

Solution combustion preparation of Fe₂O₃-nano-flakes: Synthesis and characterization

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Received: 09 April 2012, Revised: 12 May 2012, Accepted: 16 May 2012

ABSTRACT

This paper outlines synthesis of iron oxide nano-flakes and their magnetic properties. Fe₂O₃-Nano-flakes were synthesized by simple, non-expensive solution combustion method using glycine as fuel. XRD confirmed the phase purity of the sample. Surface morphology and elemental composition were determined by SEM and EDX analysis. Mössbauer studies revealed the sextet at room temperature indicating ordered crystalline long range ferromagnetism. M-H measurements showed the saturated hysteresis curve with noticeable coercivity of 300 Oe. UV-vis spectra revealed the good optical absorbance in the visible region. Copyright © 2012 VBRI Press.

Keywords: Solution combustion; mössbauer spectroscopy; nano-flakes.



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Introduction

Nowadays, semiconductor oxides at the nano level have attracted a lot of attention, as their properties can be controlled by changing by changing the surface to volume ratio, synthesis techniques, growth temperature and also by changing the crystallite size [1-2]. For the research purpose Fe₂O₃ is an important semiconductor for the study of polymorphism and the magnetic and structural phase transitions of nanoparticles. In the past decade, nanostructures of iron oxides such as α -Fe₂O₃, γ -Fe₂O₃, β -Fe₂O₃ and Fe₃O₄, have evoked remarkable interest from both theoretical and experimental point of view because of their potential applications in nanodevices [3]. Gamma and epsilon type Fe₂O₃ are ferromagnetic; alpha Fe₂O₃ is a canted antiferromagnetic while beta type Fe₂O₃ is a paramagnetic material. As alpha Fe₂O₃ has canted magnetism which means that the magnetic moments of the two magnetic sublattices do not fully cancel each other and results in small magnetic moment value in the direction of the basal plane. When the size of the magnetic particles becomes very small the magnetic moment in the domain fluctuates in direction, due to thermal agitation which leads to superparamagnetism. Among different magnetic nanoparticles, α -Fe₂O₃ is a very common magnetic material as it has potential applications in the chemical industry and also in drug delivery [4-6].

Alpha-Fe₂O₃ is also an environment friendly n-type semiconductor and thermodynamically most stable phase of iron oxide under ambient conditions. It can be used as catalyst, gas sensing material to detect combustible gases

like CH_4 and C_3H_8 , and so forth [7-8]. A lot of experiments have been carried out to make its use in composites for many useful applications [9-10]. A number of preparation techniques have been employed earlier for the preparation of Fe_2O_3 nanoparticles [11-15]. Some of them are very expensive and time consuming. Here, we have prepared Fe_2O_3 nanoflakes by simple non-expensive solution combustion method using glycine as fuel [16].

Experimental

All of the chemical reagents such as iron nitrate (Merck, $\geq 98\%$) and glycine (Merck, $\geq 99\%$). Stoichiometric composition of the redox mixture was calculated based on the total oxidizing and reducing valencies of the oxidizer (all nitrates) and the fuel (glycine) keeping the O/F ratio unity. Required amount of iron nitrate and glycine were dissolved in distilled water under vigorous stirring. The resulting solution was allowed to burn at 100°C with vigorous stirring. This low temperature synthesis results in fluffy material after complete combustion at 150°C . Then this material was dried in air oven at $300 \pm 20^\circ\text{C}$ for five hours. The obtained powder was grinded to final form of Fe_2O_3 nano-flakes. X-Ray powder diffraction analysis was conducted on XPERT-PRO Diffractometer (XRD) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) to analyze the phase structure. Surface morphology was studied by scanning electron microscope using QUANTA250 FEI D9393 of the powder sample.

Magnetization measurements were carried out using vibrating sample magnetometer ('Microsense') by applying the field of -22000 to 22000 Oe. Mössbauer spectra were recorded by using ^{57}Fe spectroscopy using cobalt as radioactive source with pc-based spectrometer equipped with weissel velocity at the room temperature and the experimental results were fitted with the NORMOS-SITE program to deduce the isomer shift and hyperfine field of the sample. Experiment to study the optical properties was done on SYSTRONICS double beam spectrophotometer 2202 by making the suspension of 2 mg of prepared sample in distilled water.

Results and discussion

The XRD pattern of prepared Fe_2O_3 nano-crystalline sample is shown in Fig. 1. The major XRD peak is obtained at $2\theta = 33.1^\circ$ while the second major peak is obtained at $2\theta = 35.67^\circ$. The 35.67° peak can be due to either of the alpha or gamma phases. The relative intensities of the two major peaks and the other smaller peaks that are observed suggests strongly that alpha Fe_2O_3 is the major phase in this material, which is further supported by Mössbauer studies. Average particle diameter D is obtained from the main peaks using Scherrer's formula for the peak width broadening as a function of the size of the particles,

$$D = k\lambda/\beta \cos\theta$$

Average particle diameter is found to be 17 nm. The lattice constants so obtained for alpha Fe_2O_3 nanoflakes are $a = b = 5.0356 \text{ \AA}$ and $c = 13.7489 \text{ \AA}$. Surface

morphology of the prepared powder was studied by scanning electron microscope (SEM).

