic iron (Fe) phase with plane [222],[321] and [420] respectively, having hexagonal and primitive lattice parameter $a= 2.45$, and $c= 3.39$ (JCPDF No. 011262). FeO phase is also confirmed by TEM-SAED pattern and some authors have also reported the ablation of iron target in DDW and reported similar type of results [10, 15].
Fig. 3.1.1: XRD pattern of iron oxide (FeO) nanocrystals at 40 mJ.

The crystalline sizes can be estimated using Scherer’s formula

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (3.1.1)$$

Where constant K and wavelength $\lambda$ of X-ray are taken to be 0.94 and 1.5043 Å, $\beta$ is full width at half maximum of diffraction peak corresponding to $2\theta$. Crystallite size is calculated using eq. 3.1.1 and found in the range of 3-5 nm.

(B) UV-Visible Absorption Spectroscopy

UV-visible absorption spectra of as synthesized FeO colloidal NPS in DDW at different pulse energies have been recorded and shown in fig. 3.1.2a. The absorption spectra show low absorbance in the range of 402-309 nm and intense absorbance near 219 nm. Liu et al [10] have got similar absorption results of FeO colloidal NPs. It is difficult to explore clear band edge in transition metal oxides due to the many narrow d-d bands in between the energy gap. UV-visible absorption spectra of agglomerated and oxidized iron oxide NPs in DDW upto 5 months are also shown in Fig. 3.1.2b. The entire spectrum consists three absorption bands 591-443, 373-252 nm and a sharp peak near 219 nm. The absorption spectra of samples at 30, 40 and 50 mJ are almost similar but the absorption spectrum of sample at 60 mJ is quite different.
The difference is in the sense of peak broadening and absorbance intensity. It is probably due to the unlike particle shape and size configuration at 60 mJ. These absorption peaks are characteristic absorption of stable iron oxide \((\text{Fe}_2\text{O}_3)\) phase. The absorption range 591-443 nm is the basic bandgap, which is originated due to pair excitation process from the transition of \(^6\text{A}_1+^6\text{A}_1 \rightarrow ^4\text{T}_1(\text{^4G})+^4\text{T}_1(\text{^4G})\). The absorption spectra in the range of 373-252 nm and a sharp peak at 219 are resulted from the ligand to metal charge-transfer transitions [16-17]. The absorption spectra of as synthesized and agglomerated iron oxide NPs indicate that, in laser ablation process FeO phase forms at first stage and after ageing during 5 months and it transits in stable \(\text{Fe}_2\text{O}_3\) phase.

UV-visible absorption spectra of as synthesized iron oxide colloidal NPs at different variable parameters are illustrated in Fig 3.1.3a-d. Fig 3.1.3a depicts absorption spectra of iron oxide NPs synthesized using 1064 and 532 nm wavelength. Absorbance of 532 nm is dominant over 1064 nm; may be due to higher NPs density. Fig.3.1.3b-d. illustrates the UV-visible absorption spectra of iron oxide NPs synthesized using 532 nm wavelength. The time dependent absorption spectra of iron oxide NPs at different days are shown in Fig.3.1.3b. As number of day’s passes away the peak position near 260 nm is red shifted and also peak intensity goes down. It is due to agglomeration and oxidation of iron oxide NPs in DDW. Fig.3.1.3c-d show UV-visible absorption spectra at different energy and ablation time duration. The whole process can be described using chemical formula as follows.

\[
\text{Fe (clusters)} + 2\text{H}_2\text{O} \rightarrow \text{Fe (OH)}_2 + \text{H}_2 \hspace{1cm} (a)
\]

\[
\begin{align*}
\text{Fe(OH)}_2 & \xrightarrow{\text{high pressure}} \text{FeO} + \text{H}_2\text{O} \\
& \xrightarrow{\text{high temperature}} \text{FeO} + \text{H}_2\text{O} \hspace{1cm} (b)
\end{align*}
\]
Fig. 3.1.2 (a) FeO phase, just after ablation (b) Fe$_2$O$_3$ phase, after five month of ageing.

Fig. 3.1.3: UV-visible absorption spectra of NPs showing effect of (a) Different wave length (b) Ageing (c) different pulse energy (d) different ablation time.

Fig. 3.1.4: (a) Optical bandgap just after ablation (b) Optical bandgap after five month ageing
Since FeO phase is highly unstable and it decomposes in the presence of H2O and it finally change in Fe2O3 during five month in H2O. The absorption bandgap $E_g$ of as synthesized iron oxide colloidal NPs can be determined by the Tauc equation given as:

$$\alpha h\nu = (h\nu - E_g)^n$$  \hspace{1cm} (3.1.2)

Where $h\nu$ is the photon energy, $\alpha$ is the absorption coefficient and $n$ is either 1/2 for a direct transition or 2 for an indirect transition. The linear portions of the curves are fitted using linear regression analysis. An extrapolation of the linear region of the plot gives the value of the bandgap as the intercept to the horizontal axis. Tauc plot of as synthesized FeO colloidal NPs phase is shown in Fig.3.1.4a, the calculated bandgap of FeO phase is well consistent as reported Alfredsson et al [18]. Fig.3.1.4b depicts the bandgap of stable Fe2O3 phase which is consisted as reported by He et al [16]. There are two bandgap as cleared from tauc plot, the larger bandgap results from inter valence charge transfer (IVCT) and Charge transfer between Fe $^{+3}$ and O$^{+2}$. The lower bandgap is due to the IVCT and pair excitations. Optical bandgap energy of as synthesized iron oxide NPs are decreased due to ageing and oxidation in DDW during five month.

**Table 3.1.1: bandgap of as synthesized and agglomerated iron oxide nanocrystals**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Pulse energy (mJ)</th>
<th>Bandgap of FeO (eV)</th>
<th>Bandgap of Fe2O3 (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Charge Transfer</td>
<td>Pair excitations</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
<td>3.37</td>
<td>2.91</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>3.91</td>
<td>3.13</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>3.60</td>
<td>3.03</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>3.81</td>
<td>3.09</td>
</tr>
</tbody>
</table>

The comparative study of energy bandgap vs pulse energy of as synthesized and agglomerated iron oxide NPs are shown in table 3.1.1 It is clear that bandgap of NPs increases on increasing pulse energy. It seems that on increasing pulse energy of laser, the particle size of iron oxide NPs become smaller and smaller.
(C) **Photoluminescence Spectroscopy (PL)**

![Pl spectrum of FeO NPs synthesized at 40 mJ.](image)

Fig. 3.1.5. Illustrates the photoluminescence spectrum of as synthesized iron oxide colloidal NPs in DD water. The PL spectrum was recorded in the range of 250-450 nm using xenon lamp of 245 nm as excitation wavelength. The PL spectrum shows a intense band near 396 nm and a kick around 328 nm. The peak at 396 nm indicates the band to band transition of iron oxide NPs and the kick at 328 nm may be due the ligand to metal charge-transfer transitions. Turro et al. [19] have reported Pl of iron oxide NPs which is compatible with our results.

