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Effect of synthesis route on the structural, optical and magnetic properties of Fe_3O_4 nanoparticles

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Abstract

Fe_3O_4 nanoparticles were prepared by the co-precipitation as well as combustion method. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV–Visible spectroscopy and vibrating sample magnetometer (VSM) were used to study the physical properties. XRD pattern revealed the formation of single magnetite phase in the compound. TEM micrographs confirmed the uniform distribution of nanoparticles. UV–Visible spectroscopy measurement exhibited that the shifting of λ_{max} with the variation of particle size which indicated that band gap is dependent on particle size. Development of well saturated magnetization loop indicated the magnetic nature of the samples. The as prepared Fe_3O_4 nanoparticles exhibited superparamagnetic behavior. The band gap as well saturation magnetization (M_s) was found to be strongly dependent on the particle size. The saturated magnetization of the superparamagnetic Fe_3O_4 nanoparticles prepared by the co-precipitation and combustion methods were found to be ~63.5 emu/g and 44.2 emu/g, respectively at room temperature which enables them to be recycled from the solution by applying a small magnet.

Keywords: Fe_3O_4; Co-precipitation; Superparamagnetic; Band gap

1. Introduction

In recent few years, considerable attention has been paid to iron oxides especially on magnetite (Fe_3O_4) nanoparticles due to their potential applications such as pigment, magnetic resonance imaging, magnetic drug delivery, Ferro fluids, recording material, catalyst and data storage media [1–3].The magnetite nanoparticles display superparamagnetic behavior which arises from the negligible energy barrier in the hysteresis of the magnetization loop of the particles as predicted by Bloch and Neel [4].There are many reports on the synthesis and characterization of magnetite, but still magnetite instigates researcher's novel ideas, this is due to its great significance in various fields, especially, when this material remains in nanosize. Fe_3O_4 nanoparticles have been prepared by various methods such as arc discharge, mechanical grinding, laser ablation, micro-emulsions and high temperature decomposition of organic precursors, etc [5]. However, the research is still going on to obtain well-dispersed Fe_3O_4 nanoparticles.

Considering the importance of Fe_3O_4 nanoparticles, the synthesis technique plays an important role in determining the optimum magnetic as well as structural, microstructural and optical properties. Till now the most popular method for the synthesis of Fe_3O_4 nanoparticles is by co-precipitation, hydrothermal and sol–gel methods [6–8]. It was reported that combustion technique can be an effective method for the synthesis of nanoparticles. This method has been used for the synthesis of different oxides; including ferrites and perovskites [9–13]. It involves a self-sustained reaction between an oxidizer (e.g., metal nitrate) and a fuel (e.g., glycine). This self-sustained reaction converts the initial mixture typically to fine well-crystalline powders of desired compositions. However, very little attention has been given towards the synthesis of Fe_3O_4 nanoparticles by using combustion technique. This route proves to be a possible alternative method since it is simple, economic and environment friendly.

In the present work, we have successfully synthesized Fe_3O_4 nanoparticles by co-precipitation as well as combustion method.

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The detail structural, microstructural, optical and magnetic properties were studied in detail. The effect of synthesis route on the various physical properties has also been discussed thoroughly.

2. Experimental

2.1. Materials

For the synthesis of magnetic nanoparticles in this study, all chemicals were of analytical grade and were used without further purification. Ferric chloride hexa-hydrate ($FeCl_3 \cdot 6H_2O$), ferrous chloride tetra-hydrate ($FeCl_2 \cdot 4H_2O$), and ammonium solution (26% of ammonia) were purchased from Aldrich. The combustion synthesis was carried out by using Ferric nitrate, glycine, starch and ammonium nitrate.

