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α-Fe₂O₃ nanospheres: Facile synthesis and highly efficient photo-degradation of organic dyes and surface activation by nano-Pt for enhanced methanol sensing

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Abstract: We report a simplified electrochemical route to synthesize thin films of nanosphere α -Fe₂O₃ from a suitable electrolytic solution. X- ray diffraction studies revealed the formation of pure phase of hematite (hexagonal structure) α -Fe₂O₃ films. Field emission scanning electron microscopy revealed a highly compact surface morphology with evenly distributed almost spherical grains. Raman, Electron Paramagnetic Resonance and Fourier transform infrared spectroscopic analyses confirmed the presence of α phase of Fe₂O₃ (hematite). Optical analysis revealed band gap energy of 2.15 eV; most suitable for visible light driven photocatalysis towards Indigo Carmine (IC) and Rhodamine B (Rh B) dyes, widely used in textile industry and was taken as model organic compounds. About 90% photodegradation was achieved at a rate of 0.0188 min⁻¹ for IC and 0.0133 min⁻¹ for Rh B. The synthesized films were used as the modified electrodes and their catalytic activity towards methanol oxidation was investigated. A comparison was also made with Pt modified FTO/Fe₂O₃ electrode was a better performer.

Keywords: α-Fe₂O₃ Nanospheres; Photocatalysis; Electrocatalytic activity; Electro-oxidation; Surface activation; Multifunctional material.

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1. Introduction

Iron oxide in the α phase, i.e. α -Fe₂O₃ (hematite) is an attractive semiconductor for many cutting edge applications, among which photo electrochemical and photocatalytic applications are of major importance due to its stability, abundance, and environmental compatibility, as well as suitable band gap and the position of valence band edge.¹⁻⁸ In general, hematite exhibits an n-type character, which can be due to the tendency of α -Fe₂O₃ to become oxygen deficient, irrespective of the preparation method. α-Fe₂O₃ is one of the promising candidates for photocatalytic applications due to its narrow band gap energy of about 2.0-2.2 eV which leads absorption mainly in visible region. It absorbs light up to 600 nm, collects up to 40% of the solar spectrum energy. α -Fe₂O₃ is cost effective with low toxicity, high photo/heat-stability and has suitable valence band edge position. This makes hematite a promising anode material for photochemical, photoelectrochemical and electrochemical studies like methanol electrooxidation⁹. Nanoparticles of α -Fe₂O₃ perform the photocatalytic reactions through the generation of electron-hole pairs upon visible light irradiation which leads to better charge transfer process between (LUMO)_{dyes} to (HOMO)_{catalyst}. Various techniques have been investigated for the synthesis of hematite nanocrystalline thin films viz. thermal evaporation,¹⁰ chemical vapor deposition,¹⁰ aqueous chemical growth¹⁰, spray-pyrolysis¹¹, ultrasonic spraypyrolysis¹¹, sol-gel method¹² and the plasma enhanced atomic layer deposition.¹³ Electrodeposition is a technique that is well-suited to the preparation of nanostructures.¹⁴ In fact, through proper parameter control, electrodeposited materials can from nanostructured to even epitaxial films with better properties.¹⁵ Moreover, the electrodeposition technique is now emerging as an important lowcost and low temperature method for preparing semiconducting thin films¹⁶.

In the last couple of years, several reports have appeared concerning the electrodeposition of iron oxide thin films onto foreign substrates like Fe₃O₄ (magnetite), α -FeOOH (goethite), and γ -FeOOH

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(lepidocrocite)¹⁷. Among the various oxides of iron, hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃) and wustite (Fe_{1-x}O), α -Fe₂O₃ is of special interest due to its unique catalytic properties, however, γ -Fe₂O₃ nanoparticles are excellent candidate for nanoscale magnetism¹⁸. Owing to its suitable electronic properties like flatband potential, surface current density and doping density, α -Fe₂O₃ is a very important material for electrooxidation of various toxic chemicals like methanol^{9,19}. It also serves as a good photocatalyst for aniline²⁰ and photo polymerization reaction promoter for acrylamide through radical mechanism²¹. α -Fe₂O₃ with different nanostructures can act as an efficient photocatalyst for the degradation of phenolic compounds and other dyes like methylene blue (MB)²², Rose Bengal (RB)²³ and Methyl Orange (MO)²⁴. Xu et al.²⁵ and Tang et al.²⁶ have also investigated the uv-light driven photocatalytic performance of hollow spindle²⁵ and flower like²⁶ α - Fe_2O_3 towards phenol degradation. α -Fe₂O₃ is also used for the improvement of photocatalytic efficiency of other semiconductors like TiO₂ by making a composite, owing to facts that Fe³⁺can act as a better electron scavenger than O₂ and significant matching of band structures between Fe₂O₃ and TiO_2^{27} . Hematite is also very important for the synthesis of composite heterostructures like Fe_2O_3/SnO_2^{28} , Fe_2O_3/CdS^{29} etc. for better photocatalytic performances through effective charge carrier separation.

