Physics

SYNTHESIS, CHARACTERIZATION AND ELECTRICAL CONDUCTIVITY OF FE₃O₄ NANOPARTICLES

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ABSTRACT Iron oxide (Fe_3O_4) nanoparticles were synthesized using Ferric chloride and ammonium hydroxide by co-precipitation technique. The precipitate product was dried at 100°C for 1 hour in vacuum to obtain black magnetite phase of Fe_3O_4 nanoparticles. The iron oxide nanoparticles were then confirmed using powder X-ray diffractometry measurements in the range 20-80°, the crystallites obtained exactly matches with the Fe_3O_4 reported in the literature The Energy Dispersive X-ray spectrometry (EDX) and Scanning Electron Microscopic (SEM) analysis were performed. The EDX results show that 90% of FeO is present in the total composition. SEM analysis shows spherical shaped iron oxide particles with an average diameter of 25.87nm are formed. The FT-IR analysis was recorded to find the characteristic vibrational peak of Fe-O band; as expected, bands appeared at 563.76 cm^{-1} as an intense peak and 446.88 cm^{-1} as a weak peak. The UV-Visible spectrum was measured in the range of 200-800nm to find the band gap in iron oxide nanomaterial. The transitions obtained are between 3.5 to 1.6 eV. Electrical conductivity was measured for different concentration of samples at the different temperature range (30°-50°C). The conductivity is good compared to previous reports.

KEYWORDS : Iron oxide, electrical conductivity, nanoliquid, nanoparticles, Fe_3O_4

1. INTRODUCTION

In recent years the synthesis and characterization of iron oxide (Fe_3O_4) nanoparticles have increased rapidly because of their wide application in a variety of fields. The choice of using a nanomaterial for a specific application largely depends on the size and shape of every individual particle. Nanomaterials of desired size between 1-100nm can be achieved by selecting a suitable controlled synthetic methodology. Recent literature reports on FeO nanoparticles of size 9-15 nm, give more insights on the electrical and magnetic properties of the materials which are widely used as catalyst, sorbents, pigments, flocculants, coating material, gas sensors, lubricants and in waste water treatment [1].

Fe_3O_4 nanoparticles of size 2-25 nm of are recommended for color imaging, magnetic recording media, soft magnetic materials, ferrofluid, spintronics and biomedical applications such as drugs delivery, cell separation, imaging and therapeutic [2]. Iron oxide nanoparticles preparation methods such as co-precipitation, sol-gel, solvothermal, hydrothermal, micro emulsion and sonochemical are promising methods available for producing nanoparticles of 1-50 nm [3-4]. These magnetic nanoparticles are also used in medical sciences such as MRI contrast agents, tissue repair, and immunoassay, detoxification of biological fluids and hyperthermia, especially, magnetite (Fe_3O_4) has excelled in research because of its biocompatibility and high magnetic saturation [5]. The magnetic nanoparticles (Fe_3O_4) prepared by co-precipitation technique possess super paramagnetic (SPIONS) property. They are useful in bioanalysis, therapeutic, drug delivery, bioimaging and a lab on chip device [6]. In addition to that iron oxide nanoparticles of order 30-35 nm size synthesized using different chemical methods are used in refrigeration systems and drug targeting. Ji Young Park [7] prepared iron (iii) oxide particles by co-precipitation method, with size between 8-10 nm, and reported that these iron oxide particles have great potential applications in information storage, color imaging, bioprocessing, magnetic refrigeration and magnetic resonance imaging. The above reviews and results inspired us to develop iron oxide nanoparticles in lesser size and interested us in studying properties such as crystallite size, shape, band gap and electrical conductivity. In the present investigation, we have synthesized Fe_3O_4 nanoparticles, characterized them by XRD, SEM-EDX, FT-IR, UV-Vis. spectra and studied electrical conductivity of the material.