2.2. Co-precipitation method

Ferric chloride and ferrous chloride were mixed in 2:1 M ratio. The solutions of Fe^{2+} and Fe^{3+} were prepared by making their aqueous solutions in distilled water and this solution containing both ions was then heated up to 50 °C for 10 min. After heating, the solution was precipitated by ammonia solution with continuous stirring on the magnetic stirrer at 50 °C. Black colored particles of iron oxide were precipitated. These particles were then separated from the solution by using a strong magnet and then were washed many times with distilled water. The precipitated magnetite is black in color. The powder was then dried in hot air oven at 100 °C for overnight. The overall reaction can be written as

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O \quad (1)$$

2.3. Combustion method

Ferric nitrate ($Fe(NO_3)_3$) was used as oxidant agent. Glycine, ammonium nitrate and starch were used as fuel. First stoichiometric amounts of the raw materials were weighed and then mixed with an agate mortar pestle. The grinding process was continued till mixing of the materials was completed. A quartz crucible was kept at ~500 °C temperature. The mixture was poured into this crucible and kept for 2 h till all the residues were evaporated. Finally, black color powders were collected and subjected for further characterizations.

2.4. Characterization

The Fe_3O_4 nanoparticles were analyzed for phase composition using X-ray powder diffraction (XRD, Bruker-axs, D8 Advance) over the 2θ ranges from 20°–70° at scan rate of 2°/min, using Cu-K_α radiation (1.5408 A°). The structure and unit cell parameters were calculated by X'pert high score plus 2.0 software. The surface morphology of the samples was taken by using JEOL JSM 6480 LV scanning electron microscope (SEM). The morphology and size of the synthesized particles were observed using transmission electron microscope (TEM, HILIPS-CM-200). Optical properties were studied by using UV CARY 100 Scan UV–Visible Spectrophotometer. Magnetic properties (M-H curve) were measured with a vibrating sample magnetometer (VSM, Quantum Design) at room temperature.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of Fe_3O_4 nanoparticles prepared by the co-precipitation method. XRD peaks are found to be sharp and distinct indicating good crystallinity and homogeneity of the sample. The absence of secondary peaks ensures the good purity of the sample. Fig. 1(b) shows the XRD pattern of the Fe_3O_4 nanoparticles prepared by combustion method. In this case, the XRD peaks are found to be relatively broad than the Fe_3O_4 nanoparticles prepared by co-precipitation method. This may be due to the more nanocrystalline nature of the Fe_3O_4 particles prepared by combustion method. The single phase formation of Fe_3O_4nanoparticle is confirmed by matching with standard JCPDS

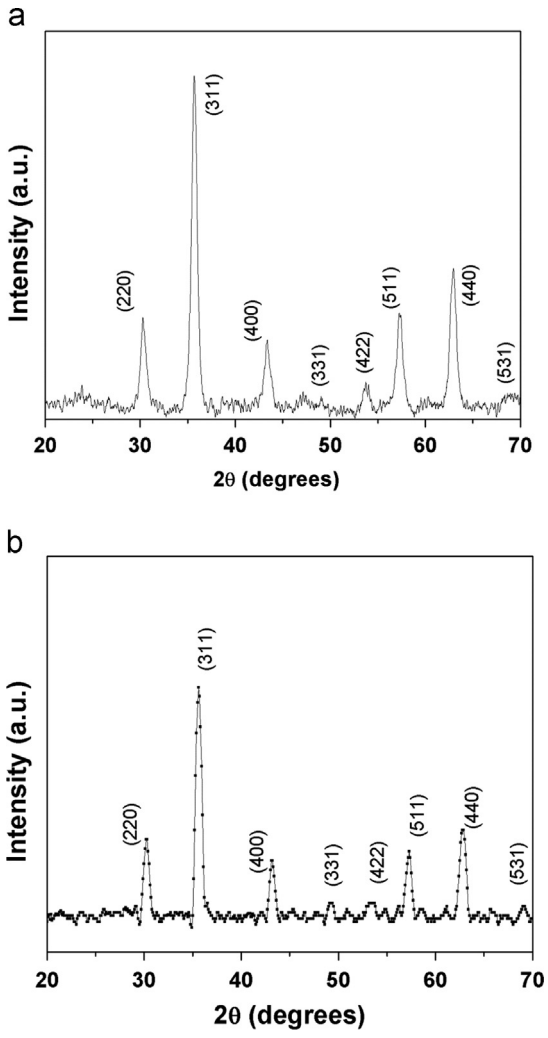

Fig. 1. (a) XRD pattern of magnetite nanoparticles by the co-precipitation method. (b) XRD pattern of magnetite nanoparticles by combustion synthesis.