Over the last few decades, our society has become increasingly sensitive towards the protection of the environment against the adverse effects of the industries. The effluents of dyeing, textile, pulp and paper industries contains various dye pigments and methanol which should be removed before discharging to the environment to avoid health hazards and protect the ecosystem. Due to low biodegradability of dyes, the conventional biological wastewater treatment pathways are not very efficient. To solve this problem, scientists have developed semiconductor photocatalysis. The main advantage of this technology is the environmental compatibility, as its main reagent, the

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electrons, is clean reagent. As well as, the semiconductor photocatalysis has faster degradation rate over biodegradation. In this regard, efficient, stable, low-cost and environment friendly photocatalysts must be developed. These are the motivations behind this work. In this work, the deposition of nanocrystalline thin films of α -Fe₂O₃ on fluorine-doped tin oxide (FTO) coated glass was carried out by a simple electrochemical method using the chemicals FeCl₂.4H₂O, KCl and H₂O₂. The method reported here is cheaper, simpler and less time consuming for large scale production. In electrochemical synthesis of iron oxides, an accurate control of growth potential and pH is necessary which have been taken care of in this work. The catalytic behavior of the deposited α -Fe₂O₃ films for the photo-degradation of hazardous organic dyes like Indigo Carmine (IC) and Rhodamine B (Rh B) has been explored. A comparison was also made between the Pt modified FTO/Fe₂O₃ and unmodified FTO/Fe₂O₃ electrodes towards methanol electrooxidation, and the latter was found to be better performer.

2. Experimental Procedure

2.1. Materials

All chemicals and solvents were of analytical reagent grade and used as received, without any further purification. Commercially available FTO substrates with ~ 10 ohm/sq surface resistivity were cleaned properly and used as the cathode for the deposition.

2.2. Deposition of α -Fe₂O₃ thin films

The working solution was prepared by mixing thoroughly 1 mL of 0.1(M) FeCl₂, 4H₂O and 1 mL 0.1(M) KCl in 100 mL double distilled water. KCl was taken as the supporting electrolyte for stabilizing the redox system. Next, 0.5 mL 0.02 (M) H₂O₂ was added drop wise with stirring at 500

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rpm for 15 minutes. The pH of the working solution was maintained around 2.5 by adding dilute hydrochloric acid (1:30) drop wise. The working solution was brownish yellow in color.

The electrochemical cell was constructed by immersing the FTO glass and a Zn rod (99.8% pure) in the solution, which were short-circuited externally through a copper wire. The Zn rod served as the self-decaying anode to produce Zn^{2+} ions and the FTO glass as the cathode (schematic is reported elsewhere³⁰). As soon as the two electrodes are short-circuited, the deposition starts very slowly , which was continued for around 24 hours at room temperature without stirring, to obtain almost pinhole free compact films with good adherence. After deposition, the films were washed thoroughly with double distilled water and dried in a hot air oven at 60°C for 15 minutes.

The mechanism for α -Fe₂O₃ deposition involves two reactions that take place simultaneously on the FTO cathode surface, when the electrodes are short circuited externally.

FeCl₂. 4H₂O dissolves in water at low pH (c.a. 2.5) and dissociates as:

$$FeCl_2.4H_2O \rightarrow Fe^{2+} + Cl^- + 4H_2O....(i)$$

Now, as we have used Zn rod as the sacrificial anode and it was dipped in to a low pH (c.a. 2.5) medium, metallic Zn will dissociate in the following manner:

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$
 $E^{0} = +0.76 V......(ii)$

The Zn^{2+} ions will come to the solution and the two electrons that were released on the Zn surface, will flow to the FTO cathode through the external path, which in turn, will reduce the Fe²⁺ ions present in the vicinity of the cathode as the E⁰ value for Fe²⁺/Fe⁰ is much lower (-0.41 V) than that of Zn^{2+}/Zn^{0} (-0.76 V).

In presence of H_2O_2 , the Fe^o formed on the FTO surface will undergo the following series of reactions to finally produce Fe₂O₃ as described earlier by Schrebler-Guzman *et al.* and Kelly *et al.*³¹⁻³² According to them, H_2O_2 first reacts with the dissolved electrons (Photo-Fenton reaction) in the following manner to produce the active species like OH- and OH*:

 $H_2O_2 + e^{-}(aq) \rightarrow OH^* + OH^- \dots (iv)$

 $Fe^{o} + OH^{-} \rightleftharpoons [FeOH] + e^{-} \dots (v)$

 $[FeOH] \quad \overleftarrow{\leftarrow} \quad [FeOH]^+ + e^- \dots \dots \dots \dots \dots (vi)$

 $[FeOH]^+ + OH^- \longrightarrow Fe(OH)_2$ (vii)

 $Fe(OH)_2 + OH^- \rightarrow [FeOOH] + H_2O + e^-$ (viii)

$$2[\text{FeOOH}] \stackrel{\frown}{\leftarrow} \text{Fe}_2\text{O}_3.\text{H}_2\text{O}$$
 (ix)

The Cl⁻ ions released by Fe^{2+} ions during reduction, captures the free Zn^{2+} ions present in the solution, and thus restricting their deposition along with Fe and enhancing the purity of the deposited films.

To avoid 'poisoning' of the catalyst, i.e. the deposited Fe_2O_3 films in this case, Pt nanoparticles were deposited on the film surface by dipping the film in a beaker containing 1% H₂PtCl₆.H₂O solution for 2 minutes. After taking out, the films were washed thoroughly with distilled water and dried at 200°C.