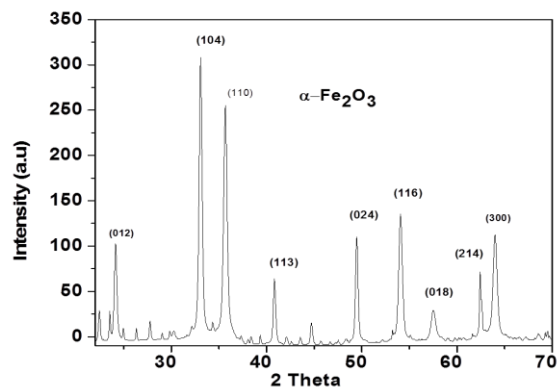


Fig. 1. XRD spectra of $\alpha\text{-Fe}_2\text{O}_3$ nanoflakes.

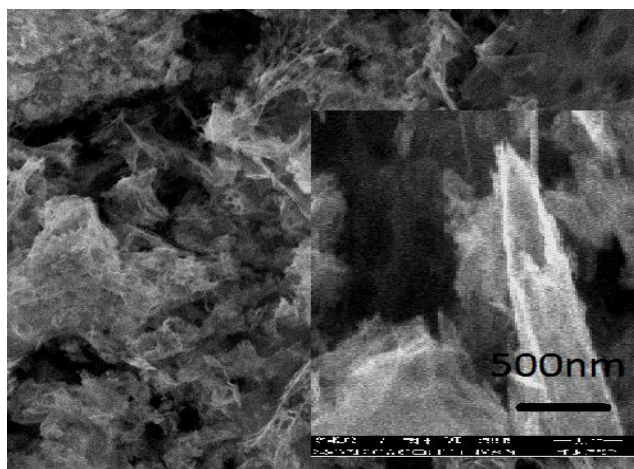


Fig. 2. SEM image of the prepared sample.

Fig. 2. shows the SEM image of prepared sample which clearly shows that the particles are roughly flake like. The size and the shape of the $\alpha\text{-Fe}_2\text{O}_3$ nanoflakes strongly depend on the preparation technique [17]. Porosity can be clearly seen from the SEM micrograph which may be due to the liberation of gases during combustion process. EDX analysis confirms the elemental composition of the sample and depicts that there are no traces of any impurity except some carbon content which may be due combustion process (Fig. 3).

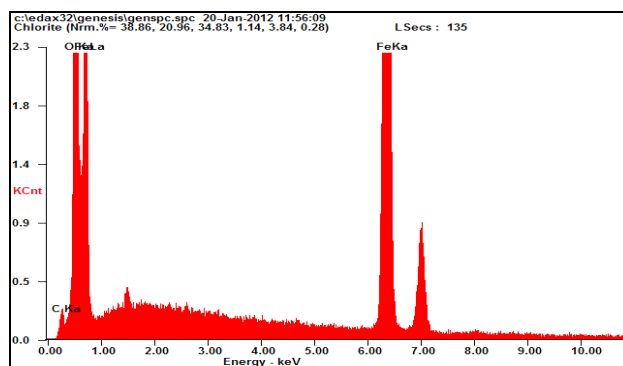


Fig. 3. EDX spectra of $\alpha\text{-Fe}_2\text{O}_3$ nanoflakes.

To study the magnetic properties, magnetic hysteresis measurements for α -Fe₂O₃ were carried out by applying the magnetic field of 20000 Oe at room temperature (Fig. 4). A clear saturated loop was obtained after the subtraction of diamagnetic part of the sample holder used for the hysteresis study. α -Fe₂O₃ exhibit hysteric feature with the remanent magnetization and coercive field of 0.67 emu/g and 300 Oe (Table 1). The obtained value of remanent magnetization is higher than the previous work but there is large variation in the value of coercive field [11, 13]. The obtained squareness ratio of 0.352 is quiet greater than previous report [17-18].

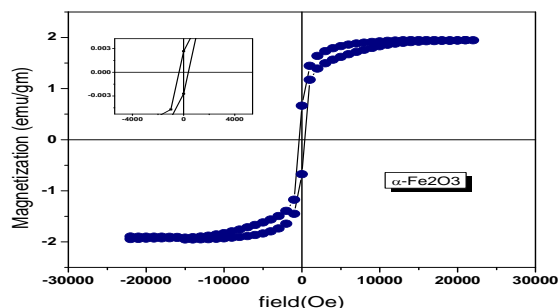


Fig. 4. Magnetic hysteresis loop of as-prepared α -Fe₂O₃ sample at room temperature.

Table 1. The best fitted Mössbauer spectra at the room temperature give the value for isomer shift and hyperfine field.

