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Nanospheres of Fe_3O_4 Synthesis through Sol-gel Technique and Their Structural & Magnetic Characterization

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ABSTRACT *Magnetite magnetic nanoparticles have been synthesized through sol-gel technique at different precursor concentrations. The synthesized magnetic nanoparticles were annealed at different temperatures (200°C, 300°C & 400°C) and they were analyzed for their structural, morphological, chemical composition and magnetic properties by using Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Diffraction Spectroscopy (XRD), Scanning Electron Microscopy (SEM) measurements and Vibrating Sample Magnetometer (VSM). The results show that the magnetic Fe_3O_4 nanoparticles are of cubic inverse spinel structure, the size of the nanoparticles lies in the range of 8 - 29 nm and crystalline in nature. The morphological and structural phase changes are not revealed by the heat treatment. However, the particle size is increased with increasing annealing temperature and precursor concentration notably. The saturation magnetization values of Fe_3O_4 nanoparticles are increased linearly with the annealing temperature to 55 emu/g at 400 °C.*

1. Introduction

Magnetic nanoparticles are class of nanoparticle, which can be manipulated for their fascinating property under the influence of magnetic field. Iron oxide nanoparticles have been of great interest, because of fundamental prospects caused by their multivalent oxidation states, abundant polymorphism and the mutual polymorphous changes in nanophase and in technological applications. Magnetite is a kind of mixed iron oxide ($FeO.Fe_2O_3$) with a cubic inverse spinel structure with oxygen forming a FCC closed packing and Fe cation occupying the interstitial tetrahedral sites and octahedral sites. In this structure, half of Fe^{3+} ions are tetrahedrally co-ordinated while the other half of the Fe^{3+} ions are octahedrally co-ordinated. Each octahedral site has six nearest neighbor O^{2-} ions arranged on the corners of the tetrahedran [1]. It has exhibited unique electric and magnetic properties based on the transfer of electrons between Fe^{2+} ions and Fe^{3+} ions in the octahedral site. However, magnetic nanoparticles show novel prospects that are different from those of the bulk materials due to their small size and their fundamental changes in the co-ordinates, symmetry and confinement [2].

Superparamagnetic nanoparticles has been widely studied and are compatible for bioapplications such as magnetic resonance imaging (MRI) contrast agents [3], medium for targeted drug delivery [4], magnetic cell separation [5] and in ultra high density, magnetic storage media etc., Numerous chemical methods can be used to synthesize magnetic nanoparticles for these applications, many efforts have been devoted to the synthesize of nano based magnetic particles, such as co-precipitation [6], micro emulsion [7], sol-gel method [8,9], laser pyrolysis [10], hydrolysis and thermolysis of precursors [11], flow injection synthesis [12], electrospray synthesis [13], hydrothermal preparation and DC thermal arc method and sonochemical synthesis [14].

The synthesis of superparamagnetic nanoparticles is a complex process because of their colloidal nature. The first main chemical challenge consists of defining experimental conditions, leading to a monodisperse population of magnetic grains of suitable size. The second critical point is to select a reproducible process that can be industrialized without any complex purification procedure, such as ultracentrifugation [15], size-exclusion chromatography [16], magnetic filtration [17] and flow field gradient [18]. These methods have been used to prepare particles with homogeneous composition and narrow size distribution. Among the various chemical synthesis methods for metal oxide, sol-gel process offers several advantages over the other method, including good homogeneity, produce materials at low temperature, able to produce large quantity at relatively cheapest cost and high purity.

Recently sol-gel method has been developed for the preparation of magnetite nanoparticles using metallo-organic precursors [8, 9]. Even though highly crystalline and uniform sized magnetite nanoparticles can be produced by the synthetic procedure mentioned above, cannot be applied to large-scale and economic production, because it requires expensive and often toxic reagents and complicated synthetic steps. A nanostructured magnetite thin film has been prepared by sol–gel method with inexpensive reagent of iron (II) chloride as starting materials [19]. The sol-gel process is a suitable wet route to the synthesis of nanostructured metal oxides [20-22]. This process is based on the hydroxylation and condensation of molecular precursors in solution, originating a "sol" of nanometric particles. Further condensation and inorganic polymerization lead to a three-dimensional metal oxide network denominated wet gel. These reactions are performed at room temperature further heat treatments are needed to acquire the final crystalline state [23, 24].