2.3. Characterization techniques

The crystalline structure and phase of the deposited films were determined by X-ray diffraction (XRD) technique using Bruker D8 advance X-ray diffractometer with Bragg-Brentano goniometer

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geometry and Cu-K_{α} X-radiation source (λ =1.5418 Å). Morphological analyses of the films were carried out by both field emissions scanning electron microscopy (FESEM) (JEOL, JSM-6700F) and atomic force microscopy (AFM) (NT-MDT Solver Next). AFM measurements were done in semicontact mode, and a silicon probe (length = 95 μ m, width = 30 μ m, thickness = 2 μ m, resonance frequency = 240 kHz, force constant = 18 N/m^2) was used for the scanning purpose. Scans were made with a scanning speed of 0.5 Hz. Electron Paramagnetic Resonance (EPR) spectra were recorded using an EPR spectrometer (JEOL-JES FA200) with X-Band frequency: 8.75-9.65 GHz, Sensitivity: 7x10⁹ spins/0.1 mT, Resolution: 2.35 µT. UV-VIS spectroscopic measurements were carried out using a Perkin-Elmer Lambda 25 UV-Vis spectrophotometer to evaluate the optical properties of the deposited films. Infrared spectrum was recorded using a Perkin-Elmer Spectrum Two with ATR Mode. Raman (NXR FT-RAMAN MODULE, Thermo electron Corporation, USA, operating with 1064 nm Nd: YVO4 excitation laser source at 0.1W power) analyses was also carried out to establish the phase of the deposited material. Perkin Elmer, LS-55 fluorescence spectrophotometer was used to study the 'OH radical trapping phenomenon. The electrochemical measurements were carried out using a CHI 620D, USA made electrochemical analyzer.

2.4. Photocatalytic measurement

Photocatalytic behavior of the deposited thin films was measured by noting the gradual decrease of the characteristic absorption peak of the test dye in presence of light. Standard aqueous solution of Indigo Carmine (IC) (100 ppm, pH c.a. 6) and Rhodamine B (RhB) (100 ppm, pH c.a. 5.5) were prepared and taken after attaining the equilibrium in dark for 30 minutes, to study the photocatalytic performance of the films. Two prototype films, each with 2 cm \times 3 cm area, were placed at the bottom of two 100 ml beakers containing 50 ml of 100 ppm IC and RhB dye solutions, respectively. The same technique was also applied for the Pt activated films. As Fe₂O₃ is a semiconductor with

main electronic transitions in the visible region, a 200W tungsten filament lamp (Philips) was used as the source of visible light, which was placed 2.0 cm above the beaker so that it can produce 1 Sun intensity. The entire experimental set up was kept in a water bath at 30°C with constant flow of air to the beaker to eliminate the effect of any probable heating that might be caused due to the light source. At certain time intervals, specific amount of the solution were withdrawn and the changes in concentration of the dye were observed using UV-Vis spectrophotometer by noting the lowering in intensity of the characteristics absorption peak of the respective dye.

2.5. Electrocatalytic activity measurement

The electrochemical oxidation and chronoamperometric detection of CH₃OH by α -Fe₂O₃ and Pt modified α -Fe₂O₃ thin films (FTO/ α -Fe₂O₃ and FTO/Pt- α -Fe₂O₃) with 1.0 cm² active areas each, were monitored with the help of an electrochemical analyzer using conventional three electrode system with Ag/AgCl as reference electrode. Cyclic voltamograms (CV) were recorded in a cell containing 10 mL of 0.1 M phosphate buffer solution (PBS) (pH c.a. 7.4, 32°C) with a scan rate of 0.1 V s⁻¹. For chronoamperometric measurements, similar cell setup was used with an applied potential of -1.0 V (vs. Ag/AgCl).

3. Results and discussions

3.2. Structural and morphological properties of α -Fe₂O₃ and Pt activated α -Fe₂O₃ thin films

The composition and purity of the deposited films were examined by X-ray diffraction (XRD) technique and the resulting diffractrograms are displayed in Figure 1. The diffraction pattern of the as deposited film (Figure 1a) showed characteristic peaks from (104), (202), (116), (214), (300), (119) and (223) planes which can be indexed to the pure hematite phase (hexagonal structure), i.e. α -Fe₂O₃ (JCPDS ID: 33-0664). The sharpness of the peak indicates the crystallinity of the deposited

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material. The diffraction peaks marked "*" correspond to the SnO₂ of the bottom FTO coated glass substrate (JCPDS ID 21-1250). However, two diffraction peaks of α -Fe₂O₃ viz. (104) and (116) were found to overlap with the diffractions from SnO₂. The crystallite size corresponding to the highest intense diffraction was estimated using the Debye-Scherrer equation³²: D = 0.9 λ/β Cos θ , where D is the crystallite size, λ is the wavelength of the Cu-K_{α} radiation used (λ = 1.5418 Å), β is the experimentally observed diffraction peak width at half maximum (FWHM), θ is the Bragg's angle; the average crystallite size was estimated to be around 10 nm. The dislocation density (δ), which is the length of dislocation lines per unit volume, was also estimated using the equation³³: δ = $1/D^2$ and found to be significantly low (0.01/nm²) indicating lesser amount of crystal defects and good crystalline nature of the deposited films. The high value (3.83×10⁻²) of microstrain (ϵ) as obtained using the relation ϵ = (β cos θ)/4, again supports the formation of crystallites with low dimension.