Table 1
Unit cell parameters and particle size of the Fe_3O_4 nanoparticles.

Synthesis method	$a=b=c$ (Å)	Structure	Vol. (Å^3)	Particle size from XRD	Particle size from TEM
Co-precipitation	8.330 (6)	Cubic	578.01	39 nm	35 nm
Combustion	8.366 (4)	Cubic	585.55	24 nm	20 nm

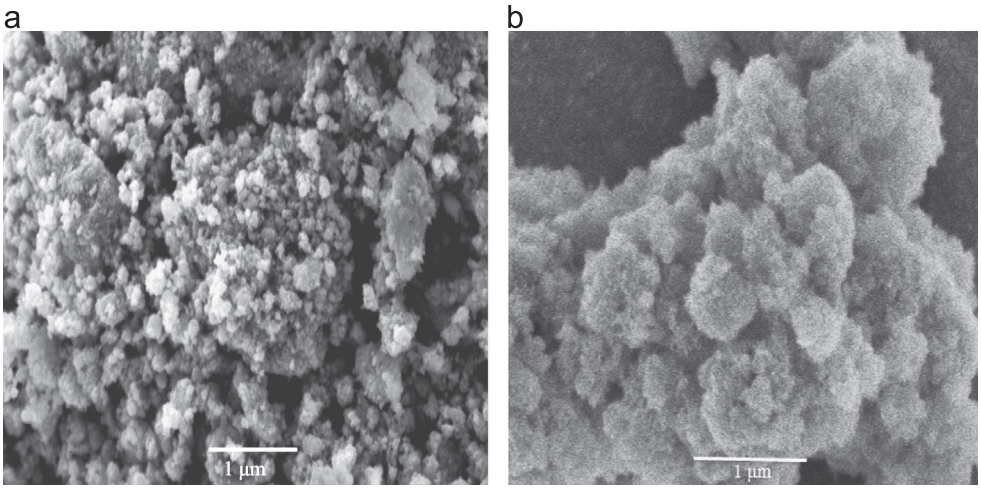

Fig. 2. SEM micrographs of the Fe_3O_4 nanoparticles prepared by (a) co-precipitation method and (b) combustion method.

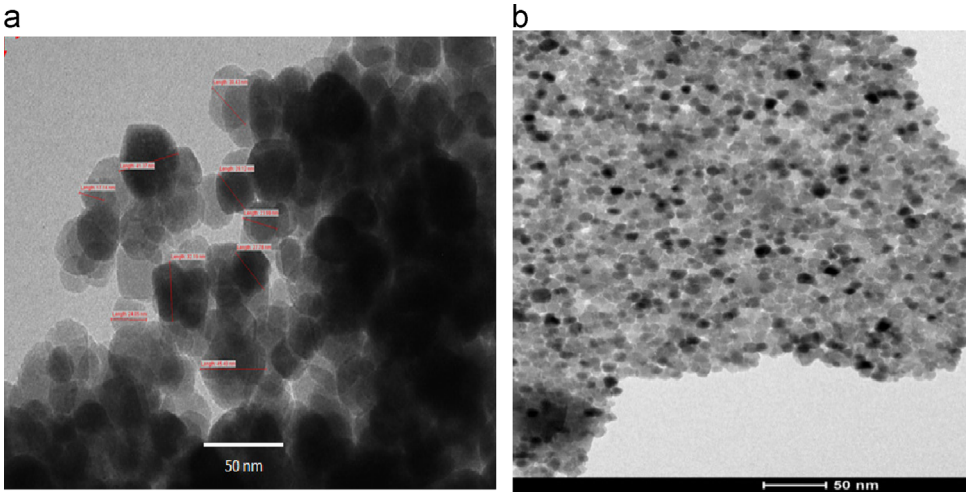

Fig. 3. TEM micrographs of the Fe_3O_4 nanoparticles prepared by (a) co-precipitation method and (b) combustion method.