In this paper, magnetic nanoparticles are successfully synthesized via sol-gel method combined with annealing under vacuum using inexpensive, non-toxic ferric nitrate and ethylene glycol as starting material. The present route is easy to control during the reaction process without considering Fe (II)/Fe (III) molar ratio control and basic condition. The sizes of the obtained magnetic nanoparticle can be easily tailored by concentration of the precursor and by controlling the annealing temperature.

2. Experimental

2.1. Synthesis of Fe_3O_4 nanoparticles

In the typical experiment, different concentration (0.2M, 0.5M & 1M) of ferric nitrate in ethylene glycol precursors were prepared to study the effect of concentration on the nanoparticles formation using the procedure [25] with slight modifications, vigorous stirring for 2 h at 50° C and then the sol was heated to 75° C and kept to obtain gel, which was

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brown in colour. The gel was aged for 5 h and dried at 120° C for about 8 h. After drying, the xerogel was annealed at different temperatures 200, 300 and 400° C. Finally, Fe_3O_4 nanoparticle powders were stored in vacuum desicator for further studies.

2.2. Characterization

The magnetite nanoparticles produced were then characterized by various techniques. X-ray diffraction Spectroscopy (Panlytical X'Pert Pro Diffractometer) was used to study the structural phase identification and the mean crystalline size of the nanoparticles. From the XRD data, the size of the nanoparicles was also calculated through Scherrer formula. The Fourier Transform Infrared Spectroscopy (FTIR-Thermo Nicolet 380, Thermo Nicolet) was used to find out the chemical bonds in the Fe_3O_4 nanoparticles. The morphology and size analysis were made by using Scanning Electron Microscopy (S – 3000H, version = 1, Four Vision Instrument). The magnetic property of the synthesized Fe_3O_4 nanoparticles was measured by Vibrating Sample Magnetometer.

3. Results and Discussion

3.1. XRD pattern of Magnetite nanoparticles

Magnetite, Fe_3O_4 nanocrystals are with the cubic inverse spinel structure. The large oxygen ions are closely packed in a cubic arrangement and the smaller Fe ions are filled in the gaps. In Fe_3O_4, the Fe ions are surrounded by four and six oxygen ions in the tetrahedral and octahedral arrangement respectively.

The tetrahedral and octahedral sites form the two magnetic sub lattices are A and B respectively. The spins on the A sub lattice are anti parallel to those on the B sub lattice. The two crystal sites are very different and result in complex forms of exchange interactions of the iron ions between and within the two types of sites. The structural formula of magnetite is $[Fe^{3+}]$ A $[Fe^{3+}, Fe^{2+}]$ B O_4.This particular arrangement of cations on the A and B sub lattice is called an inverse spinel structure [26].

The X-ray diffraction patterns taken for the magnetite nanoparticles synthesized at 0.2M, 0.5M and 1M concentrations and annealed at 200°C, 300°C & 400°C are presented in the Figures 1. A very sharp and high intensity peaks were appeared at an angle 2θ = 32.13 °, 35.48 °, 43.83 °, 50.24, 62.20 °, 64.32 ° in the spectra of at higher concentration annealed at all the temperatures, however the other two concentrations and different annealing temperatures, a clear peak is appeared only around 32.13 ° and 35.48 ° and the remaining peaks are diminished while reducing the concentration. The diffraction peaks appeared at different angles (2θ) is corroborate with the (JCPDS 85-1436) JCPDS values which can be correlated with the (311), (400), (511) and (440) planes of Fe_3O_4 [27, 28]. This reveals that the resultant particles are pure without the presence of diffraction peaks for other impurities and also other forms of iron oxide phases. Broad nature of the diffraction pattern is an indication of the smaller particles, Scherrer formula gives a relationship between the peak broadening in XRD and the particle size.

Using the Scherrer formula, the particle size of the synthesized Fe_3O_4 nanoparticles have been calculated and plotted as a function of concentration and temperature which is presented in the Fig. 2I. The particle size annealed at 200 °C is lies between 7.8 nm and 13.8 nm for the 0.2M and 1M concentration respectively and when increasing the annealing temperature, the particle sizes are increased to around 17.1 nm and 28.7 nm at concentration 0.5M and 1M concentrations respectively. The smallest particle size is around 8 nm synthesized by using 0.2M concentration at 200° C annealing temperature. However, when the concentration of precursor solution increases which influences on the particle size growth. The nucleation of magnetite nanoparticles at lower concentration is less and it's less growth impacts on the smaller particle size. In the case of higher precursor concentration, the growth of the particle is dominating than the nucleation; hence the bigger particle size is the result. The full width half maximum (FWHM) of the reflection peaks decreases and the peaks become sharper with increasing annealing temperature, indicating the size of the Fe_3O_4 nanoparticles increased. The crystallinity of the Fe_3O_4 nanoparticles improved with the increase in annealing temperature. From the Fig.5, it can be seen that the particle size of the Fe_3O_4 is increased with in precursor concentration and with annealing temperature as discussed.