After activating the surface of the deposited Fe₂O₃ films with Pt, the samples were also subjected to the XRD analysis and the result is given as Figure 1b, which reveals the presence of diffractions from the (111), (200) and (220) planes of metallic Pt (JCPDS ID: 04-0802) corresponding to the 2 θ values 39.76, 46.24 and 67.45 degrees, respectively. The deposition of metallic Pt leads to the suppression of some peaks corresponding to α -Fe₂O₃. The standard diffraction ID indicates the presence of quasi spherical metallic platinum on the surface of the deposited α -Fe₂O₃ film. The small intensity of the diffraction peaks indicates the presence of metallic platinum in small amount.

The 2D and 3D surface morphology and the average particle size of the as deposited α -Fe₂O₃ films were investigated using field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM), which are shown in Figure 2. One can see from the FESEM image (Figure 2a) that the FTO surface is fully covered with uniformly distributed spherical grains of α -Fe₂O₃ with diameter in the range 40 to 60 nm. The grains are distinct and the grain boundaries are prominent. To

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study the nature of an individual grain, high magnification image (Figure 2a inset) was captured and it has been found that, such a grain is composed of crystallites with average 15 nm diameter. This value of crystallite diameter agrees well with what we have obtained from the XRD analysis. However, the average grain size as obtained from low magnification FESEM is somewhat larger than that was calculated from XRD analysis, which is attributed to the formation of larger grains from smaller crystallites, essential for spontaneous lowering of Gibb's free energy in the system to gain stability. The total free energy of a system containing nanoparticles (NPs) is given by:

$$G_{\text{total}} = \mu_{\text{NP}\times} N_{\text{NP}} + \gamma \times S$$

Where, μ_{NP} is the chemical potential of the nanoparticles and N_{NP} is the total number of nanoparticles. γ is the interfacial tension (or the interfacial energy per unit area) and S is the surface area. Thus $\gamma \times S$ denotes the total surface energy of the system. As we know, NPs have higher surface-to-volume ratio, making the total surface energy of the system significantly high. As every system has a tendency to lower down the free energy spontaneously, this $\gamma \times S$ part of free energy for a system consisting of nanoparticles also has a tendency to get lowered down by means of forming larger grains (which reduces the value of S) from smaller crystallites by agglomeration. For this reason, from FESEM image analysis we see the grains to have somewhat larger size then the crystals.

AFM studies were also carried out to find the salient topographical and surface features of the as deposited films and the typical 3D AFM image is shown in Figure 2b. From this image also, we can see the average grain size to be about 50 nm, which is in good agreement with the value obtained from the FESEM analysis. AFM revealed a significantly undulated topography along with the presence of numerous finer crystallites in the grains of the as deposited α -Fe₂O₃ films.

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On the other hand, the FESEM image of the Pt activated α -Fe₂O₃ film (Figure 2c) clearly reveals the presence of numerous almost spherical Pt nanoparticles with an average diameter of 50 nm. This is in good agreement with the x-ray diffraction from quasi-spherical Pt nanoparticles (JCPDS ID: 04-0802), as explained before. The spikes in the 3D AFM image of the Pt activated α -Fe₂O₃ sample (Figure 2d) also indicate the growth of distinct nanoparticles on the surface of the deposited semiconductor. Various parameters as obtained from XRD, FESEM and AFM analyses, relating to the structure of the deposited α -Fe₂O₃ thin films before and after Pt activation are summarized in Table 1. It has been observed from the AFM measurements and can be seen from Table 1 that both Root Mean Square (RMS) and average (Ra) roughness increased significantly after Pt activation. The increase in surface roughness indicates that, Pt activated α -Fe₂O₃ thin films may serve as a better candidate towards photochemical and electrochemical activities.

3.3. Electron paramagnetic resonance studies (EPR)

The room temperature electron paramagnetic resonance (EPR) spectrum of α -Fe₂O₃ is shown in Figure 3 which exhibits an intense resonance signal at g ≈ 2.30 within 300 to 325 mT. This confirms the oxidation state of +3 in the deposited material as the Fe³⁺ ions belong to d⁵ configuration with ⁶S as ground state, and there is no spin-orbit coupling. The theoretical g value for the free Fe³⁺ ion is 2.0023. Our experimentally observed value is in good agreement with the theoretical value. The slightly high experimentally obtained g value might be attributed to the formation of clusters of Fe³⁺ ions which causes exchange interactions between the coupled ions³⁴. Previous report³⁴ indicates, if the Fe₂O₃ crystallites stay within few nanometers of domain, as the case here (Section 3.2), a broad spectrum of g (≈ 2.3) may be observed. Therefore, the observed resonance signal at g ≈ 2.3 in this study justifies that the oxidation state of Fe in the deposited iron oxide is +3, which is in good agreement with the XRD analysis confirming the presence of α -Fe₂O₃. The broad nature and slightly

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higher value of g also indicate the formation of small clusters of Fe₂O₃ with nano-dimension, which in turn supports the findings from FESEM and AFM studies.