2. Experimental details

2.1 Synthesis of Fe₃O₄ nanoparticles

100ml deionized distilled water was taken in the Round Bottom Flask (RBF). The water was heated to 90°C in a heating mantle. 3g of $FeCl_2.4H_2O$ was added into the RBF and the contents were continuously stirred with a magnetic stirrer. 100ml ammonium hydroxide solution was prepared by mixing 35ml NH_4OH and 75 ml of distilled water, the prepared solution was taken in a burette and added drop wise into RBF at the rate of 0.5ml/min continuous stirring. The total volume of the mixture was 200ml in the end of the process. After the system reached a precipitation state, it was allowed to cool and settle. The precipitate was then filtered with whatman qualitative filter paper no.1004-042 with pore size 20-25μ. The product was first washed in water and later in ethanol for 4-5 times to remove the water contents in the product. Then the product was dried in air at room temperature for 24 hours, until the colour of the product turned into black magnetite phase. Finally the product was dried at 100°C for 1 hour in vacuum [8].

3. Experimental characterization

X-ray diffraction pattern for Fe_3O_4 nanoparticle was measured on PAN Analytical x'Pert PRO powder X-Ray Diffractometer at 25°C temperature and generator setting about 30mA. The XRD was recorded at the Science Park Department of Physics, Alagappa University, Karraikudi. FT-IR spectrum of transmittance mode was measured using Perkin Elmer in the range of 400 cm^{-1} to 4000 cm^{-1} at the Arch bishop Casimir Instrumentation Centre (ACIC), St. Joseph College, Trichy. UV-visible absorbance spectrum was measured using double beam UV visible spectrometer in the range of -200 to 800 nm, the electrical conductivity was measured using SYSTRONIC water analyzer at the Central Instrumentation Facility, Centre for Research and Development, PRIST Deemed University, Vallam, Thanjavur. SEM was measured on Carl ZEISS EV015 Scanning electron microscope at the 100nm magnification and energy dispersive X-Ray (EDX) analysis was done on Bruker X-Flash 6160 EDX detector, at the Central Analytical Laboratory, University of Hyderabad.

4. RESULTS AND DISCUSSION

4.1 XRD Analysis

X-Ray diffraction patterns were recorded for the sample using Mo-Kα

radiation (λ=0.7092Å) in the range of 2θ diffraction angle between 20° to 80°. X-Ray pattern of iron oxides nanoparticles is shown in Figure 1. The measured 2θ peak values were compared with previously reported results [9], the peaks obtained matches well with Fe_3O_4 nanoparticles. The obtained 2θ peaks are 30.11, 35.49, 57.09, 43.21 and 62.75. Its corresponding crystal planes are 220, 311, 511, 400 and 440.

The size of crystallite were measured by Scherer equation [10]

$$D_n = \frac{k\lambda}{\beta \cos\theta}$$

Where, D_n is the crystallite mean size, k is a shape function for which a values of 0.9 is used, λ is the wavelength of the radiation, β is full width at half maximum (FWHM), in radian, the 2θ scale and is the Bragg angle.

As recorded in X-ray pattern, the size of crystallites are 27.86 (2θ=30.11), 33.90 (2θ=35.49), 28.94 (2θ=43.21), 11.49 (2θ=57.09) and 31.51 (2θ =62.75), the average size of particle is 26.74 nm. The crystallite size was determined using the full width half maximum and θ the Bragg's angle, the strongest peak obtained at 35.49 belongs to (311) plane is due to Fe-O composite.