3.2. FTIR spectra of Magnetite nanoparticles

The FTIR analysis was performed for the synthesized magnetite nanoparticle to characterize the sample's nature and to confirm the samples are pure Fe_3O_4, which is shown in the Fig.2II. The peaks at 575 and 375 cm^{-1} are due to the vibration of Fe – O functional group that matches well with the characteristic peak of Fe_3O_4 [29]. The peaks observed in the region 1650 cm^{-1} were due to the stretching vibration of the remainder H_2O. The intense and broad band appeared in the range of 3200-3600 cm^{-1} corresponding to O – H stretching vibration, since that the iron oxide surfaces are readily covered with hydroxyl groups in an aqueous environment. The absorption bands in 2925 cm-1 is due to C – H stretching vibration which present in all the spectra studies [30].

3.3. Field Emission-Scanning Electron Microscopic Studies of Fe_3O_4 nanoparticles The FE-SEM micrographs for the synthesized Fe_3O_4 nanoparticles at different concentrations and annealed at different temperatures (200 & 400° C) were taken and selected representative images are (x20k) presented in the Figures 3. All the nanoparticles are almost spherical in shape. The mean sizes of Fe_3O_4 agglomerated particles from the figures are determined to be 100 – 200 nm. Crystallinity of the particles improved with increasing the annealing temperature and consequently agglomeration of the particles is decreased tremendously. However, the particle sizes of the synthesized magnetite nanoparticles are in the range of 17 – 28 nm at higher annealing temperatures. The agglomeration of the particles has to be controlled for conducive application.

3.4. Magnetic measurements of magnetite Fe_3O_4 nanoparticles

The VSM study was carried out on the samples synthesized using 1M concentration and annealed at 200, 300 & 400° C used to evaluate the magnetic properties. The zero magnetic remanence and the anhysteresis loop feature indicate that the magnetite nanoparticles are in superparamagnetic behaviour. The saturation magnetization values (Ms) of the Fe_3O_4 nanoparticles annealed at 200, 300, and 400° C are found to be 36, 48, and 55 emu/g respectively, which are presented in the Fig.4. The results indicate that the saturated magnetization value increases continuously with increasing the annealing temperature in the temperature range studied. The magnetic behavior of Fe_3O_4 nanoparticles is very sensitive to particle sizes, at higher annealing temperature increased crystallinity and increase in Fe_3O_4 nanoparticles leads to the increased saturated magnetization values of Fe_3O_4 nanoparticle [31]. An ideal superparamagnetic material has zero co-ercivity and zero remenance of the particles below 20 nm [32].

4. Conclusions

A better size controlled sol-gel method is reported in this paper for the synthesis of Fe_3O_4 magnetite nanoparticle, which is extremely simple and cost effective. The FT-IR results of the synthesized magnetite nanoparticles at various experimental conditions show the formation of Fe-O metal oxide bond. The XRD peaks correspond to Fe_3O_4 are found and the magnetite nanoparticle size is lies between 8-11 nm and the aggregated particles are in the range of 100-200 nm with respect to the precursor concentration and annealing temperature which is represented by the SEM pictures. The XRD and SEM results show that various sized Fe_3O_4 nanoparticles

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can be obtained simply by varying the concentration. The VSM measurement shows that the saturation magnetisation increases with increasing annealing temperature and without the loop opening reflects the superparamagnetic character. Important advantage of this synthetic process is the size of the nanoparticle can be easily tailored by annealing temperature. Moreover, by this economical and environment friendly viable method, other metal oxides synthesis can be made.