3.4. Fourier transform infrared (FTIR) and Raman spectroscopy

For further detection of phase and purity of the deposited iron oxide films, FTIR analysis was carried out within the range 500-4000 cm⁻¹ (Figure 4). The absorption band at ~3340 cm⁻¹ is assigned to the presence of adsorbed water moiety.³⁵ The band around ~1626 cm⁻¹ might be attributed to the O-H bending vibrations of the adsorbed H₂O molecules (moisture) and the band around 1100 cm⁻¹ is attributed to the Fe-OH vibrational mode of iron oxide in presence of moisture. The bands ~540 and ~462 cm⁻¹ correspond to the characteristic metal-oxygen (Fe-O) vibrational modes of spinel iron oxide. The small intensity of the Fe-O bands agrees well with the previous report.³⁶ The observed shift is gradual and depends on the particle size. The main band has been attributed to the Fe-O or Fe-O-Fe bindings of hematite. This confirms the formation of Fe₂O₃ films with α phase.

Raman spectra of various phases of iron oxides (viz. α -Fe₂O₃, Fe₃O₄ and γ -Fe₂O₃) are distinctly different from each other and this technique can be used effectively to determine the phase of deposited iron oxide.³⁷ Iron oxide belongs to D₃d⁶ space group and typically seven phonon lines are expected in the Raman spectrum, viz. two A_{1g} and five E_g phonon modes.³⁸ The spectrum is normally dominated by the overtones of the longitudinal optical (LO) phonons. First of all, a background scan within 200-700 cm⁻¹ was performed, taking a blank FTO glass and then for the iron oxide sample deposited on FTO glass. The spectrum (Figure 5) reveals the presence of five strong resonant Raman peaks at 220, 285, 408, 491 and 608 cm⁻¹. These values are typical for α -Fe₂O₃ and are in well agreement with the previous reports. The Raman lines are broader and are found to be

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shifted to low wavenumbers with respect to the values obtained for commercial hematite (α -Fe₂O₃). The broader line width and the shifting of wavenumbers of the Raman peaks are due to phonon confinement effect in the nanocrystals, as was described previously. Bersani *et al.*³⁹ proved that the peak that appears at 660 cm⁻¹ is typical for the hematite iron (α -Fe₂O₃) and seems to be related to the disorder effects and/or to the presence of nanocrystals. Xu *et al.*⁴⁰ recorded Raman spectrum of α -Fe₂O₃ nano leaves synthesized by oxygenating pure iron and observed A_g at 225 and 498 cm⁻¹ and E_g at 252, 293, 411, 612 cm⁻¹. So, in our case, Raman analysis confirms the presence of α -Fe₂O₃ in the deposited films.

3.5. UV-Vis analysis

As displayed in Figure 6, the absorption spectrum showed a moderately sharp onset in absorbance around 580 nm which represents the typical band to band transition for α -Fe₂O₃. The band gap energy for the α -Fe₂O₃ thin film was calculated using the Tauc's relation: $[(\alpha hv)^{1/n} = A(hv-E_g)]$, where A is a constant related to the effective masses of charge carriers, h is the Planck constant, E_g is the band gap energy, *hv* is the incident photon energy and 1/n is the exponent that depends on the nature of the optical transition (n = 0.5 and 2 for direct and indirect transition, respectively). The Tauc's plot (Figure 6 inset) indicates the direct band gap energy of 2.15 eV for the deposited α -Fe₂O₃ films. The higher band gap energy compared to that of the bulk material (~1.8 eV) is due to the presence of smaller particles (~50 nm) in our case. The band structure of semiconductors changes from continuous to discrete pattern with the reduction in crystallite size and the lowest transition energy (E₁) is blue shifted with respect to the original band gap energy (E_g). The quantum confined or blue shifted energy (ΔE) can be expressed by the standard equation as:

$$\Delta E = E_{l} - E_{g} = (\hbar^{2} \pi^{2} / 2 \mu R^{2}) - (1.8 e^{2} / 4 \pi \epsilon R)$$

where, E_l is the lowest transition level, E_g is the original band gap energy, \hbar is the reduced Planck's constant, R is the radius of the nanocrystal, μ is the effective mass of electron, ε is the permittivity of the material and e is the electronic charge. Since (ΔE) is inversely proportional to R, the reduction of crystallite size leads to an increase in the band gap energy, what we have also observed in this case.

3.6. Photochemical activities toward toxic organic dyes

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The photocatalytic activity of α -Fe₂O₃ thin films was evaluated by observing the photodegradation of Indigo Carmine (IC) and Rhodamine B (RhB) dyes under simulated irradiation as mentioned in Section 2.4. The photocatalytic degradations were evaluated by measuring the successive lowering of characteristic absorbance peaks for IC and RhB at different time intervals in presence of light and the catalyst. Significant decrease in the absorption intensity with increasing irradiation time was observed, which are shown in Figure 7a and 8a respectively for the IC and RhB. Two sets of blank experiments by taking the dye solution in absence of α -Fe₂O₃ films but presence of light and dye solution in presence of α -Fe₂O₃ but absence of light were also carried out for each dye to confirm the role of both catalyst and light in the degradation process.