Card no. 88-0315. The crystallite size of the Fe_3O_4 nanoparticles are calculated by using Scherrer's formula and are presented in Table 1 [6]. It is found that average crystallite size of the Fe_3O_4 nanoparticles prepared by the combustion method is lower than the co-precipitation method. The unit cell parameters of Fe_3O_4 in both the cases have been calculated by using X'pert high score plus software and listed in Table 1. It can be seen that the value lattice parameters are increased with the decrease in particle size for combustion process. The SEM micrographs of the Fe_3O_4 nanoparticles prepared by co-precipitation as well as combustion method are shown in Fig. 2. It is evident that the relatively small nanoparticles are obtained in case of the combustion process. It is very difficult to find out exactly the particle size of the samples from the SEM micrographs. Hence, TEM micrographs of the sample are collected. Fig. 3 shows the TEM micrographs of both the samples. Spherical shaped nanoparticles are obtained in case of both the methods. It can be seen that the particle size of Fe_3O_4 nanoparticles prepared by the co-precipitation and combustion method are found to be ~35 nm and 20 nm, respectively.

To determine the optical properties of the synthesized Fe_3O_4 nanoparticles, the UV–vis Spectra (with DRS) was collected and are shown in Fig. 4. A single absorption is observed in both the samples, which indicates the formation of a single phase compound. The absorption peak ($\lambda_{max.}$) is found to be shifted towards the lower wavelength side in case of the nanoparticles synthesized by combustion method which indicates that band gap is dependent on particle size. The direct

band gap of the Fe_3O_4 nanoparticles are calculated by using tauc plot and are shown in Fig. 5(a) and (b).The band gap of Fe_3O_4 nanoparticles synthesized by combustion technique is found to be higher than the co-precipitation method. The band gap of Fe_3O_4 nanoparticles synthesized by co-precipitation and combustion technique are observed to be ~1.88 and 2.08 respectively. This is due to the fact that with decrease in particle size the band gap of the material increases.

Fig. 6 shows the magnetization vs. magnetic field loop of the Fe_3O_4 nanoparticles. Development of saturated loop confirms the magnetic nature of the samples. However, it is evident here that unlike ferromagnetic samples where a remnant magnetization and coercive field is observed, but in this case no such behavior is noticed. These samples show perfect superparamgnetic behavior and hence, are believed to be promising for wide range of engineering applications, such as drug delivery, bio-separation and magnetic resonance imaging [14]. The present results are compared with the reported results to have a better understanding and a deeper insight into the results, and it is found that M_s value is higher than the reported one [15,16].

The saturation magnetization (M_s) is found to be strongly dependent on the synthesis method. The value of M_s (63.5) is found to be higher in case of Fe_3O_4 nanoparticles synthesized by co-precipitation method. It can be observed that the smaller particle sizes display smaller values of M_s as expected due to the surface disorder and modified cationic distributions [17]. In other words, the decrease in M_s at smaller sizes is attributed to the noticeable surface effects in these nanoparticles. The surface of the nanoparticles is considered to be composed of some canted or disordered spins that prevent the core spins from aligning along the field direction resulting in decrease of the saturation magnetization of the small sized nanoparticles [18].