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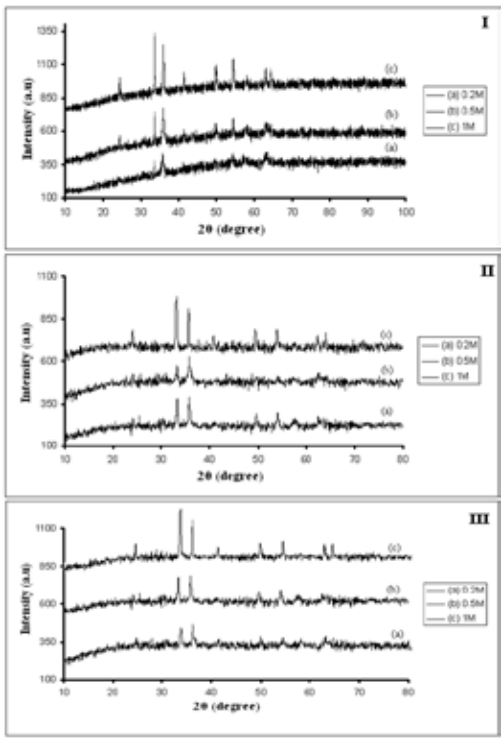

Fig.1 XRD patterns of Fe_3O_4 Nanoparticles synthesized at different concentrations and annealed at (I) 200°C (II) 300°C (III) 400°C.

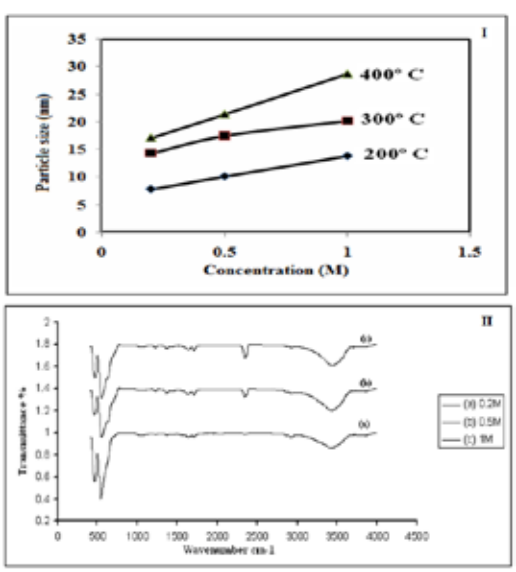

Fig.2 (I) Particle size of Fe_3O_4 nanoparticles at different concentrations and annealed at 200, 300 & 400°C (II)

FT-IR Spectra of Fe_3O_4 Nanoparticles synthesized at different concentrations and annealed at 400°C.

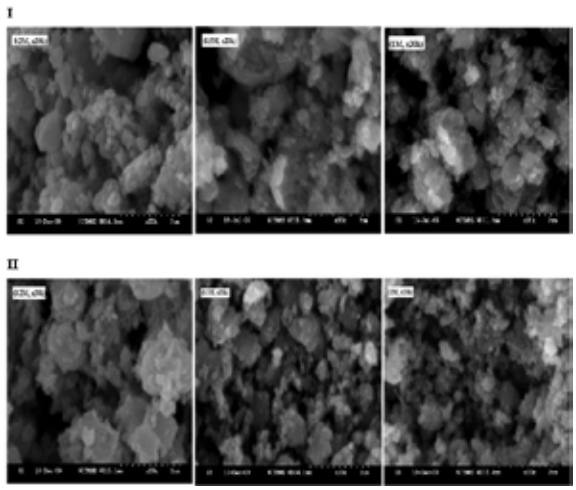

Fig.3. SEM photographs of Fe_3O_4 Nanoparticles prepared at different concentrations and annealed at (I) 200°C (II) 300°C.

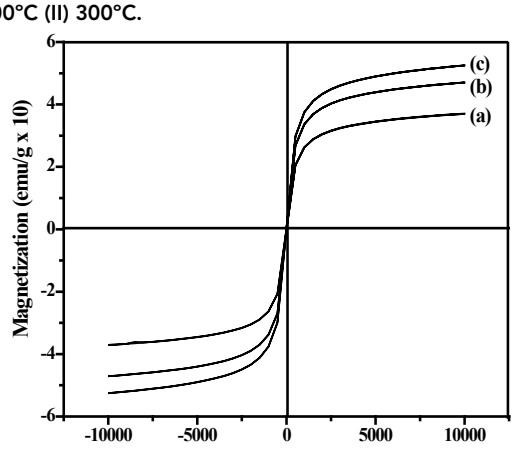

Fig.4 Magnetization loops of Fe_3O_4 nanoparticles synthesized at 1M annealed at different temperatures: (a) 200, (b) 300 and (c) 400 ºC.

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