Appearance of no new absorption peak during the whole process indicates the complete photolysis in presence of the proposed catalyst. No degradation of these dyes was observed in dark and very slow degradations were observed in absence of the catalyst, i.e. α -Fe₂O₃ thin films. About 90% degradation of the dye IC was observed after 150 minutes and about 95% degradation of RhB was achieved after 225 minutes, which is evident from Figure 7b and 8b. Figure 7c and 8c show the extent of photocatalytic degradation of IC and RhB respectively, by the α -Fe₂O₃ thin films in the form of relative concentration (C_t/C₀) change with irradiation time under three different conditions viz. (a) in absence of both light and catalyst. Here C₀ is the initial concentration of the dye and C_t is the

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concentration of the dye at time 't'. To determine the nature of the degradation kinetics, Ln (C_0/C_t) was plotted against irradiation time (Figure 7d and 8d) and the negative slopes in each case indicate pseudo-first order kinetics. The rate constant 'k' for IC was found to be about 0.0188 min⁻¹ and the same for RhB was about 0.0133 min⁻¹. These two values are notably higher than many other previous reports (Table 2) on the degradation of IC and RhB. Significant enhancement of degradation rate in presence of both catalyst and light, as seen from the Figures 7c and 8c, indicate that α -Fe₂O₃ thin films can act as an excellent photocatalyst towards the degradation of Indigo Carmine and Rhodamine B dyes under visible light irradiation.

Figure 9 depicts the plausible schematic band structure and charge transfer process for the generation of active species leading to the photodegradation of organic dye molecules on the surface of α -Fe₂O₃ nanoparticles. Firstly, electron-hole pairs are generated in α -Fe₂O₃ nanoparticles on light irradiation^{49,50} and the electrons occupy the conduction band (CB) and holes the valence band (VB). The photogenerated electrons (e⁻) thus produced in the conduction band of α -Fe₂O₃ is scavenged by O₂ to produce O₂^{• –} anion radical which on protonation yields HOO[•] in presence of water. On the other hand, the holes (h⁺) which are produced in the valence band of α -Fe₂O₃ reacts with H₂O or ⁻OH ions coming from H₂O to produce highly active species [•]OH radical. The hydroxyl radicals thus produced are responsible for the complete mineralization of dye thereby producing products like CO₂ and H₂O. The degradation processes normally follow both oxidative (using holes) and reductive (using heles) pathways which may be summarized as follows:⁵¹⁻⁵³

$$\alpha - Fe_2O_3 + h\nu \rightarrow e^-_{CB} + h^+_{VB}$$
$$e^-_{CB} + O_2 \rightarrow O_2^{\bullet -}$$
$$O_2^{\bullet -} + H^+ \rightarrow HOO^{\bullet}$$
$$HOO^{\bullet} \rightarrow H_2O_2 + O_2$$

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 $H_2O_2 + e^- \rightarrow {}^{\bullet}OH + {}^{-}OH$ $h^+_{VB} + OH^-/H_2O \rightarrow {}^{\bullet}OH$ ${}^{\bullet}OH + dye-intermediates \rightarrow CO_2 + H_2O$

3.6.1. Evaluation of active oxidative species:

In the studies photocatalysis, there are two common ways for the degradation of organic pollutants, through direct oxidation reaction by the photogenerated holes and the other one is through oxidative radicals. It can also be concluded that the activity of a particular catalyst will be considered as higher if it generates reactive species like $O_2^{\bullet-}$ and $\bullet OH$ at higher rate^{54,55}. Here, the hydroxyl radicals perform the key role for the decomposition reactions mentioned above. So, it is necessary to investigate the presence of hydroxyl radicals in the medium produced by the catalyst, to support the above mechanism. We have used fuorescence probe technique to establish the formation of [•]OH radicals by the deposited α -Fe₂O₃ films, where terephthalic acid (TPA) was taken as the fuorescence probe. TPA was illuminated in the same light source used for photocatalysis in slightly alkaline medium (pH \approx 8). The fuorescence intensity was measured by a fluorescence spectrophotometer and the emission spectrum upon excitation at 320 nm was measured every 10 min. interval during irradiation (Figure 10). TPA is directly attacked by the 'OH radicals to form 2-hydroxy-terephthalic acid (TPAOH), giving the fluorescence signal at ~425 nm. The fluorescent intensity is directly related to the number of hydroxyl radicals formed by the photocatalyst, i.e. α -Fe₂O₃ in this case. This means, higher the rate of hydroxyl radical formation, more is the yield of TPAOH and more intense will be the fluorescence peak. Intense fluorescence signal on the other hand indicates enrichment in degradation efficiency.

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3.6.2. Reactive Oxygen Species (ROS) scavenging studies:

In order to get an insight of the mechanism of photocatalytic dye degradation by α -Fe₂O₃ thin films, specific ROS scavengers e.g., tertiary butyl alcohol (TBA) as hydroxyl radical scavenger was added in the reaction medium. As the ROS generation study was based on scavenging action, it is necessary to confirm that the evidence for the photocatalytic mechanism, so, TBA has been chosen for the detection and quantification of °OH radicals. The effect of different concentrations of TBA (0.01M, 0.1M and 1M) on dye degradation was observed and the results showed quenching of degradation efficiency of both IC and Rh B with increase in the concentration of the scavenger (Figure 11). Therefore, it can be concluded that the drastic inhibition of dye degradation is due to the scavenging of hydroxyl species (°OH) which were produced in the reaction medium by the α -Fe₂O₃ films. The consequences of mimicking hydroxyl radical generation towards dye degradation with radical scavenger in various concentrations affect the rate of the reactions. These are the evidences behind proposed photocatalytic mechanism.