4.2. FTIR spectrum
Fourier Transform Infrared (FTIR) spectrum was recorded in the visible range (4000-400 cm⁻¹) for Fe_3O_4 nanoparticles. FTIR spectrum is shown in S1 (Supporting information). In this spectrum, there are several vibrational peaks absorbed, in which bands at 563.76 cm⁻¹ (intense peak) and at 446.88 cm⁻¹ is (weak peak) for Fe-O composite [11-12]. The remaining bands observed are of less intensity. The peak at 3435.36 cm⁻¹ corresponds to O-H stretching vibration [3], and peak at 2923.61 cm⁻¹ is attributed to the asymmetric CH_2 stretching vibration. The H_2O deformation mode appeared at 1628.77cm⁻¹ [3, 13], and the CH_2 is in-plane bending (scissoring) vibration observed in the range of 1400.30 cm⁻¹ [14], the peak at 1035.25 cm⁻¹ is assigned to C-O stretching vibration [12].

4.3 UV band gap analysis
The UV-Visible Spectrum was recorded to analyze the electronic transitions and band gap energy of Fe_3O_4 nano crystallite, shown in S2 (Supporting information). The result reveals that transition in the ranges of λ=358.28, 449.41, 518.78, 615.96 and 792.70 nm, corresponds to band gap energies 3.46, 2.76, 2.39, 2.01 and 1.56 eV respectively. The values of both direct and indirect band gap of the magnetite semiconducting samples falls between 0-3eV [15].The results confirm that Fe_3O_4 nanoparticles possess magnetic behavior and behaves as a semiconducting material, since the band gap falls between 3.46 and 1.56eV. The UV-transition spectrum is shown in S2 (Supporting information).

4.4 EDX and SEM analysis
The sample was analyzed using SEM and EDX spectra. The result shows that, 90% of the total composition is of Fe-O with Fe, 59.61% and O, 30.29%, The EDX spectrum is shown in S3 (Supporting information).

The SEM analysis was done to investigate the morphology, grain size and shape of nano composite. SEM images of Fe_3O_4 nanoparticles are shown in Figure 2. The morphology of Fe_3O_4 sample is composed of spherical shaped particles with diameters, 23.35, 31.78, 17.92, 23.92 and 32.35nm. The average size of the particle size is 25.87nm. The size matches with the mean particle size observed in X-ray diffraction analysis [10].

4.5 Electrical conductivity
The DC electrical conductivity of the iron oxide nano liquid was measured using SYSTRONIC water analyzer, which consists of conductivity cell with accuracy of ±1% of FS ± 1 digit. The conductivity ranges from 0 to 100mS/cm (micro Siemens/Centimeter) for the concentration from 0 ppm to 100 ppt. This instrument measures both temperature and conductivity simultaneously. Initially, the conductivity of deionized water was measured as σ=34.3μS/cm at room temperature. Then, 100ml of deionized water taken in a beaker and 0.1g of iron oxide (Fe_3O_4) composite was dissolved. This nano liquid was stirred until it completely dissolved. Then conductivity was measured by immersing the conducting cell into the nanoliquid. The conductivity was measured for different concentration 0.1g (I), 0.2g

(II), 0.3g (III), 0.4g (IV) and 0.5g (V), on different temperature ranges between 30 and 50°C. While observing the conductivity of nanoliquid, when the concentration of iron oxide increases the conductivity also increases with respect to the temperature. Previous report shows that the conductivity of nano liquid consisting particles size about 15.3 and 22.3 nm are 19 μS/cm and 1.62 μS/m respectively [16-17]. In the present investigation the conductivity for 0.1g of solution at 30°C is observed about 101μS/cm., whereas, when the temperature was raised (up to 50°C) the conductivity increases to 151μS/cm. Similarly, for the sample II, III, IV and V, the conductivity increases; maximum conductivity reaches to 432μS/cm for 0.5g of nanoliquid at 50°C. From this measurement, the conductivity of iron oxide indicates that at low concentration the mobility of charge carrier is low, whereas, when the concentration of iron oxide increases, the mobility of charge carrier also increases and the hence conductivity of the nanoliquid increases. On comparing our results with the previous reports [16-17], our sample with particle size 25.87nm, shows enhanced electrical conductivity. Figure 3 shows the conductivity measurements at different concentration and temperature.