(D) **ATR-FTIR Spectroscopy**

FTIR spectra of FeO NPs dissolved in DDW and DDW as background are recorded which are shown in Fig.3.1.6. Strong bands at 545, 586 and 670 cm\(^{-1}\) are attributed to the Fe -O stretching vibration mode. The transmittance at 1524 and 1654 cm\(^{-1}\) are related to the O-H stretching vibration modes and the broad band 3600 - 3800 cm\(^{-1}\) is related to the O-H stretching vibration mode due to water vapor [20-21]. The intense transmittance at 2362 cm\(^{-1}\) is due to the CO\(_2\) molecules present in atmosphere. The transmittance near 3747 and 3865 cm\(^{-1}\) are due to the H\(_2\)O.
Fig. 3.1.6: FTIR spectra of as synthesized colloidal solution of iron oxide NPs at 40 mJ.

(E) Transmission Electron Microscopy (TEM)

Fig. 3.1.7: TEM and SAED image of iron oxide colloidal NPs at 40 mJ.

TEM image of as synthesized iron oxide NPs in DDW at the bar scale of 50 nm is shown in Fig. 3.1.7. The picture shows that particles are dispersed in liquid medium with spherical shape. Majority of the particles are in the range of 1-5 nm while some of them are
in the range of 5-10 nm in diameter. SAED pattern of as synthesized iron oxide colloidal NPs are also shown in Fig.3.1.7b. The SAED pattern confirms the formation of FeO phase of iron oxide NPs which has been also confirmed by XRD pattern. The SAED pattern shows ring as well as spots which is due to crystalline and amorphous nature of FeO NPs. The plane [111], [200] and [220] are well consistent as indexed in XRD pattern.

(F) Magnetic Property

![Magnetic Property Graph](image)

Fig.3.1.8: Magnetic measurement at 40 mJ (a) M-H loop of FeO NPs at RT (b) dM/dH.

The hysteresis loop of iron oxide (FeO) NPs at room temperature is shown in Fig. 3.1.8a. Initial susceptibility was calculated by derivative of M-H loop as shown in Fig. 3.1.8b. The FeO NPs show antiferromagnetic character with coercivity (H_c) 47 Oe and remanence (M_r) 0.009 emu/gm. The magnetic domain size can be calculated using magnetization curve from the following formula derived from Langevin function [22].

\[
D_m = \left[ \frac{18K T \chi_i}{\pi \rho M_s^2} \right]^{1/3}
\]  

(3.1.3)

Here, \( \chi_i \) is initial magnetic susceptibility \( \chi_i = (dM/dH)_{H \to 0} \) and \( \rho \) is the density (5.74 g/cm\(^3\)) of FeO. Initial slope near origin was determined from differentiating M-H loop, M_s
saturation magnetization was found to be 0.97 emu/g at 300 K. Magnetic particle (domain) size $D_m$ of FeO NPs is calculated about 7.0 Å at 300 K, which is about 10$^\text{th}$ times smaller than TEM particle size ($D_{\text{TEM}}$). Because $D_{\text{TEM}}$ can contain multi domains while $D_m$ has only single magnetic domain. Another deference between $D_m$ and $D_{\text{TEM}}$ are most likely the contribution of a magnetically `dead' layer which may arise due to canted surface spin present on the surface of $D_{\text{TEM}}$, and also amorphous nature of FeO NPs [23].

![Fig.3.1.9: Temperature dependent magnetization (a) ZFC and FC of FeO NPs (b) $dM/dT$ of FC.](image)

Fig.3.1.9 shows the temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of iron oxide NPs. In the ZFC measurement, the sample is cooled from 350 to 50 K without applying an external magnetic field. After reaching 50 K, a 1 K Oe field was applied and the magnetization has been recorded on increasing temperature. When the sample is cooled at zero-field (ZFC) the spin moments are totally disordered and show zero-magnetization. For FC experiments, the sample is cooled from 350 K under an applied field of 1 K Oe; then the magnetization is recorded as the temperature increased. When the sample is cooled at non-zero field (FC), the spin moments are ordered almost parallel to the direction of applied field, so that sample shows
non-zero magnetization even if the field decreases to zero. It is clear from Fig (3.1.9a) on increasing the temperature, the ZFC magnetization increases and reaches a maximum where the temperature is referred to as the blocking temperature \((T_B)\). Fig.3.1.9b shows derivative of magnetization vs temperature, the peak shows the Néel transition temperature. The blocking temperature is defined as the temperature at which the NPs moments do not relax (known as blocked) during the time scale of the measurement. Khurshid et al. [24] have reported blocking temperature 340 K of FeO / Fe_{3}O_{4} at 30 nm particles size. It is also observed that blocking temperature of FeO NPs increases on increasing particle size. In our case blocking and Neel temperature of FeO NPs found to be 245±2 K and 181±2 K respectively which are lower than reported values as shown in the Fig 3.1.9b. Reduced values of \(T_B\) and \(T_N\) may be due to smaller particle size and canted surface spin of FeO NPs [25].

(G) **Thermal Conductivity**

![Thermal conductivity measurement of FeO Colloidal NPs in water at 40 mJ.](image)

The thermal conductivity recorded in the range of 20-70 °C of as synthesized FeO colloidal NPs is shown Fig. 3.1.10. It is clear that thermal conductivity of FeO colloidal NPs increases continuously as temperature increases with respect to reference DDW.
Temperature dependent thermal conductivity of nanofluids can be explained on the basis of Brownian motion.

\[ K_{\text{brownian}} = (\phi C_N V_N l)^{1/3} \]  

(3.1.4)

where \( C_N \) is the heat capacity per unit volume of the NPs, ‘l’ is the mean free path, \( V_N \) is root mean square velocity of the particles and \( \phi \) is the volume fraction [26].

If the temperature increases the root mean square velocity also increases which is temperature dependent, therefore Brownian motion of dispersed NPs increases in base liquid, this boost up the thermal conductivity of nanofluids [27]. The other factors which enhance the thermal conductivity of nanofluids are NPs density and size. As the size of NPs decreases the heat capacity per unit volume (\( C_N \)) of NPs increases, which raises the thermal conductivity.

