A simple solid-state method to synthesize nanosized ferromagnetic α -Fe₂O₃ with enhanced photocatalytic activity in sunlight

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Abstract. α -Fe₂O₃ was synthesized by preparing a mixture of Fe(III) nitrate with urea as a precursor. The yellowish coloured precursor was calcined at 400°C for 2 h, resulting in the formation of bright red coloured hematite. The surface properties and catalytic activity were compared with a reference sample prepared without the use of urea. It was observed that urea-induced synthesis resulted in a sample having nanosize and large lattice strain, accompanied by the development of ferromagnetic behaviour. The catalytic activity was evaluated for the decomposition of H₂O₂ through the photo-Fenton process in sunlight. The urea-synthesized sample showed an usually large photo-Fenton effect and the catalyst could be easily recovered and reused due to its ferromagnetic behaviour.

Keywords. Hematite; ferromagnetism; lattice strain; photo-Fenton process; H₂O₂.

1. Introduction

Iron is one of the most abundant elements in the Earth's crust. Its oxide exists in different polymorphic forms, such as hematite and magnetite. Like various transition metal oxides, iron oxides exhibit different bulk properties, such as magnetism and surface properties. The properties of an iron oxide depend on the method of synthesis e.g., co-precipitation method is a simple and efficient technique which also include good homogeneousness, low cost and low time consumption [1–3].

Among the various iron oxides, the hematite or α -Fe₂O₃ form is a thermodynamically stable oxide. Hematite is an important and widely investigated polymorph of iron oxide. It has a hexagonal close-packed crystal structure with a band gap of 2.1 eV. It is known to have a large number of applications in the area of sensors, capacitors and as a catalytic material and also in energy conversion through a photoelectrochemical process. It is particularly relevant as compared to other transition metal oxides due to its ease of synthesis and non-toxic nature. Hematite is generally antiferromagnetic however, its oxygen deficient form is known to exhibit significant ferromagnetic or superparamagnetic behaviours [4]. At temperatures below 948 K, bulk hematite is an antiferromagnetic material with slightly canted spins and at 200 K, spins flip 90° and the hematite phase becomes pure antiferromagnetic. The phenomenon of magnetism in hematite was explained by Zubov *et al* [5] based on the investigation of natural faces of the hematite band calculating the energy of surface anisotropy for the faces of types (100) and (111). Weak ferromagnetic moment within the basal plane of hematite natural crystals at low temperatures was explained by Hernandez [6].

Apart from the magnetic properties of α -Fe₂O₃, it can also be used as a good candidate for use in a heterogeneous Fenton like process because they are reactive at neutral pH which avoids the need for the acidification and neutralization steps used in the homogeneous Fenton process. Also their low-band gap and magnetic property help to undergo a facile advanced oxidation process and to separate out from the reaction mixture easily [7–12].

In the present study, we have synthesized iron oxide by a combustion method. The synthesized samples were further investigated for their surface and magnetic properties. The results are also discussed in relation to the catalytic activity towards decomposition of hydrogen peroxide.

In the present investigation, we report a urea-induced synthesis of hematite with ferromagnetic properties.

2. Experimental

2.1 Synthesis of α -Fe₂O₃

All the chemicals used were of analytical grade. Fe(NO₃)₃ · 9H₂O, 99–101% and urea CO(NH₂)₂, 99–100.5% were purchased from Thomas Baker (Chemicals), Pvt. Ltd. (Mumbai). Iron oxides were synthesized by heating an intimate solid mixture of ferric nitrate $\pm$ urea such that ferric nitrate:urea molar compositions were 1:0 and 1:5. The mixtures were preheated uniformly on a water bath. This resulted in the formation of molten liquid at 60°C. Thereafter (within $\sim$ 1–2 h), the mixture becomes semisolid. When the temperature was raised to $\sim$ 90°C, the reaction mixture is converted into a dry powdery mass within $\sim$ 2 h. The resulting precursors were

Scheme 1. Urea-induced synthesis of magnetic α -Fe₂O₃.

subsequently heated in a muffle furnace at 400°C for 2 h to obtain the final samples (scheme 1). The samples in general were designated as F-xy where xy is the molar ratio of ferric nitrate and urea. Their respective sample codes were F-10 and F-15.