5 CONCLUSIONS
Iron oxide nanoparticles were synthesized, and characterized by Powder X-ray diffraction, EDX, SEM, FT-IR and UV-Vis., spectrometry. The XRD pattern confirms that the material consist of Fe_3O_4 nano composite crystallites. The elemental analysis confirms that 90% of the composition is FeO nanoparticles. The size of particles was measured by XRD and SEM confirms that the particles are of same diameter (26.74 nm from XRD and 25.87nm from SEM analysis). FT-IR spectrum show Fe-O band appears at the characteristic regions. Band gap of this nano composite is in agreement with materials exhibiting semiconducting nature. The conductivity of nanoliquid prepared by this composite was measured at different concentration of sample and temperature (30°-50°C); it showed increasing conductivity when increasing the concentration and temperature. The maximum conductivity was observed for 0.5.g of sample out of 0.1g-05.g. It is observed from our study that for 0.1g of solute at 30°C the conductivity is 101μS/cm, whereas for 0.5g of solute at 50°C, the conductivity is 432μS/cm. It clearly shows that the number of charge carriers and the mobility of charge carrier increases, when, the concentration is more.
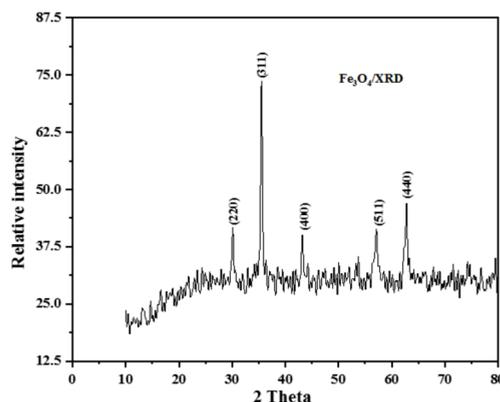
Figure 1 The X-Ray Diffraction pattern of Fe_3O_4 nanoparticles
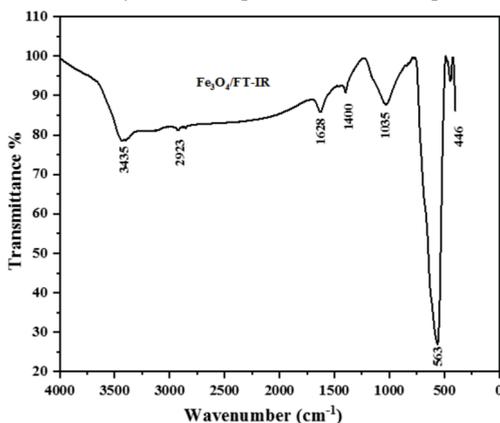
Figure S1 FT-IR Spectrum of Fe_3O_4 nanoparticles
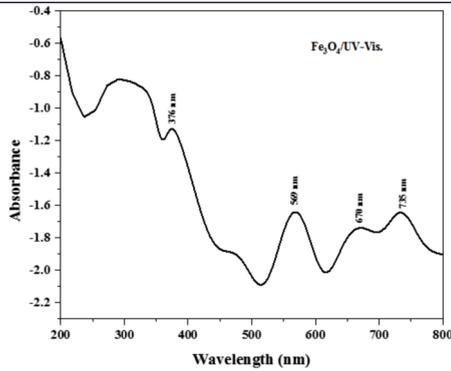
Figure S2 The UV-Visible spectrum for Fe₃O₄ nanoparticles
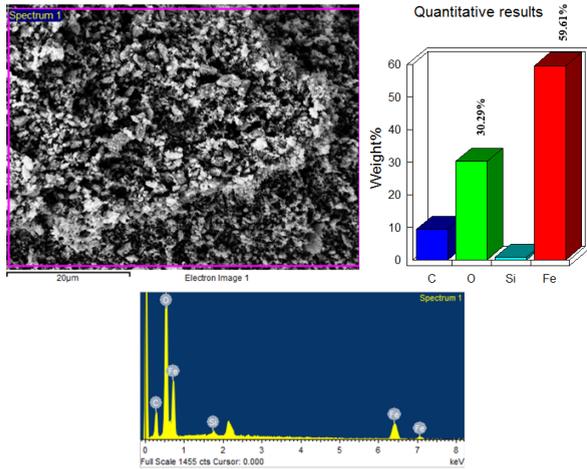
Figure S3 The SEM-EDX analysis of Fe₃O₄ nanoparticles
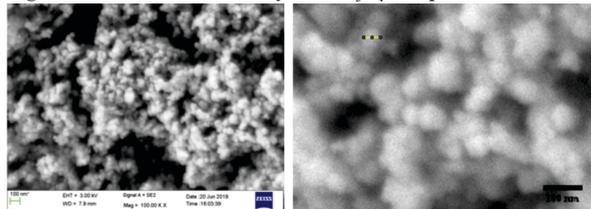
Figure 2 The SEM image of Fe₃O₄ nanoparticles
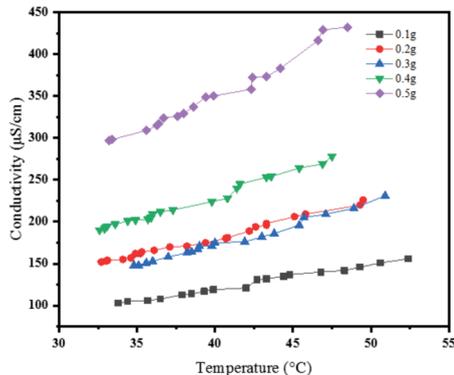
Figure 3 Electrical conductivity of Fe₃O₄ nano liquid for different concentration and temperature