3.1.4 Conclusion

The colloidal solution of FeO NPs has been successfully synthesized using PLA in DDW. The absorption bandgap of as synthesized and agglomerated FeO NPs have been estimated using tauc plot. The PL spectroscopy and IR spectroscopy employed to investigate defect level and vibrational states of iron oxide NPs. Particle shape, size and phase have been confirmed by TEM and SAED pattern and found spherical in the range of 1-10 nm in diameter. The FeO NPs show antiferromagnetic character with coercivity 47 Oe, remanence 0.009 emu/gm. As synthesized iron oxide NPs show blocking and Neel temperature 245±2 K and 181±2 K respectively. Thermal conductivity measurement confirms that iron oxide ferrofluids have larger thermal conductivity than base fluid.
3.2.1 Introduction

There are many different phases of iron oxide (Fe₂O₃) such as γ-Fe₂O₃ (maghemite), α-Fe₂O₃ (hematite), β-Fe₂O₃, δ-Fe₂O₃, η-Fe₂O₃, ε-Fe₂O₃ and oxyhydroxide such as α-FeOOH (goethite) and γ-FeOOH (lepidocrocite) [28]. Among these oxides α-Fe₂O₃ semiconducting commonly known as hematite, is the most stable oxide having many useful applications in pigments, adsorbents, photocatalysts, solar energy conversion, lithium ion batteries and sensors [29-33]. Further most usually explored oxide is γ-Fe₂O₃, known as maghemite having many applications in magnetic recording and storage, magneto-optical device, magnetic refrigeration, magnetic resonance imaging [34-39].

The reports on synthesis of β-Fe₂O₃ and ε-Fe₂O₃ phases of iron oxide nanocrystals are very rare, because specific condition i.e. high temperature and pressure [40-42]. There is insufficient information available on synthesis of iron oxide NPs using (CTAB) as cationic surfactant that provides detailed understanding of its surface properties. Since rate of adsorption of cationic capping agent is higher than the non-ionic or anionic capping agent, the size, shape and composition of iron oxide nanocrystals must differ from those in non-ionic or anionic surfactant. Keeping above points in view, the synthesis of iron oxide NPs by PLA with varying concentration of CTAB as surfactant has been discussed here.

3.2.2 Material Synthesis and Characterization

The experimental procedure and arrangement of laser ablation of metal target in aqueous environment are similar as described earlier in chapter-2 [43-47]. The synthesis conditions are same as disused in section 3.1.2. Here CTAB cationic liquid media with different concentrations are used as capping agent. XRD pattern of as synthesized powder
sample was recorded using synchrotron radiation source having wavelength $\lambda = 1.1294 \, \text{Å}$. Synchrotron radiation source is inherently advantageous compared to laboratory XRD, as discussed in chapter -2. The other characterizations are same as discussed in section 3.1.2.

3.2.3 Results and Discussion

(A) X-ray Diffraction

Fig.3.2.1 shows the XRD pattern of as synthesized iron oxide NPs in CTAB cationic liquid media. The diffraction pattern confirms mix phases of $\beta$-Fe$_2$O$_3$, $\varepsilon$-Fe$_2$O$_3$ and FeO (OH). The highest intense peak at $15.56^\circ$ corresponds to the FeO (OH) phase (JCPDS No. 03-0251), which also coincides with $\beta$-Fe$_2$O$_3$ but FeO (OH) is most dominant. The diffraction pattern at $15.56^\circ, 17.88^\circ, 21.90^\circ, 22.70^\circ$ and $24.70^\circ$ present the $\beta$-Fe$_2$O$_3$ phase corresponding planes $[105], [006], [017], [0112], \text{and} [116]$ respectively; having hexagonal structure and lattice parameters $a=5.92, c=35.69$ (JCPDS No. 40-1139).

The peak positions at $2\theta = 13.62^\circ, 16.20^\circ, 20.07^\circ, 21.83^\circ$ and $30.02^\circ$ present $\varepsilon$-Fe$_2$O$_3$ phase with planes $[221], [220], [202], [022], \text{and} [411]$ respectively; having monoclinic structure and lattice parameters $a=12.97, b=10.21$ and $c=8.44$ (JCPDF No. 16-0653). Crystallite size can be estimated using Scherer’s equation 3.1.1. Calculated crystalline size corresponding
to $2\theta=15.58^\circ$ and $17.88^\circ$ are found to be 6.60 and 5.64 nm respectively.

(B) **UV-visible Absorption Spectroscopy**

UV-visible absorption spectra of as synthesized mix phases of iron oxide / hydroxide ($\text{Fe}_2\text{O}_3$, FeO (OH)) just after ablation in different CTAB concentrations are shown in Fig.3.2.2a inset picture depicts normalized absorption spectra. Fig.3.2.2b shows the UV-visible absorption spectra of agglomerated NPs after five month of synthesis in CTAB liquid media. The absorbance intensity decreases with concentration of CTAB due to self ageing of NPs. The rate of ageing of smaller NPs is faster than large particles, due to larger surface energy. Gaussian fitted curve describes two absorption peaks at 260 and 354 nm for $\text{Fe}_2\text{O}_3$ and FeO (OH) shown in Fig.3.2.2c. This absorption spectrum corresponds to ligand field transition [48-49].

The absorption bandgap is calculated using tauc equation 3.1.2 and it has been found in the range of 2.86-2.99 eV as shown in table 3.2.1 and Fig.2.2.3a-b. These results confirm that bandgap energy decreases after agglomeration of NPs in CTAB liquid media but at 0.5, 1 and 5 mM CTAB (near CMC of CTAB), there is nominal change in absorption bandgap, due to better capping and stable particle formation. Optical bandgap of $\text{Fe}_2\text{O}_3$, and FeO (OH) have been reported by a number of authors in the range of 2.12-2.50 eV [48-51].

**Table 3.2.1: bandgap analysis with respect to crystalline size of as synthesized NPs.**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample name</th>
<th>Crystalline size (nm)</th>
<th>Bandgap (eV) after Ablation</th>
<th>Bandgap (eV) after five month</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1 mM</td>
<td>-</td>
<td>2.97</td>
<td>2.90</td>
</tr>
<tr>
<td>2</td>
<td>0.5 mM</td>
<td>-</td>
<td>2.87</td>
<td>2.87</td>
</tr>
<tr>
<td>3</td>
<td>1.0 mM</td>
<td>6.60, 5.54</td>
<td>2.91</td>
<td>2.87</td>
</tr>
<tr>
<td>4</td>
<td>5.0 mM</td>
<td>6.25, 5.07</td>
<td>2.88</td>
<td>2.86</td>
</tr>
<tr>
<td>5</td>
<td>10 mM</td>
<td>6.38, 5.23</td>
<td>2.99</td>
<td>2.86</td>
</tr>
</tbody>
</table>
Fig. 3.2.2: UV-visible absorption spectra (a) Just after ablation (b) After five month of ageing, inset picture shows normalized data. (c) Gaussian fitted spectra.

Fig. 3.2.3: Tauc plot of NPs (a) just after ablation (b) after five month ageing.

(C) Photoluminescence Spectroscopy

Fig. 3.2.4: PL spectrum of as synthesized iron oxide/hydroxide NPs in 1 mM CTAB.
PL spectrum of as synthesized mix phases of Fe$_2$O$_3$ and FeO (OH) is shown in Fig. 3.2.4. After Gaussian fitting of experimental curve, two peaks were observed around 560 and 604 nm, these peaks are emission spectrum of Fe$_2$O$_3$ and FeO(OH) composite. The peak broadening also indicates the formation of mix phases. Zhang et al. [52] have reported photoluminescence spectrum of iron oxide in the range of 510-558 nm.