H _r (T)	QS (mm/s)	IS (mm/s)	LW (mm/s)	Area%	Particle size(nm)	M _r	M _r /M _s	H _c (Oe)
3	-0.22	0.23	0.35	100	17	0.67	0.35	300

The graph suggests that α -Fe₂O₃ nanoflakes exhibit ferromagnetic character at room temperature. Since symmetrically shaped nanoparticles such as spheres, do not have any net shape anisotropy. So the high value of remanance and coercivity can be attributed to the shape anisotropy in addition to the crystalline anisotropy of nanoflakes which is playing a role in modifying the magnetic properties. The presence of minor traces of γ -Fe₂O₃ can be ruled out because of slightly large coercivity and small magnetization because at the room temperature the gamma phase being a soft phase has a much higher moment and low coercivity. XRD also supports the non-formation of any peak of γ -Fe₂O₃.

To further support the phase purity of the prepared sample, we have performed Mössbauer spectroscopy at the room temperature which further gives the nature of the internal magnetic field of the prepared nanoflakes (Fig. 5). Mössbauer data was collected by using a ⁵⁷Co (Rh-matrix) source (initially activity of 25 mCi) in transmission geometry. We obtained a clear sextet at the room temperature indicating long range ferromagnetism. The fitting of the data was carried out by Normoss dist/site program. The parameters of the best fitted spectra clearly indicate the presence of only one phase i.e alpha phase Fe₂O₃. The best fitted spectra give the value for isomer

shift and hyperfine field of 0.23 mm/s and 53T (Table 1). The value of HF so obtained is slightly greater than 52 T which is for the bulk α -Fe₂O₃. This may be due to low electron density at the interfacial in this sample. Less value of isomer shift clearly indicates the iron presents in Fe³⁺. So the possibility of Fe₃O₄ is also ruled out as in Fe₃O₄-phase, iron presents in both 2⁺ and 3⁺ states.

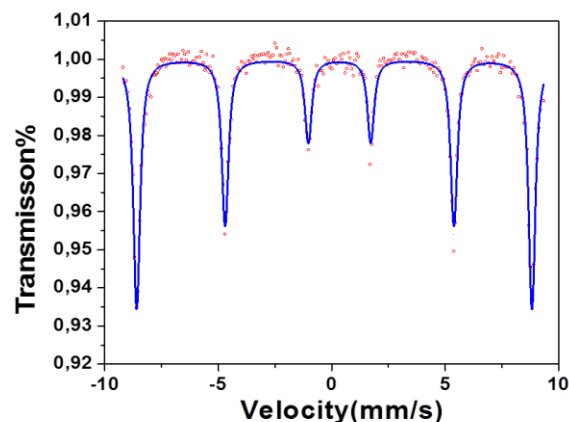


Fig. 5. Mössbauer spectra of α -Fe₂O₃ nanoflakes at room temperature.

Fig. 6 shows the UV absorption spectra of the prepared sample. Unlike all other II-IV group semiconductors, hematite nanocrystals also possess a broad absorption in the 200-700 nm. Iron oxides have three kinds of optical transitions: (1) the Fe³⁺ ligand field transition or the d-d transition, (2) the ligand to metal charge-transfer transitions, and (3) the pair excitations resulting from the simultaneous excitations of two neighboring Fe³⁺ cations that are magnetically coupled.

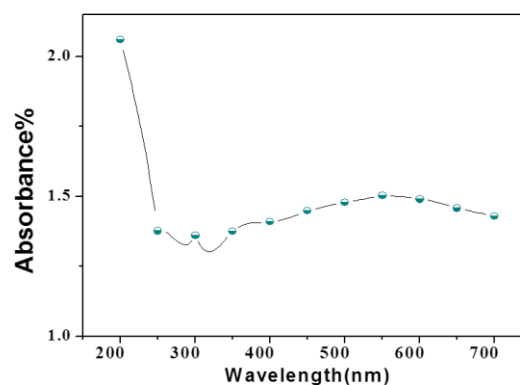


Fig. 6. UV-vis spectra of as-prepared α -Fe₂O₃ sample.

A good optical response is observed in the visible region which is good from the application point of view. The band gap, E_g (for a direct transition between the valance and conduction band), is obtained by fitting the experimental absorption data with the following equation: $(\alpha h\nu)^2 = A (h\nu - E_g)$, for a direct band gap semiconductors, where $h\nu$ is the photon energy, α is the absorption coefficient, E_g is the band gap, and A is the characteristic parameter independent of photon energy [20]. The

obtained band gap E_g value is found to be 2.4 eV which is in good agreement to earlier reports.

Conclusion

We have successfully synthesized single phased α - Fe_2O_3 nanoflakes at low temperature by simple solution combustion technique. Magnetic studies clearly show the ferromagnetic state for the nanoflakes. Local environment of the Fe atom has been probed by Mössbauer spectroscopy indicating long range ferromagnetism at room temperature which further supported the formation of single phased Fe_2O_3 nanoflakes. UV-vis spectra depict the good optical absorbance in the visible region which is a key factor for photocatalytic behaviour.

Acknowledgements

We appreciate the financial support from UGC New Delhi in the form of Rajiv Gandhi Junior Research fellowship. The authors would also like to thanksUSIC facility, Himachal Pradesh University Shimla for providing research facilities.

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