3.7. Comparative study on the methanol oxidation by as deposited and Pt-activated α -Fe₂O₃ thin films:

Electrocatalytic activities of bare FTO/ α -Fe₂O₃ and Pt-activated α -Fe₂O₃/FTO electrodes (will be designated as FTO/ α -Fe₂O₃-Pt hereafter) towards methanol were also studied. These measurements were carried out using conventional three electrode systems where a platinum wire acted as the counter and an Ag/AgCl electrode was acted as the reference electrode. The FTO/ α -Fe₂O₃ and FTO/Pt- α -Fe₂O₃ electrodes were taken as the working electrodes, for each case. The reaction bath was prepared by taking 10 mL 0.1 M phosphate buffer solution (PBS, pH= 7.4) and 10 mL of 1 M CH₃OH in a 25 mL beaker, in which the electrodes were dipped and the solution was degassed by

purging pure N₂ for 15 mins. Figures 12a, 12b and 12c represent the cyclic voltammograms (CV) of blank FTO, FTO/ α -Fe₂O₃ and FTO/ α -Fe₂O₃-Pt electrodes in this working solution. The characteristics CV curve for the FTO-PBS system shows maximum current in nano-ampere range (Figure 12a), whereas, when the FTO electrode was modified with α -Fe₂O₃, it was found to show moderate enhancement in current to micro-ampere (Figure 12b). Notable increase in peak current was observed (Figure 12c) when the FTO/ α -Fe₂O₃ electrode was further modified with nano-Pt to produce FTO/ α -Fe₂O₃ electrode towards methanol is highest among the three. The less reactivity of FTO/Pt– α -Fe₂O₃ electrode towards methanol might be attributed to the restricted movement of electrons from the surface to the bulk and also due to the poisoning of the electrode in presence of the oxidized byproducts.

Figure 12d represents the cyclic voltammograms of FTO/ α -Fe₂O₃-Pt in the same working solution with gradual addition of 10, 30, 50, 100, 200, 300, 400, 500, 1000, 1500 and 2000 micromolar methanol solutions respectively. Steady increase in current occurs with increasing methanol concentration which indicates stability of the FTO/ α -Fe₂O₃-Pt electrode even with gradual addition of methanol. In this process, the anodic current (i_{pc}) increases sharply due to the fast electrooxidation of methanol on the electrode surface and reaches the anodic current height (i_{pa}) at the peak potential around -1.0 V (Vs. Ag/AgCl). The electro-oxidation of methanol was significantly fast within the potential range -0.85 to -1.0 V (Vs. Ag/AgCl). The CV curves also indicate the quasireversibility of the electro-oxidation process using FTO/ α -Fe₂O₃-Pt electrodes with progressive increase in analyte concentration where, the anodic peak current (i_{pa}) increases with concomitant increase in cathodic peak current (i_{pc}) to achieve the quasi-reversibility. Thus, the Pt nanostructures

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on the α -Fe₂O₃ serve as the foreign domains for modifying the physicochemical properties and consequently enhance the methanol electro-oxidation reactions.

3.7.1. Explanation for enhanced electro-oxidation by Pt-activation:

The activity of FTO/ α -Fe₂O₃ electrode may be enhanced by modifying the electrode surface with noble metal nanoparticles like Pt, which helps in the chemisorption of oxidized byproducts like carbon monoxide (CO) on the metal surface by the following reactions^{9,19,56}, thus minimizing catalyst (α -Fe₂O₃) poisoning.

$$Pt + CH_3OH \rightarrow Pt-CO_{ads} + 4H^+ + 4e^-$$

$$\alpha$$
-Fe₂O₃ + H₂O $\rightarrow \alpha$ -Fe₂O₃-OH + H⁺ + e⁻

Coupling Pt with α -Fe₂O₃ increases the rate of methanol oxidation by decreasing the cathodic peak current and increasing the anodic peak current. Continuous removal of adsorbed CO from the Pt active sites also favors the oxidation. During the electrochemical process, reactions between the chemisorbed CO and OH⁻ take place to produce CO₂, which is removed from the electrode surface according to the following scheme and the Pt active sites roll back to their initial positions:

$$Pt-CO + \alpha - Fe_2O_3 - OH \rightarrow Pt + \alpha - Fe_2O_3 + CO_2 + H^+ + e^-$$

From AFM analyses (Section 3.2), it has been observed that the activation of α -Fe₂O₃ film surface by Pt nanoparticles increases both RMS and average roughness significantly. Enhanced surface roughness in turn helps in better adsorption of the analyte molecules on the electrode surface, leading to better electrochemical performances.

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On the other hand, the decoration of α -Fe₂O₃ surface by noble metal, in this case Pt nanoparticles, can enhance the electro-oxidation performance due to the difference in Fermi levels (E_f) of α -Fe₂O₃ and the metal nanoparticles, where the energy difference at the semiconductor/metal interface drives the electrons from the CB of the α -Fe₂O₃ into the metal nanoparticles (Figure 13). In other words, the metal acts as an electron trap, promoting interfacial charge transfer and therefore minimizing recombination of the e⁻/h⁺ pairs, as shown in Figure 13. The effective band alignment between the semiconductor (Fe₂O₃) and metal (Pt) in presence of the redox system helps in better electrocatalytic activity towards methanol oxidation.