Table1 The 2 theta, d-spacing and particle size of the Fe₃O₄ nanoparticles

S.No	Position [2θ]	FWHM	d-spacing [Å]	Size of the particle (nm)
1	30.1134	0.2952	2.96771	27.86
2	35.4888	0.2460	2.52956	33.90
3	43.2089	0.2952	2.09382	28.94
4	57.0901	0.7872	1.21335	11.49
5	62.7506	0.2952	1.48074	31.51

Table S1 The FT-IR spectral values and assignments of Fe₃O₄ nanoparticles

S.No	Wavenumber [cm⁻¹]	Functional group Assignments
1	446.88	νFe-O
2	563.76	νFe-O
3	1035.26	νC-O
4	1400.30	νC-O
5	1628.77	βCH₂
6	2923.61	νCH₂
7	3435.36	νO-H

Table 2 The average particle size of Fe₃O₄ nanoparticles using by SEM analysis

S.No	Area	Mean	Min	Max	Angle	Length
1	68.05	91.15	81.51	98.64	-130.60	23.36
2	88.47	199.62	171.54	212.41	-138.37	31.79
3	54.44	167.28	161.98	171.99	-90.00	17.94
4	68.05	191.28	172.90	199.83	-90.00	23.92
5	88.47	127.61	116.97	131.53	-34.99	32.35
Mean	73.50	155.39	140.98	162.88	-96.79	25.87
SD	14.75	45.51	40.33	47.47	41.18	6.12
Min	54.44	91.15	81.51	98.64	-138.37	17.94
Max	88.47	199.62	172.90	212.41	-34.99	32.35

Table 3 The conductivity of iron oxide nano liquid at different concentration and temperature range

Temperature	Conductivity (µS/cm) for different concentration of sample				
	I	**II**	**III**	**IV**	**V**
30°C	101	150	155	196	270
35°C	106	164	166	203	309
40°C	119	180	184	228	350
45°C	137	206	200	264	383
50°C	151	226	231	278	432

I→0.1g, II→0.2g, III→0.3g, IV→0.4g, V→0.5g;

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