Optical and Magnetic Properties of Superparamagnetic Fe₃O₄ Colloidal Nanoparticles

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Abstract Magnetic nanomaterials gained widespread interest due to remarkable future applications in various fields. The purpose of present work is to explore magnetic and optical properties of ultra pure superparamagnetic Fe₃O₄ nanoparticles. Nowadays, superparamagnetism is receiving considerable interest in terms of biomedical and engineering applications. Herein, Fe₃O₄ superparamagnetic nanoparticles have been successfully synthesized by pulsed laser ablation method in the presence of anionic surfactants in liquid environments. The structural, morphological, optical and magnetic properties have been studied using X Ray diffraction (XRD), transmission electron microscope (TEM), UV-visible absorption, ATR-FTIR and vibrating sample magnetometer (VSM), respectively. The optical band gaps of as synthesized and after agglomeration Fe₃O₄ nanoparticles have been estimated in the range of 2.27–2.86 eV and 2.27–2.87 eV, depending on surfactant concentration. TEM image showed Fe₃O₄ nanoparticles possess mean diameter in the range of 5–25 nm. The saturation magnetization and coercivity of Fe₃O₄ nanoparticles have been estimated 0.36 emu·g^{−1} and 33 Oe at room temperature, respectively. Therefore, as synthesized Fe₃O₄ nanoparticles showed superparamagnetic character at room temperature.

Keywords magnetite, superparamagnetic Fe₃O₄ nanoparticles, optical properties, magnetic properties

Introduction

Recently, significant research has been focused on iron oxide nanomaterials due to their potential uses such as pigment, magnetic drug targeting, and magnetic resonance imaging for clinical diagnosis, tissue repair, recording material and catalyst.^[1–4] Large surface to volume ratio afterward quantum size effect in magnetic nanomaterials dramatically changes some magnetic properties. Consequently, they show superparamagnetic property, which never happens in bulk counterparts. Superparamagnetic nanoparticles (SPMNs) have shown great potential in different applications such as ferrofluids, information storage, color imaging and cell leveling, etc.^[5–9]

There are many various methods for synthesis of Fe₃O₄ nanoparticles such as energy milling,^[10] co-precipitation,^[11] ultrasonic assisted impregnation,^[12] and using emulsion.^[13] In this paper, we have employed a physical method for synthesis of Fe₃O₄ colloidal magnetic nanoparticles, which is known as liquid phase pulse laser ablation. A magnetic nanoparticle agglomerates effectively due to magnetic dipole-dipole attraction. An anionic surfactant sodium dodecyl sulphate (SDS), preventing further agglomeration of magnetic nanoparticles, was used as a capping agent. Zeng *et al.* described pulse laser ablation mechanism in liquid environments earlier.^[14,15]

Experimental

The experimental procedure of the laser ablation of the metal target in aqueous environment is described earlier.^[16–20] XRD pattern of as synthesized powder sample was recorded using Indus-2, beam line-12 synchrotron radiation source

having wavelength $\lambda = 1.1294$ Å. Synchrotron radiation is inherently advantageous to laboratory sources for several reasons such as high brightness, high intense, high collimation and large tunability in wavelength.

The UV-visible absorption spectrum of Fe₃O₄ colloidal solution was recorded using a Perkin Elmer Lambda 35, double beam spectrophotometer. Thermo scientific FT-IR (ATR) was used for Infrared spectroscopy. TEM imaging has been performed using TEM (model number FEI Tecnai G2F30STWIN). A drop of Fe₃O₄ colloidal solution was placed on the copper grid and dried at 60 °C before imaging the particle shape and size. The magnetic measurement performed by a VSM (Lakeshore, USA) at room temperature.

X-ray diffraction

Figure 1a shows X-ray diffraction of as synthesized Fe₃O₄ nanoparticles. 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° correspond to [210], [121], [212], [122], [220], [023], [214], [231], and [422] plane, respectively. As synthesized Fe₃O₄ nanoparticles are orthorhombic primitive lattice with cell parameter $a = 11.86$ Å, $b = 11.85$ Å and $c = 16.75$ Å, $\alpha = \gamma = \beta = 90^\circ$ (JCPDF No. 76-0956).