2.2 Characterization

Phase identification was carried out from the X-ray powder diffraction (XRD) patterns recorded on a Rigaku Ultima IV diffractometer, using Ni filtered CuK α radiation ($\lambda = 1.5406$ Å). The crystallite sizes were determined using the Scherrer formula $t = 0.9\lambda/\beta \cos \theta$, where λ is the wavelength characteristic of CuK α radiation, β is the full-width at half maximum (in radians) and θ is the angle at which the 100 intensity peak appears. Thermal studies were carried out on a NETZSCH STA 409 PC by using a Al₂O₃ crucible at a heating rate of 10°C min⁻¹ under an oxygen atmosphere. Transmission electron microscopy (TEM) analyses were carried out to find the particle size of the synthesized catalyst on Phillips CM 200 at operating voltages of 20–200 kV and a resolution of 2.4 Å. The Brunauer–Emmett–Teller (BET) surface area was determined by a multipoint BET method and Barrett–Joyner–Halenda pore size distribution

analysis was performed on the Quantachrome Autosorb iQ and Asiqwin gas sorption system. The band gap energies were determined using a UV–Vis spectrophotometer (Shimadzu UV-2450). The Fourier-transform infrared spectrum was recorded in the range of 4000–400 cm⁻¹ on Shimadzu IR Prestige-21 by diluting a few milligrams of the sample in KBr. The magnetic properties were measured on a Quantachrome Versa Lab vibrating sample magnetometer at 300 K. X-ray photoelectron spectroscopy (XPS) spectra of the representative sample was recorded on a microtech multiple ESCA 3000 spectrometer.

2.3 Catalytic activity

The catalytic activity was measured by the ability of the catalyst to decompose H₂O₂. The decomposition of H₂O₂ was carried out on 10 mg of the catalyst containing 5 ml of 0.1 M H₂O₂ and measuring the evolved gas at various time intervals. The reactions were carried in the dark as well in sunlight. The pH of the reaction mixture was 5.

3. Results and discussion

3.1 Synthesis and characterization

The urea-induced synthesis of iron oxide is illustrated in scheme 1. It is known that Fe(III) nitrate when calcined produces the hematite phase. When this calcination is carried out in the presence of urea, the surface features of the oxides are altered. In the present investigation, the synthesis was carried by using a salt:urea ratio of 1:5, which is close to the stoichiometric ratio required for the combustion synthesis [13,14]. Calcination of the precursors was carried out at 400°C. XRD patterns of the synthesized samples are shown in figure 1. In the case of both the samples F-10 and F-15, all

Figure 1. XRD pattern of the synthesized samples F-10 and F-15.

Table 1. Synthesis and structural properties of the α -Fe₂O₃ samples prepared by calcination of an iron nitrate $\pm$ urea mixture.

Catalyst code	Urea (mol)	Phase composition	Particle size (nm)	Lattice parameters (Å)			Lattice strain	Surface area (m ² g ⁻¹)	Pore volume (cc g ⁻¹)	Pore radius (Å)	Band gap (eV)
				$a = b$	c	c/a					
F-10	0	α -Fe ₂ O ₃	23	5.03	13.77	2.73	0.063	44	0.185	17.03	2.1
F-15	5	α -Fe ₂ O ₃	37	5.02	13.75	2.73	0.165	43	0.090	21.55	2.1

Figure 2. TG curves of the synthesized precursors of samples F-10 and F-15.

the peaks correspond to the hematite or α -Fe₂O₃ phase. These are in agreement with JCPDS file no. 33-0664. Table 1 shows the synthesis and the structural parameters of the samples. As seen from the thermogravimetric (TG) curves (figure 2), the decomposition of the iron oxide precursors is completed at 400°C, resulting in stable phase formation.

Figure 3 shows TEM images of the synthesized samples and their respective particle sizes are shown in table 1. The TEM particle sizes were 23 and 37 nm, respectively. Thus, the urea-synthesized sample F-15 showed a larger particle size. This could be due to increase in the temperature caused by the use of urea during the synthesis leading to formation of crystallites of larger size. The high temperatures during combustion synthesis can cause lattice disorder and cation displacements resulting in strain in the lattice.