(D) ATR-FTIR Spectrum of Iron Oxide/Hydroxide

![ATR-FTIR Spectrum of Iron Oxide/Hydroxide](image)

Fig.3.2.5: ATR-FTIR spectra of as synthesized iron oxide/hydroxide NPs in 1 mM CTAB.

Fig.3.2.5 illustrates the ATR-FTIR spectra of as synthesized iron oxide/ oxyhydroxide NPs and pure CTAB as background. Transmittance at 2364.20 is due to O–C–O antisymmetric stretching vibration of CO$_2$ in air. Transmittance 3746 and 3848 cm$^{-1}$ is raised due to the symmetric and antisymmetric O–H stretching mode of water. Broad and intense band at 3365 cm$^{-1}$ is attributed to FeO (OH) due to intermolecular hydrogen bonding [43]. Transmittance at 1504, 1609 and 1677 cm$^{-1}$ assigned to O–H bending vibration [47]. Peak positions at 589 and 670 cm$^{-1}$ are due to the Fe – O vibration.
(E) Transmission Electron Microscopy

Iron oxide NPs shape and size have been determined using TEM with 200 KV electron energy. Fig.3.2.6a-b shows the TEM picture and selected area electron diffraction (SAED) pattern at the bar scale of 50 nm and 5 nm respectively. TEM picture shows that a few particles have diameter in the range of 15-20 nm while rest of the particles lie in the range of 5-15 nm.

Fig.3.2.6: TEM and SAED pictures of iron oxide/hydroxide NPs in 1 mM CTAB.

All the particles are spherical in the shape, it is clear that smaller particles are making assembly to form larger particles; it may be due to dipole-dipole attraction or Colombian attraction between magnetic NPs. Dipole- dipole attraction takes place due to magnetic nature of iron present in core of NPs, while Colombian attraction cases due to opposite charge present at surfaces. The magnetic particle size (domain) was also calculated with help of Langevin function which is in good agreement with TEM picture. SAED pattern shows spot as well as ring structure which depicts that the Fe₂O₃/ FeO (OH) has polycrystalline nature, which is also justified by XRD.
(F) Magnetic Characterization

Fig.3.2.7: M-H loop of NPs at different temperature inset shows enlarge version at origin.

Fig.3.2.8. Temperature dependent (a) M-H loop (b) dM/dH of M-H loop (c) coercivity (d) particle size.

Magnetic measurements were carried out using (VSM) at different temperature.

Fig.3.2.7a-d shows the hysteresis loop of as synthesized iron oxide/oxyhydroxide nanopowder at 80 K, 150 K, 250 K and 300 K in the field range of -3000 to 3000 Oe. The
inset picture depict the enlarge version at origin to clarify the value of coercivity. The magnetic domain size has been calculated using equation 3.1.3 derived from Langevin function [53]. Density of iron oxide/oxyhydroxide has been taken 4.50 gm/cm³. Value of \(dM/dH\) has been calculated by taking derivative of magnetization as shown in Fig.3.2.8a and calculated diameter is shown in table 3.2.2. Temperature dependent magnetic domain size and coercivity is also plotted in Fig.3.2.8a-b, which shows that the magnetic domain size increases on increasing temperature, it may be due to crossover from single domain to multidomain behavior [54]. Coercivity decreases with increasing temperature due to exchange biasing and magnetocrystalline effect [55-56].

Table 3.2.2: Magnetic measurement with respect to temperature

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Temperature</th>
<th>magnetic particle size (nm)</th>
<th>Coercivity (H_c) (Oe)</th>
<th>Saturation magnetization (M_s) (emu/gm)</th>
<th>Remanence (M_r) (emu/gm)</th>
<th>Remanence ratio, (M_r/M_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80 K</td>
<td>3.0</td>
<td>193.50</td>
<td>0.039</td>
<td>0.014</td>
<td>0.35</td>
</tr>
<tr>
<td>2</td>
<td>150 K</td>
<td>4.0</td>
<td>95.23</td>
<td>0.038</td>
<td>0.0011</td>
<td>0.028</td>
</tr>
<tr>
<td>3</td>
<td>250 K</td>
<td>5.0</td>
<td>118.21</td>
<td>0.044</td>
<td>0.01</td>
<td>0.2272</td>
</tr>
<tr>
<td>4</td>
<td>300 K</td>
<td>5.0</td>
<td>114.3</td>
<td>0.045</td>
<td>0.0073</td>
<td>0.162</td>
</tr>
</tbody>
</table>

3.2.4 Conclusion

We have successfully synthesized mix phases of \(\beta\)-Fe\(_2\)O\(_3\), \(\varepsilon\)-Fe\(_2\)O\(_3\) and FeO (OH) NPs using pulse laser ablation of iron target in different concentration of CTAB liquid medium. Colloidal stability of as synthesized NPs has been checked during 5 months by UV-visible absorption spectroscopy and found that it is unstable in CTAB liquid environment. Absorption bandgap of as synthesized colloidal NPs have been calculated using tauc relation. Temperature dependent magnetic properties have been studied. It was found that coercivity, remanence, saturation magnetization and domain size of as synthesized NPs highly depends on temperature.
3.3.1 Introduction

Quantum size effect and large surface to volume ratio in magnetic nanomaterials dramatically change some magnetic properties and show superparamagnetic character, which never happens in bulk counterpart. Recently, considerable research has been focused on iron oxide nanomaterials due to their potential applications in different field such as pigment, magnetic drug targeting and magnetic resonance imaging (MRI) for clinical diagnosis, tissue repair, recording material and catalyst [57-66]. There are many various ways to prepare Fe$_3$O$_4$ NPs such as energy milling [67], co-precipitation [68], ultrasonic assisted impregnation [69], and using emulsion. In the present study an anionic surfactant SDS has been used as capping agent for synthesis of Fe$_3$O$_4$ NPs. SDS is a widely used as amphipathic anion surfactant and plays vital roles upon interaction with Fe$_3$O$_4$ NPs.

Anionic Surfactant SDS is most commonly used and it dissociates in water in an amphiphilic anion lauryl sulfate which is generally used as a foaming agent and a cation which is an alkaline metal Na$^+$. It is used often than any other surfactant as an excellent denaturing or “unfolding” surfactant [70]. However, the mechanism governing the stability of NPs in surfactant solutions is not well understood. The purpose of this investigation is to provide structural and optical information with the influence of SDS to furnish insights into the mechanisms for both SDS– Fe$_3$O$_4$ interactions and the stability of Fe$_3$O$_4$ in surfactant solutions.