The crystallite sizes are estimated using Scherrer's formula

$$D = K\lambda/\beta_{2\theta} \cos\theta \quad (1)$$

where the constant K is 0.9, λ is the wavelength (1.1294) of synchrotron X-ray used, and $\beta_{2\theta}$ is the full width at half maximum of the diffraction peak corresponding to 2θ . The crystalline size of samples (5, 10 and 20 mM) was calculated and shown in Table 1. Williamson-Hall plot is employed to

Table 1 Crystalline sizes of Fe₃O₄ nanocrystals

No.	Sample concentration	Peak position 2θ/degree	FWHM (β)	Crystalline size range/nm
1	5 mM	12.88, 14.50, 15.44, 15.98	0.187, 0.165, 0.366, 0.349	2.77—5.64
2	10 mM	12.88, 14.50, 15.44, 15.98	0.235, 0.178, 0.3637, 0.220	2.82—5.97
3	20 mM	12.88, 14.50, 15.44, 15.98	0.151, 0.161, 0.3687, 0.1518	2.82—6.77

Figure 1 (1a) X-ray diffraction pattern of as synthesized Fe₃O₄ SPMNPs in SDS liquid media (1b) W-H plot at different surfactant concentrations.

calculate lattice strain and effective particle size with zero strain through the following relation:^[21]

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{\varepsilon} + \frac{\eta \sin \theta}{\lambda} \quad (2)$$

where β , ε and η are the full width at half maximum (FWHM) in radians, the effective particle size and the effective strain, respectively. Figure 2b shows plot between $\beta \cos \theta / \lambda$ versus $\sin \theta / \lambda$. The intercept on the $\beta \cos \theta / \lambda$ axis gives the effective particle size corresponding to zero strain, where the plot gives the positive slope, indicating the presence of tensile strain.

UV-visible absorption

Figure 2a shows the UV-visible absorption spectrum of as synthesized Fe₃O₄ colloidal nanoparticles in different concentrations (1, 5, 10, 20 mM) of the SDS liquid medium. The absorption spectra in 1, 5, and 10 mM SDS are almost similar, but the absorption spectrum in 20 mM SDS is quite different. SDS is an anionic surfactant with 8 mM critical micelle concentration,

Figure 2 UV-visible absorption spectra of as synthesized Fe₃O₄ colloidal SPMNPs in SDS liquid media at different concentration, (a) just after ablation (b) after five months.

which means that SDS has good capping ability near 10 mM. When SDS concentration increases beyond its critical micelle concentration value, the molecules of SDS makes micelles due to self ageing. Due to micelle formation, the absorption spectra in 20 mM SDS change. For instance, growth of Fe₃O₄ nanoparticles takes place smoothly and forms larger particle size. During self ageing of SDS molecules, they can make templates with different shape and size due to high concentration, thus, the growing nanoparticles can form shapes like templates. It is very clear from UV-visible absorption spectra in 20 mM SDS that the absorption peak is shifted to the higher wavelength side. The whole absorption spectrum in Figure 2a 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 due to slow or a little oxidation of iron nanoparticles due to SDS anionic surfactants. This absorption is attributed to the pair excitation

Table 2 Optical band gap of as synthesized Fe₃O₄ colloidal nanoparticles

No.	Sample name	Band Gap (E_g) just after ablation/eV	Band gap (E_g) after five months /eV
1.	1 mM	2.78	2.60
2.	5 mM	2.81	2.55
3.	10 mM	2.86	2.87
4.	20 mM	2.27	2.27

Figure 3 Tauc plot for calculation of optical band gap of Fe₃O₄ SPMNPs (a) Just after ablation (b) After five months ageing.

process. The absorbance in the range of 300–375 nm and peak at 240 nm are due to the ligand to metal charge transfer transitions.^[16,17] Figure 2b shows the absorption spectrum of Fe₃O₄ nanoparticles after 5 month of ageing in SDS liquid media. The absorption intensity is high due to complete oxidation of iron colloidal nanoparticles in the form of Fe₃O₄. It is very clear from the picture that three sharp absorption peaks at 244, 371 and 583 nm are red shifted as compared to Figure 2a. After ageing, absorption spectrum of Fe₃O₄ nanoparticles in 10 mM SDS is almost different from other concentration of SDS. This shows that 10 mM SDS (near critical micelle concentration) produces smaller particle size and shield oxidation due to better capping ability, while other concentrations produce different particle sizes.