Table 1 also shows the values of the lattice strain calculated with reference to Williamson–Hall plots [15]. As expected, F-15 showed much larger strain (a value of 0.165) as compared to (0.063) only for F-10 and the latter was synthesized by calcination of the precursor without the use of urea. Figure 4 shows infrared (IR) spectra of the synthesized samples. IR vibrations obtained in the region of 400–1000 cm⁻¹ were due to the Fe–O bonds [16]. The bands between 1200

Figure 3. TEM images of F-10 and F-15 samples.

and 1800 cm⁻¹ are attributed to solid-state defects or lattice imperfections, which generally arise in samples prepared by the combustion method. Solid-state defects could be oxygen defects and the absence of some lattice oxygen around Fe³⁺. The sample F-10 also showed bands around 3460 and 1636 cm⁻¹ due to O–H stretching and bending absorptions. These bands were absent in F-15 during urea-induced synthesis; the high temperature causes complete dehydroxylation followed by *in situ* sintering of some particles. This explains the larger particle size and higher lattice strain in the F-15 sample.

Figure 4. IR spectra of the synthesized samples F-10 and F-15.

Figure 5. UV-Vis profiles of the α -Fe₂O₃ samples F-10 and F-15.

In α -Fe₂O₃, Fe³⁺ is a 3d⁵ complex surrounded by O²⁻ ions in an octahedral environment. Figure 5 shows the UV-Vis spectra of the synthesized α -Fe₂O₃ samples F-10 and F-15. The spectra show absorptions at wavelengths around (i) $\sim$ 350 nm, mainly due to the ligand to metal charge transfer process (LMCT), (ii) $\sim$ 530 nm in the range of 450–600 nm, due to transitions associated with magnetically coupled cations which is pair excitation processes of the type ${}^6A_1 + {}^6A_1 \rightarrow {}^4T_2(4G) + {}^4T_2(4G)$ as well as d–d transition associated with high spin Fe³⁺ and (iii) a weak absorption in the spectral range of 600–800 nm which is due to the ligand field transition of Fe³⁺.

In F-15, the UV-Vis absorption intensities in the range of 200–600 nm are significantly lower than those of F-10, due to O²⁻ vacancies, causing incomplete coordination around the metal ion, which in turn affect the LMCT.

Figure 6 shows N₂ adsorption–desorption isotherms with respective pore size distributions (profiles in the inset). F-10 and F-15 show hysteresis from a relative pressure of 0.3 to 1. The respective surface areas are given in table 1. There is not

Figure 6. N₂ adsorption–desorption isotherms of F-10 and F-15 with the inset showing pore size distribution profiles.

Figure 7. Hysteresis profile for F-10 and F-15 samples.

Table 2. Magnetic properties of the samples.

Catalyst code	Particle size (nm)	Magnetic properties		
		M_s (emu g ⁻¹)	M_r (emu g ⁻¹)	H_c (Oe)
F-10	23	0.783	0.103	1978.22
F-15	37	15.431	3.216	271.76

Figure 8. XPS spectra of the F-15 sample.

much difference observed in the case of the surface area of the samples F-10 and F-15, but the pore size distribution profiles of F-15, differ from those of F-10. F-15 exhibits different pores of different sizes ranging from 10–20, 20–30 and 40–60 Å. The observed wide range of porosity in F-15 is due to the use of urea during the synthesis process. The large amounts of gases evolved during the calcinate stage induce a wider porosity range.

3.2 Magnetic properties

Figure 7 shows the magnetization curves and the corresponding hysteresis parameters. The respective magnetic values are given in table 2. The sample F-10, synthesized without urea, as expected, shows essentially anti-ferromagnetic behaviour or very weak ferromagnetism due to a small spin canting effect.

In fact, its room temperature saturation magnetism is very weak (~ 0.8 emu g⁻¹). On the other hand, the sample synthesized in the presence of urea showed large ferromagnetism (~ 15.4 emu g⁻¹).

As urea-mediated synthesis induces O²⁻ vacancies, it results in an incomplete coordination environment of O²⁻ ligands for Fe³⁺. It thus destroys the antiferromagnetic super-exchange interaction of Fe³⁺–O²⁻–Fe³⁺, resulting in uncompensated magnetism.

Figure 8 shows the XPS spectra of F-15. The peaks due to 2p 3/2 and 2p 1/2 were observed at binding energies of 709 and 718 eV, respectively, and spaced apart with a binding energy difference of 13 eV as observed in α -Fe₂O₃ nanostructures [17,18]. Further, satellite shake-up peaks were observed at the higher binding energy side of the above two main peaks. Thus, these peaks were observed at 718 and 731 eV which were about + 9 eV upside in energy and are due to the presence of Fe³⁺. Thus, there were no traces of Fe or Fe²⁺ or γ -Fe₂O₃ in the F-15 sample that could have contributed to its ferromagnetic property.