It is of great interest to know fundamental understanding of anionic surfactant SDS aqueous micellar system. Micellar media have been widely used in materials chemistry due to properties of micelles which passivate the surface of NPs [71].
3.3.2 Material Synthesis and Characterization

The experimental procedure for the laser ablation of iron target in aqueous SDS environment is same as described earlier chapter-2. High purity iron slice was emerged in 20 ml SDS at different concentrations and 40 mJ laser pulses were used throughout experiment. Obtained colloidal suspension of NPs after ablation was centrifuged, dried and used for further characterization. X-ray diffraction pattern of as synthesized powder sample was recorded using synchrotron radiation source having wavelength $\lambda = 1.1294 \, \text{Å}$. The other characterization techniques are similar as discussed in section-3.1.2.

3.3.3 Results and discussion

(A) X-ray diffraction

XRD pattern of Iron oxide (Fe$_3$O$_4$) NPs as synthesized in SDS liquid media is shown in Fig.3.3.1. The peak positions at $2\theta=12.21^\circ$, $12.88^\circ$, $14.42^\circ$, $14.50^\circ$, $15.44^\circ$, $15.98^\circ$, $19.76^\circ$, $20.25^\circ$ and $24.74^\circ$ correspond to the planes [210], [121], [212], [122], [220], [023], [214], [231] and [422] respectively. The system is orthorhombic with primitive lattice and cell parameters $a=11.86$, $b=11.85$ and $c=16.75$, $\alpha=\gamma$, $\beta= (\text{JCPDF No. 76-0956})$.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample name</th>
<th>Peak position (2θ)degree</th>
<th>FWHM (β)</th>
<th>Crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5 mM</td>
<td>12.88, 14.50, 15.44, 15.98</td>
<td>0.187, 0.165, 0.366, 0.349</td>
<td>2.77 - 5.64</td>
</tr>
<tr>
<td>2</td>
<td>10 mM</td>
<td>12.88, 14.50, 15.44, 15.98</td>
<td>0.235, 0.178, 0.3637, 0.220</td>
<td>2.82 - 5.97</td>
</tr>
<tr>
<td>3</td>
<td>20 mM</td>
<td>12.88, 14.50, 15.44, 15.98</td>
<td>0.151, 0.161, 0.3687, 0.1518</td>
<td>2.82 - 6.77</td>
</tr>
</tbody>
</table>

The crystallite size can be estimated using Scherer’s formula 3.1.1. The crystalline size of samples (5, 10 and 20 mM) was calculated corresponding to maximum intense diffraction pattern detail is given in table 3.3.1.
Chapter 3
PLA of Iron in Aqueous media

Fig. 3.3.1: XRD pattern of as synthesized Fe3O4 NPs in SDS liquid media.

(B) UV-visible Absorption Spectroscopy

Fig. 3.3.2: UV-visible absorption spectra of Fe3O4 NPs (a) Just after ablation (b) after five month.

Fig. 3.3.3: Tauc plot of Fe3O4 NPs (a) Just after ablation (b) After five month ageing.
UV-visible absorption spectra of as synthesized Fe$_3$O$_4$ colloidal NPs in different concentrations (1, 5, 10, 20 mM) of SDS liquid media are shown in Fig.3.3.2a. The absorption spectra of iron oxide colloidal NPs in 1, 5, and 10 mM SDS are almost similar but in 20 mM SDS, it is quite different. Since SDS is an anionic surfactant having 8 mM critical micelle concentration (CMC) which means SDS has good capping ability near 10 mM. When SDS concentration increases beyond it’s CMC value the molecules of SDS make micelles due to self ageing. It seems that due to micelle formation the absorption spectrum of 20 mM SDS changes i.e. growth of Fe$_3$O$_4$ NPs takes place smoothly and forms larger particle size. Another possibility, during self ageing of SDS molecules due to high concentration, they can make templates with different shape and size so that the growing NPs can take shape like templates.

It is clear from UV-visible absorption spectra of 20 mM SDS, the absorption peak is red shifted due to larger particle size and shape. The whole absorption spectrum can be divided into three segments which are 550-450, 300-375 and a sharp peak near 240 nm. The absorbance in the range of 550-450 nm is low. The absorbance in the range of 300-375 nm and peak at 240 nm are due to the ligand to metal charge transfer transition [72-73]. Fig.3.3.2b shows the absorption spectrum of Fe$_3$O$_4$ NPs after 5 month of ageing in SDS liquid media. It is very clear from the picture that three sharp absorption peaks at 244, 371 and 583 nm are red shifted as compared to initial sample.

After ageing, absorption spectrum of Fe$_3$O$_4$ NPs in 10 mM SDS is almost different than other concentration of SDS. This shows that 10 mM SDS (near CMC) produces smaller particle size and partially shielded oxidation of iron NPs due to better capping ability. While other concentration produces different particle size and not able to guard oxidation. The estimated energy bandgap of as synthesized and agglomerated Fe$_3$O$_4$ NPs is
found in the range of 2.86-2.27 eV and 2.64-2.27 eV respectively as given in table 3.3.2.

These results confirm that bandgap energy decreases after agglomeration of nanocrystals in SDS liquid media. The bandgap energy of Fe₃O₄ NPs has been reported in the range of 2.0-2.87 eV by earlier work [74]. The inset pictures show bandgap that is calculated by log methods, which also support the bandgap as obtained by tauc relation.

Table 3.3.2: Data of bandgap of Fe₃O₄ NPs calculated from tauc plot

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample name</th>
<th>Bandgap (E₇) (eV) after ablation</th>
<th>Bandgap(E₇)(eV) after five month</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1 mM</td>
<td>2.78</td>
<td>2.60</td>
</tr>
<tr>
<td>2.</td>
<td>5 mM</td>
<td>2.81</td>
<td>2.55</td>
</tr>
<tr>
<td>3.</td>
<td>10 mM</td>
<td>2.86</td>
<td>2.87</td>
</tr>
<tr>
<td>4.</td>
<td>20 mM</td>
<td>2.27</td>
<td>2.27</td>
</tr>
</tbody>
</table>

(C) ATR-FTIR Spectroscopy

Fig.3.3.4: Fourier transform spectra of as synthesized Fe₃O₄ colloidal NPs in SDS liquid media.

Fig.3.3.4. shows the ATR-FTIR spectra of as synthesized Fe₃O₄ NPs and SDS liquid media as background, inset picture shows resolved spectrum of Fe₃O₄ in the range of 520-700 cm⁻¹. The transmittance at 537, 559, 586 and 611 cm⁻¹ are assigned to iron-
oxygen (Fe-O) vibration [76]. The transmittance assigned at 1528, and 1640 cm\(^{-1}\) are due to bending vibration of water, 2351 cm\(^{-1}\) is due to CO\(_2\) of atmosphere. The transmittance at 3215, 3739 and 3854 cm\(^{-1}\) are due to the asymmetric vibration of CH\(_2\) present in SDS.