The band gap of as synthesized and agglomerated Fe₃O₄ nanoparticles is calculated using following equation:

$$\alpha h\nu = K(h\nu - E_g)^n \quad (3)$$

where α is the absorption coefficient, K is a constant depending on material, E_g is the band gap, and n is a value that depends on the nature of the transitions (1/2 for a direct allowed transitions or 2 for an indirect allowed transitions). The estimated energy band gaps of as synthesized and agglomerated Fe₃O₄ nanoparticles are found in the ranges of 2.86–2.27

Figure 4 Fourier transforms spectra of as synthesized Fe₃O₄ colloidal SPMNPs in SDS liquid media.

and 2.87–2.27 eV as shown in Figures 3a and 3b, respectively. The optical band gap of Fe₃O₄ nanoparticles quantitatively reported is shown in Table 2. These results confirm that band gap energy decreases after agglomeration of nanocrystals in SDS liquid media. The optical band gap energy of Fe₃O₄ nanoparticles is reported in the literature in the range of 2.0–2.87 eV.^[18]

ATR-FTIR spectroscopy

Figure 4 shows the ATR-FTIR spectra of as synthesized Fe₃O₄ nanoparticles and SDS liquid media as background, where the inset picture shows resolved spectrum of Fe₃O₄ in the range of 520–700 cm⁻¹. The peak positions situated at 537, 559, 586 and 611 cm⁻¹ are assigned to metal oxygen (Fe–O) vibration.^[19,20] The peak positions assigned at 1528, 1640, 2351, 3739, and 3854 cm⁻¹ are due to SDS liquid media. The transmittance at 1528, and 1640 cm⁻¹ is due to the asymmetric vibration of CH₂.

Transmission electron microscopy

Figures 5a and 5b show the TEM image of as synthesized Fe₃O₄ colloidal nanoparticles in the SDS liquid medium at the bar scale of 0.2 μ m and 50 nm using 200 kV electron energy. All the particles seem that spherical shape and diameter is below 10 nm, which is compatible with calculated XRD data, but some of them have range 20–30 nm. Crystals are of made ordered assembly of some atoms, while nanoparticles are assembly of few crystals, therefore, crystallite size is smaller than particle size. XRD patterns always estimates crystallite size, however, TEM determines image of particles. It is very clear that few particles are not isolated, but they are agglomerated to form bigger particles in the form of chain like structures. It is also confirmed by UV-visible absorption spectra. The agglomeration of these magnetic nanoparticles is due to magnetic dipole-dipole attraction of Fe present at the core of Fe₃O₄ nano-

Figure 5 Transmission electron microscopy image (a) Fe_3O_4 SPMNPs at 2 μm bar scale (b) Fe_3O_4 SPMNPs at 50 nm bar scale.

Figure 6 Magnetic measurement of Fe_3O_4 SPMNPs at room temperature (a) Hysteresis loop (M-H loop) (b) Derivative of M-H loop for initial susceptibility.

particles. Agglomeration may occur due to an opposite charge present at the surface of Fe_3O_4 nanoparticles.

Magnetic properties

Figure 6a shows the hysteresis loop (M-H loop) of Fe_3O_4 nanoparticles and the inset picture depicts enlarged version on origin at room temperature. The coercivity and remanence magnetization of Fe_3O_4 nanoparticles are found to be 33.65 Oe and 0.010 emu/gm, respectively. Saturation magnetization (Ms)

is 0.35 emu/gm, which is very small as compared to bulk.^[22] Wu *et al.* has already reported Ms of Fe_3O_4 nanoparticles (65 emu/gm) at room temperature.^[23] Small value of coercivity confirms that as synthesized Fe_3O_4 nanoparticles are small and very close to superparamagnetic. Small coercivity may also lead to weak dipole-dipole interaction between nanoparticles, low crystallinity and disordered surface spin of nanoparticles.^[24,25] Figure 6b shows a derivative of M-H loop as a result susceptibility is 0.00027 emu/gm.

Conclusion

Fe_3O_4 superparamagnetic nanoparticles are synthesized successfully using LP-PLA technique in anionic surfactants liquid media. Phase and crystalline size of as synthesized magnetite nanoparticles is estimated by the XRD pattern using synchrotron radiation source. The Fe_3O_4 nanoparticles are not stable even in SDS liquid environment up to 5 months. The estimated energy band gap of as synthesized and agglomerated Fe_3O_4 nanoparticles are found in the range of 2.86–2.27 and 2.87–2.27 eV, respectively. The particle size and shape are determined by TEM image. The magnetic measurement was performed using VSM at room temperature, which shows superparamagnetic property with coercivity 33 Oe and saturation magnetization 0.36 emu/gm.

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Author Contributions

B. K. P. performed the experiments and wrote the manuscript. R. K. K. and J. S. did magnetic measurement. R. G. and A. S. participated in scientific discussion on this manuscript.

Conflict of Interest

The authors declare no conflict of interest.

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