3.3 Catalytic activity for decomposition of H₂O₂

The catalytic activity of the samples was studied for their ability to decompose H₂O₂. The investigation was carried out by keeping the reaction mixture first in the dark (absence of sunlight) and another mixture in sunlight. The relative activities were compared at different time intervals and the results are summarized in table 3. It can be seen from figure 9 that both the samples showed similar reactivity in the dark. A slightly higher activity of F-10 may be attributed to its slightly larger surface area available for the adsorption of H₂O₂ prior to its decomposition. The hematite iron oxide known to be active for the decomposition of H₂O₂ via the Fenton like process. The Fenton reagent is a mixture of FeSO₄ + H₂O₂ which acts as an oxidizing agent. In the case of this catalysed

Table 3. Surface area and decomposition of H₂O₂ on the synthesized samples.

Catalyst code	Surface area (m ² g ⁻¹)	Pore volume (cc g ⁻¹)	Pore radius (Å)	Volume of O ₂ gas after 50 s (ml)		Enhancement in reactivity in sunlight, ΔV (ml)
				Dark	Sunlight	
F-10	44	0.185	17.033	9.3	14.3	5
F-15	43	0.090	21.550	7.8	49	41.2

Figure 9. Decomposition of H_2O_2 on F-10 and F-15 catalysts with exposure to sunlight or without exposure to sunlight (dark).

Scheme 2. Decomposition of H_2O_2 on the Fe_2O_3 catalyst in the presence of sunlight.

reaction, the surface ferric ions (Fe^{3+}) interact with H_2O_2 in acidic media by the release of Fe^{2+} and thus, generating Fenton reagent $\text{Fe}^{2+}(\text{H}_2\text{O}_2)$ *in situ*. The general decomposition reaction on the iron oxide catalyst can be written as in equation (1) in scheme 2 by taking up Fe^{3+} ions from the catalyst surface. Fe^{2+} thus generated, catalyse further decomposition of H_2O_2 through intermediate formation of HO^* and HO_2^* [19]. While the catalytic activity in the dark was similar for both the samples, the urea synthesized sample F-15 showed a large difference in reactivity when the reaction mixture was exposed to sunlight. It can be seen from table 3 that F-10 showed an enhancement in reactivity in sunlight by liberating additional volume (ΔV) of 5 ml of oxygen gas. Under the same conditions, F-15 showed additional liberation of 41 ml of oxygen. Thus, F-15 was eight times more reactive in sunlight. Other iron oxides are also being reported with ferric nitrate and urea molar ratios of 1:2 and 1:3 showing comparatively low-catalytic activity compared to F-15 [20].

Therefore, the following mechanism is proposed for the observed photo-Fenton process (scheme 2).

Earlier it is seen that both the samples showed a similar band gap (2.1 eV). Hence, the high photo-Fenton activity of F-15 could not be explained by relative band gap values. It is seen that F-15 has much larger lattice strain indicating the presence of large number of solid-state defects associated with the presence of oxygen vacancies which cause an incomplete coordination environment for Fe^{3+} . This facilitates the capture of conduction band electrons at such defect centres and thus, enhances the rates of the intermediate reactions as shown in scheme 2 and consequently enhances the decomposition of H_2O_2 . The high ferromagnetic character of F-15 can help in easy recovery and reuse of the catalyst.

4. Conclusion

- (i) Hematite or $\alpha\text{-Fe}_2\text{O}_3$ was synthesized by calcination of a Fe(III) nitrate–urea precursor in air at 400°C . The sample was designated as F-15 to signify the 1:5 molar ratio of salt:urea.
- (ii) The samples were characterized by XRD for the identification of the hematite phase and IR for the presence of the Fe–O bond and solid-state defects. A band gap of around 2.1 was observed from a UV–Vis spectroscopic technique.
- (iii) The observed TEM particle size of 37 nm was larger for sample F-15 than for the sample F-10 prepared without the use of urea.
- (iv) F-15 showed ferromagnetic behaviour with a saturation magnetism of 15.4 emu g^{-1} with a significant remanence of 3.2 emu g^{-1} .
- (v) It also showed large catalytic activity for the decomposition of H_2O_2 , due to the photo-Fenton effect, which was at least eight times larger than the F-10 sample. The F-15 catalyst being ferromagnetic, could be easily recovered from the reaction mixture.

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