(D) Transmission Electron Microscopy

Fig 3.3.5a-b illustrate the TEM images of as synthesized Fe\(_3\)O\(_4\) colloidal NPs in SDS liquid medium, at the bar scale of 50 nm and 0.2 \(\mu\)m using 200 kV electron energy. Most of the particles are spherical in shape, with diameter below 10 nm, which is compatible as calculated with XRD data, except few particles with 20-30 nm diameters. It is clear that smallest particles are not isolated to each other, but they are agglomerated and make bigger particles. The agglomeration of these magnetic NPs can take place due to magnetic dipole-dipole attraction due to presence of Fe in the core of Fe\(_3\)O\(_4\) NPs. Another way agglomeration may occur due to opposite charges present at surface of Fe\(_3\)O\(_4\) NPs.

![TEM images of Fe\(_3\)O\(_4\) NPs](attachment:image.jpg)

Fig. 3.3.5: TEM of Fe\(_3\)O\(_4\) NPs (a) At the bar scale of 0.2 \(\mu\)m (b) At the bar scale of 50 nm.

(E) Magnetic Measurement

The hysteresis loop of Fe\(_3\)O\(_4\) NPs and inset picture depicts enlarge version at origin are displaced in Fig.3.3.6a. The coercivity (Hc) and remanence magnetization (M\(_r\)) of Fe\(_3\)O\(_4\) NPs are found to be 33.65 Oe and 0.010 emu/gm respectively. While saturation
magnetization (Ms) is 0.36 emu/gm, which is very small as compared to bulk [77]. Wu et al [78] have already reported Ms of Fe$_3$O$_4$ NPs 65 emu/gm at room temperature. Small value of Hc, and $M_R$ may be due to canted surface spin and defects on the NPs surfaces. Small coercivity may also lead to week dipole-dipole interaction between NPs, low crystallinity and disordered surface spin of NPs [47, 79]. Fig.3.3.6b shows derivative of M-H loop and the initial susceptibility found to be 0.00027 emu/gm. The magnetic particle size was calculated using equation 3.1.4 and found to be 5.0 Å, using density 5.1 gm/cm$^3$.

Fig.3.3.6: M-H loop of Fe$_3$O$_4$ NPS at RT (a) Hysteresis loop (M-H loop) (b) Derivative of M-H loop.

### 3.3.4 Conclusion

Fe$_3$O$_4$ (magnetite) is one of the magnetic NPs and it has been synthesized using PLA in anionic surfactant liquid media. Phase and crystalline size of as synthesized magnetite NPs have been determined by XRD pattern using synchrotron radiation source. Optical bandgap have been calculated in the range of 2.86-2.27 eV and 2.64-2.27 eV of as synthesized and agglomerated NPs. Particle size found in the range of 10-30 nm. The coercivity (Hc) and remanence magnetization ($M_R$) of Fe$_3$O$_4$ NPs are found to be 33.65 Oe and 0.010 emu/gm, respectively.
3.4.1 Introduction

Laser induced ablation/fragmentation in liquid media is one of the powerful techniques used for synthesis of NPs with special anisotropy which is otherwise difficult to produce by conventional methods [80-82]. The size and shape of the NPs can be controlled by changing the laser wavelength [82-83] laser fluence [84-85] liquid environment [86-87] and surfactants [88-90]. Iron can form several oxides of different stoichiometry and crystalline structure depending upon synthesis technique. These oxides are Wüstite (FeO), magnetite (γ-Fe₃O₄), hematite (α-Fe₂O₃) and magnetite (γ-Fe₂O₃). Hematite is thermodynamically most stable phase of Fe₂O₃, and is the subject of this work. Hematite (α-Fe₂O₃) has been considered as promising material since α-Fe₂O₃ is inexpensive, abundant, nontoxic, and stable in most alkaline electrolytes [91-93].

In order to prepare homogenous nano-particles of iron oxide, researchers have employed in different routes to facilitate single-phase iron oxide nano-particles such as sol–gel processes [94], microemulsion [95], combustion [18], solvothermal [96], hydrothermal [97] and precursor [98]. In the absence of any surface coating, magnetic iron oxide particles have hydrophobic surfaces with a large surface area to volume ratio. Due to hydrophobic interactions between the particles these particles agglomerate and form large clusters, resulting in increased particle size. These clusters exhibit strong magnetic dipole–dipole attractions between them and show ferromagnetic behavior. When two large-particle clusters approach one another, each of them comes into the magnetic field of the neighbor. Besides the arousal of attractive forces between the particles, each particle is in the magnetic field of the neighbor and gets further magnetized. To avoid further agglomeration cationic and anionic surfactants are subject of present study used.
3.4.2 Material Synthesis and Characterization

The experimental setup of laser ablation/fragmentation is shown in Fig.3.4.1 [90]. High pure (Qualigens, India) bulk powder of iron oxide (Fe₂O₃) was dispersed in a test tube containing 50 ml aqueous solution of SDS and CTAB. The suspension was continuously stirred using magnetic stirrer. Nd: YAG laser (Spectra Physics, USA) operated at 1064 nm wavelength, 40 mJ/pulse energy, and 10 Hz repetition rate was focused to a spot size of 2 mm at the centre of the glass tube using a lens for 1 hour. Obtained colloidal suspension of iron oxide NPs after ablation was separated, dried and used for further characterization. Samples R2, R3, and R4 were prepared in DDW, SDS and CTAB, respectively, while R1 (Fe₂O₃) bulk powder purchased commercially.

![Experimental setup for laser ablation/fragmentation of Fe₂O₃ bulk Powder.](image)

XRD pattern of as synthesized samples were recorded using synchrotron radiation source having wavelength $\lambda = 0.7306$ Å. The other characterization techniques are similar as described in section 3.1.2.
3.4.3 Results and Discussion

(A) X-Ray Diffraction

Fig.3.4.2a-b shows XRD pattern of samples R1 and R2, peak positions at 2θ=11.377°, 2θ=15.543°, 2θ=16.771°, 2θ=19.042°, 2θ=22.869°, 2θ=24.877°,
2θ=26.395°, 2θ=28.434°, 2θ=29.085°, 2θ=32.328°, 2θ=33.709°, 2θ=35.749°,
2θ=36.586°, 2θ=37.717° and 2θ=38.637° correspond to the plane [012], [104], [110],
[113], [024], [116], [018], [214], [300], [1010], [220], [128], [0210], [134] and [226]
respectively having Rhomb – centered, hexagonal lattice parameters, a= 5.035,=b ,c=
13.74, α=β=γ of Fe₂O₃ (JCPDF No. 86-05500).

Fig.3.4.2: XRD pattern of Fe₂O₃ powder ablated in different liquid medium.