4. Conclusions

Fe_3O_4 nanoparticles are prepared by chemical co-precipitation as well as combustion method. XRD patterns confirm the development of magnetite phase in the sample. UV–Vis spectra shows a blue shift in case of combustion method. The band gap of Fe_3O_4 nanoparticles synthesized

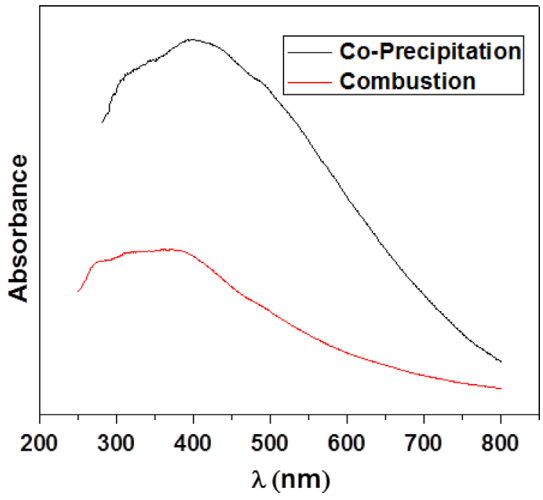

Fig. 4. UV–vis spetra of the Fe_3O_4 nanoparticles.

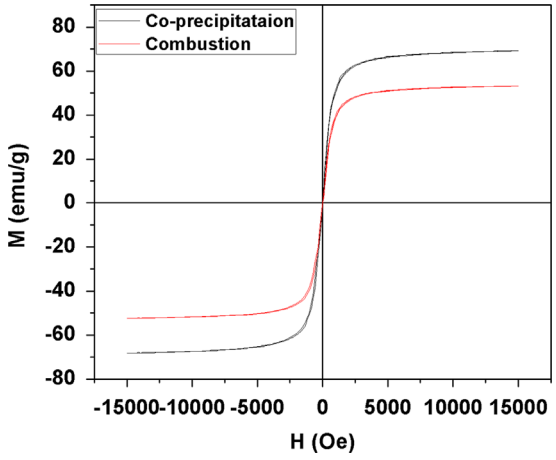

Fig. 6. Magnetic hysteresis loop of the Fe_3O_4 nanoparticles.

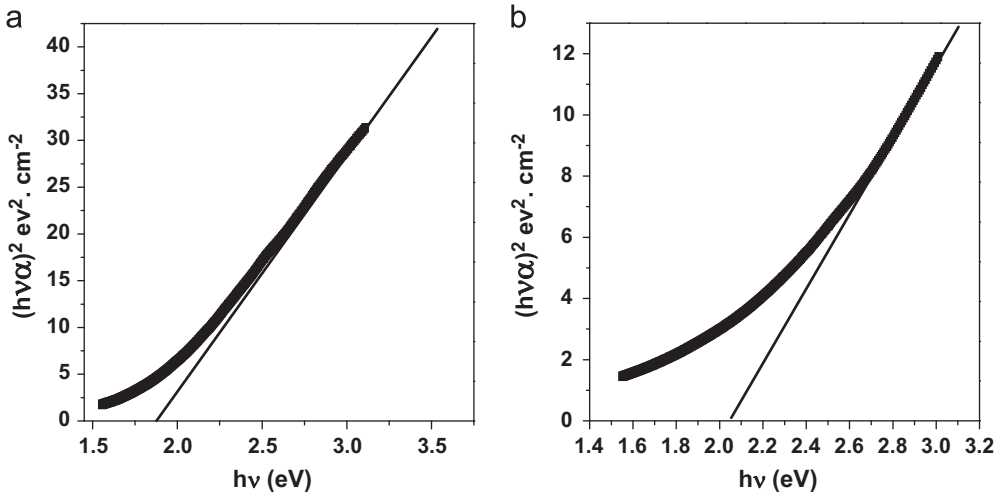

Fig. 5. Tauc plots of the Fe_3O_4 nanoparticles prepared by (a) co-precipitation method and (b) combustion method.

by co-precipitation and combustion technique are observed to be ~1.88 and 2.08 respectively. This is due to the fact that with decrease in particle size the band gap of the material increases. The magnetization measurements confirm that the sample is superparamagnetic in nature and has no hysteresis loop. The saturation magnetization (M_s) is found to be higher ~63.5 emu/g for the Fe_3O_4 nanoparticles synthesized by the co-precipitation method, which is very high in comparison to the earlier reports.

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