Fig.3.4.2c-d) shows XRD pattern of samples R3 and R4. Fig.3.4.2d shows mix
phases of FeO (OH), Fe₂O₃ and C₂H₄ Fe₂O₃. The peak position indicated by symbol H at
2θ=9.996° corresponds plane [107], Iron oxide hydroxide [FeO (OH)] with orthorhombic,
primitive lattice \( a=4.618, b=9.952, c=3.023 \) (JCPDF No. 81-0462). Peak positions are indicated by symbol C at \( 2\theta=12.708^\circ, 2\theta=13.670^\circ, 2\theta=13.861^\circ \) and \( 2\theta=15.804^\circ \) corresponds to plane [002], [211], [311], and [120] respectively for iron maleate (\( C_2H_4Fe_2O_3 \)) anorthic primitive lattice \( a=9.659, b=5.309, c=7.378 \alpha =87.72^\circ, \beta = 65.34^\circ, \gamma =105.35^\circ \) (JCPDF No. 35-1710). The peak positions of iron oxide (\( Fe_2O_3 \)) are indicated by symbol O. XRD result reveals that CTAB plays dual role i.e. reducing particle size as well as changing phase of \( Fe_2O_3 \).

Furthermore Using Williamson–Hall (W-H) plot, we have calculated the lattice strain and effective particle size using the following relation [99]

\[
\frac{(\beta \cos \theta)}{(\lambda)} = \frac{1}{\varepsilon} + \eta \sin \theta / \lambda \quad (3.4.1)
\]

Where \( \beta, \) is full width at half maximum (FWHM) in radians, \( \varepsilon \) is the effective crystalline size and \( \eta \) is effective strain. Fig 3.4.3a-d show the W-H plot, i.e. the plot between \((\beta \cos \theta) / \lambda, \) versus \( \sin \theta / \lambda. \) Negative slope in the plot indicate the presence of compressive strain whereas the appearance of positive slope indicate the possibility of tensile strain.

 Intercept on the \( \beta \cos \theta / \lambda \) axis gives effective particle size, with zero strain [100-105].

**Table 3.4.1: Optical bandgap, effective particle size, effective strain and Magnetic properties of \( Fe_2O_3 \).**

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>crystalline size(( \varepsilon )) nm</th>
<th>bandgap energy (eV)</th>
<th>Particle size(nm)</th>
<th>Effective strain(( \eta ))</th>
<th>( H_c ) (Oe)</th>
<th>( M_s ) (emu/gm)</th>
<th>( M_r ) (emu/gm)</th>
<th>Ratio ( M_r/M_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Fe_2O_3 ) (R1)</td>
<td>27.93</td>
<td>1.92</td>
<td>-----</td>
<td>0.0105</td>
<td>239.84</td>
<td>0.024</td>
<td>0.0051</td>
<td>0.212</td>
</tr>
<tr>
<td>( Fe_2O_3 ) (R2)</td>
<td>29.23</td>
<td>1.98</td>
<td>8.85</td>
<td>0.0018</td>
<td>209.33</td>
<td>3.41</td>
<td>0.51</td>
<td>0.149</td>
</tr>
<tr>
<td>( Fe_2O_3 ) (R3)</td>
<td>21.23</td>
<td>2.01</td>
<td>7.22</td>
<td>0.00126</td>
<td>298.36</td>
<td>0.21</td>
<td>0.041</td>
<td>0.195</td>
</tr>
<tr>
<td>( Fe_2O_3 ) (R4)</td>
<td>16.54</td>
<td>2.03</td>
<td>6.53</td>
<td>0.032</td>
<td>206.91</td>
<td>0.013</td>
<td>0.0023</td>
<td>0.176</td>
</tr>
</tbody>
</table>

Table 3.4.1 displays the enhancement in strain with the reduction of crystalline size; this result confirms that particle size and strain depend on particle size and different surfactant media [106]. In sample R2 and R3 strain is reduced while in sample R4 strain increases reasonably in respect to sample R1. This effect is arisen due to the reduced
crystallite size and mix phase respectively. The crystallite size is measured using both methods Scherrer’s formula and Williamson–Hall plot are well consistent.

![Williamson–Hall plots](image)

**Fig.3.4. 3:** Williamson–Hall plots of Fe$_2$O$_3$ powder as ablated NPs, size and strain analysis.

### (B) UV-visible Absorption

Fig.3.4.4 shows the absorption spectrum of Samples R1, R2, R3 and R4 defined earlier. The maximum absorption peak of sample R1 is near 792 nm, R2 has maximum absorption near 590 nm while onset absorption starts at 895 nm. The absorption edge is red shifted due to improvement in crystallinity and crystallite size as clear from table 3.4.1, R3 has maximum absorption near 580 nm and onset absorption starts at 802 nm.

The absorption spectrum of sample R3 is blue shifted than R2 due to smaller crystalline size and capping of SDS molecules. Sample R4 has broad absorption in the range of 588-793 nm. Mitra et al.\cite{110} have reported two absorption edges of \(\alpha\)-Fe$_2$O$_3$ nanocrystals around 540–560 and 670–680 nm. The broadness in absorption is due to formation of mix phases i.e. FeO (OH), Fe$_2$O$_3$ and C$_2$H$_4$ Fe$_2$O$_3$. 
The sample R4 has smallest crystalline size as confirmed from. The absorption bandgap $E_g$ of the as synthesized samples can be determined by the Tauc equation 3.1.2.

The bandgap energies of sample R1, R2, R3 and R4 are found to be 1.92, 1.98, 2.01, and 2.03 eV respectively considering indirect transition as shown in Fig.3.4.5 which is well consistent with previously reported value [108-109]. Here it is clear that on decreasing crystalline size optical bandgap increases. Sample R2 shows larger crystalline size than R1, but also higher bandgap energy. It may be due to sample R2 get more oxidized and optical bandgap widen. Direct bandgap energy of Fe$_2$O$_3$ nano wire and thin film have been reported in range of 2.14 -2.22 eV and 2.21-2.23 eV respectively [100]. It is already reported that three types of electronic transitions occur in the optical absorption spectra of Fe$^{3+}$ substances: (a) the Fe$^{3+}$ ligand field transition or the d–d transitions, (b) the ligand to metal charge–transfer transitions and (c) the pair excitations resulting from the simultaneous excitations of two neighboring Fe$^{3+}$ cation that are magnetically coupled.
In our case the transition in the range of 600 to 750 nm is assigned due to the single 
$d-d$ transition of Fe$^{3+}$ and inter valence charge transfer transitions $^6A_1 \rightarrow ^4T_2 (^4G)$ [114].

The optical particle size from bandgap is calculated using effective mass formula given as

$$E_g = E_0 + n^2 \hbar^2 \Pi^2 / 2\mu R^2 + 1.8e^2 / \varepsilon R$$  

(3.4.2)

Where $E_0$ is the bandgap of the bulk Fe$_2$O$_3$ and $R$ is the size of the nanocrystallites.

In above equation, $e$ is the electron charge, $\varepsilon$ is the effective dielectric constant and $\mu$ is the 
reduced effective mass of electron and hole of Fe$_2$O$_3$. In the above equation, we used $\varepsilon$ 
=5.7, $\mu =0.08m_0$ ($m_0$ is the electron’s rest mass) [112]. For bulk bandgap ($E_0^0$) has been 
taken 1.92 eV measured in our experiments. Calculated particle size for sample R2, R3 and 
R4 are given in table 3.4.1.

---

**Fig.3.4.5: Tauc plot to determined bandgap of Fe$_2$O$_3$ NPs synthesized in different liquid medium.**
(C) FTIR Spectroscopy

Fig.3.4. 6: FTIR spectra of as synthesized Fe₂O₃ NPs in different liquid media.

Fourier transform infrared (FTIR) transmittance spectrum of samples R1, R2, R3 and R4 are shown in Fig 3.4.6. Fig.3.4.6a shows spectrum in the range of 500 – 4000 cm⁻¹ while Fig.3.4.6b shows spectrum in the range of 480- to 660 cm⁻¹. The peak positions assigned to 499, 515, 536 and 573 cm⁻¹ are due to Fe−O stretching vibration of bulk sample (R1) [113-117]. Intense and wide peak at 497, 547 and 699 cm⁻¹ for sample R2 are again due to Fe−O stretching vibration, peak position at 497 cm⁻¹ is intense and wide it may due to enhancement of crystalline size and percentage of crystallinity.

The peak positions for sample R3 are assigned at 511, 540, 563, and 584 are due to iron – oxygen stretching vibration. Sample R4 shows intense and wide peak position at 495, 522, 565, and 588 cm⁻¹, are again due to Fe−O stretching vibration. Sifting of respective peak positions of samples R1, R2, R3 and R4 may arise due to different crystalline size. Peak position at 1363, 1520 and 1736 cm⁻¹ are due to H−O−H bending
and deformation vibrations of adsorbed water [47]. An intense peak at 2362 cm\(^{-1}\) is assigned to atmosphere CO\(_2\) or nitrogen oxide. Positions at 3336, 3643, 3739 and 3862 cm\(^{-1}\) are assigned H-OH stretching vibrations [86].

**D) Magnetic Properties**

Magnetic properties of as synthesized samples R1, R2, R3 and R4 at room temperature (RT) have been shown in Fig.3.4.7. The coercivity and other magnetic properties such as ferromagnetism have a direct relationship with the crystalline shapes and sizes [118]. Sample R1 shows low value of saturation magnetization (M\(_S\)) and remanence (M\(_r\)) while coercivity 239.84 Oe. Sample R1 shows maximum remanence ratio (M\(_r\)/M\(_S\)), which is found to be 0.212 emu/gm. The low value of remanence and saturation magnetization are observed for sample R1, due to low degree of crystallinity and spin disordering on surfaces, while in sample R3, and R4 it is due to capping, amorphous and diamagnetic nature of SDS and CTAB [119]. Sample R2 has largest value of remanence (M\(_r\)=0.51), and saturation magnetization (M\(_S\)=3.41) due to the greater degree of crystallinity, and crystalline size as shown in table 3.4.1. Sample R2 has smaller value of coercivity and sample R3 has larger coercivity as compared to sample R1.

It is previously reported that coercivity of hematite increases with decreasing grain size [120-123]. On the other hand, induced larger magnetic coercivity is attributed to magnetic spin are preferentially aligned along the long axis, crystalline size and coercivity variation [121] is shown in Fig.3.4.8a. Sample R4 shows lowest value of coercivity and crystalline size, this result is not consistent with above result; it may due to mix phases of iron oxide NPs. The enhance coercivity may caused by magneto crystalline anisotropy and easy axis of magnetization. Saturation magnetization (M\(_S\)) and remanence (M\(_r\)) increases due to increase of crystalline size, shown in Fig.3.4.8 b-c [124].
Fig. 3.4.7: Hysteresis loop characterization of Fe$_2$O$_3$ powder as synthesized in different liquid medium.

Fig. 3.4.8: Variation of crystallite size (a) coercivity (b) magnetization ($M_r$ and $M_s$) (c) remanence ratio.
(E) Effect of Anionic and Cationic Surfactant

Positively charged surface of the ablated iron oxide ($\text{Fe}_2\text{O}_3$) surface electostatically attracts the anionic head ($\text{SO}_4^{2-}$) of the SDS molecules are making its tail away from the surface [45]. However, anionic surfactant SDS usually does not show a significant effect towards reduction of particle size. It may be attributed due to weak interaction between ablated iron oxide ($\text{Fe}_2\text{O}_3$) and SDS [125]. So SDS is playing important role for enhancing coercivity due to the surface coating and spin ordering along long axis [126].

Since it is well known that as particle size decreases magnetization also decreases which is well consistent with present result [127-128]. In aqueous solution, CTAB dissociates into a bromide ion ($\text{Br}^-$) and a cetyltrimethylammonium ion ($\text{CTA}^+$) such that the surface charge property could be modified [129]. When $\text{CTA}^+$ is adsorbed onto the ablated iron oxide ($\text{Fe}_2\text{O}_3$) surface, it behaves as positively charged surface and due to colombian repulsion it restrict further agglomeration and stabilized. Further it cases reduction in particle size of sample R4. Sample R1, R3 and R4 have low value of $M_S$ and $M_R$ due to magnetically disordered surface layer around the particles.

(F) Scanning Electron Microscopy

SEM images were recorded by using JEOL SEI having 15.0 kV energy. Fig.3.4.9 show the SEM image of samples R1, R2, R3 and R4 provided with bar scale of 1 $\mu$m. Particle size of sample R1 and R2 are in the range of 100-200 nm but sample R2 has uniformity in size due to recrystallization or oxidation in presence of water and R1 has non uniformity towards particle size distribution due to bulk sample. In sample R3 particles are embedded in SDS matrix and having smaller particle size than samples R1 and R2. Particle size of sample R4 surrounded in CTAB environment is in the range of 50-100 nm. Smaller particle size may be attributed due to capping of CTAB.
3.4.4 Conclusion

In present work commercially purchased Fe₂O₃ bulk powder is ablated by laser ablation technique in DDW, SDS, and CTAB liquid media. Williamson–Hall plot and Scherrer’s formula employed for effective particle size and strain calculation. The optical bandgap energy is found in the range of 1.98-2.03 eV, while 1.92 eV is bandgap of bulk powder of Fe₂O₃. Crystallinity of as synthesized sample R2 is enhanced due to oxidation in the presence of oxygen in DDW. While surfactant supports to reduce crystalline size due to its capping effect. Mix phases of iron oxide are formed in presence of cationic surfactant CTAB. Optical bandgap and magnetic properties such as coercivity, saturation magnetization and remanence have been tailored by pulse laser ablation in different aqueous media. The coercivity has been found in the range of 206-298 Oe, though 239 Oe is bulk sample coercivity. Ablated Fe₂O₃ NPs can be used for numerous in vivo applications such as MRI contrast enhancement agent, tissue repair, hyperthermia, drug delivery and in cell separation.
Chapter-3

PLA of Iron in Aqueous media

Bibliography

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