4. Conclusion

Polycrystalline α -Fe₂O₃ thin films with hematite (hexagonal) phase were deposited on FTO coated glass substrates by a modified electrochemical technique. The morphology of the deposited films was highly dense with a regular distribution of the spherical nanoparticles. The material showed direct band gap energy of about 2.2 eV. Such films were found to degrade efficiently to toxic dyes, viz. Indigo Carmine and Rhodamine B in presence of visible light. The degradation followed pseudo first order kinetics and the measured rate coefficient has been found to be 0.0188 min⁻¹ for Indigo Carmine and 0.0133 min⁻¹ for Rhodamine B respectively. After activating the surface of the FTO/ α -Fe₂O₃ electrodes with Pt nanoparticles, significant enhancement in methanol oxidation has been observed. This indicates, the deposited thin films can act as a good photocatalyst for the degradation of Indigo Carmine and Rhodamine B, as well as it is a good candidate for the methanol detection and electro-oxidation.

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Figure Captions:

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Figure 1: X-ray diffraction patterns of (a) as deposited α -Fe₂O₃ thin film and (b) Pt-activated α -Fe₂O₃ thin film.

Figure 2: Microstructural analyses. (a) FESEM and (b) AFM images of as deposited α -Fe₂O₃ thin films. (c) FESEM and (d) AFM images of Pt-activated α -Fe₂O₃ thin films.

Figure 3: EPR analyses. Plots for (a) Lande g-factor vs. intensity and (b) magnetic field strength vs. intensity.

Figure 4: FTIR spectrum of as deposited α -Fe₂O₃ thin film.

Figure 5: Raman Spectrum of as deposited α -Fe₂O₃ thin film.

Figure 6: Absorption spectrum of as deposited α -Fe₂O₃ thin film (inset: Tauc's plot for band gap determination).

Figure 7: For Indigo Carmine (a) Spectrophotometric degradation curves in presence of light and catalyst (b) degradation efficacy with respect to time (c) relative change in concentration with time and (d) rate kinetics curves.

Figure 8: For Rhodamine B (a) Spectrophotometric degradation curves in presence of light and catalyst (b) degradation efficacy with respect to time (c) relative change in concentration with time and (d) rate kinetics curves.

Figure 9: Schematic of active species formation by the absorption of light in α -Fe₂O₃ nanoparticles.

Figure 10: Fluorescence spectrum upon excitation at 320 nm showing [•]OH radical trapping in 2×10^{-5} M alkaline solution of terephthalic acid.

Figure 11: Relative concentration profile of photocatalytic degradation of (a) IC and (b) Rh B as a function of irradiation time in presence of α -Fe₂O₃ thin films and different concentration of the scavenger.

Figure 12: Cyclic Voltammograms in 10 mL 0.1 M PBS and 10 mL 1.0 M CH₃OH for (a) blank FTO (b) FTO/α -Fe₂O₃ (c) FTO/α -Fe₂O₃-Pt electrodes and (d) Cyclic Voltammograms of FTO/α -Fe₂O₃-Pt electrode with successive addition of CH₃OH with different concentrations.

Figure 13: Schematic for energy level alignment and electron trapping by Pt nanoparticles towards enhanced methanol electro-oxidation.

Table Caption:

 Table 1: Comparative discussion on the parameters obtained from XRD, FESEM and AFM analyses.

Table 2: Comparison of photocatalytic performances of different systems towards RhB and IC.**Table 3:** Comparison of methanol electrooxidation properties.

Name of the sample	Crystallite size (nm) calculated from XRD	Grain size (nm) obtained from FESEM	Grain size (nm) obtained from AFM	Root mean square (RMS) roughness (nm) obtained from AFM	Average (Ra) roughness (nm) obtained from AFM
α-Fe ₂ O ₃ thin film	10	40 - 60	50	8.055	6.208
Pt activated α- Fe ₂ O ₃ thin film	20 for Pt	50 for Pt	70 for Pt	14.648	9.148

Table 1:

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Table 2:

Sl. No.	Type of Catalysts	Dyes	Degradation	Degradation	References
			time (min)	Rate (min ⁻¹)	
1	Titania-Silica Nanosol	RhB	240	0.01719	41
	SiO ₂ @TiO ₂ (590 nm)		720	0.00348	
	SiO ₂ @TiO ₂ (470 nm)		480	0.00465	
	SiO ₂ @TiO ₂ (220 nm)		480	0.00473	
2	Peptide I Xerogel	RhB	1440	Not Mentioned	42
3	50 At% Bi ₂ WO ₆ /BiOBr	RhB	150	Not Mentioned	43
4	LaFeO ₃	RhB	180	0.01237	44
5	Bi ₂ WO ₆	RhB			45
	$1 \times 10^{-4} \text{ ML}^{-1}$		60	0.0146	
	5×10 ⁻⁵ ML ⁻¹		60	0.0218	
	$1 \times 10^{-5} \text{ ML}^{-1}$		60	0.0517	
	5×10 ⁻⁶ ML ⁻¹		60	0.0592	
	1×10 ⁻⁶ ML ⁻¹		60	0.0714	
6	TiO ₂ - Zeolite (TZ)	RhB	360	0.0155	46
	Composite				
7	Nb_2O_5	IC	90	Not Mentioned	47
8	Ti/TiO ₂	IC	90	0.33	48
9	α -Fe ₂ O ₃	IC	150	0.0188	This Work
10		D1-D	225	0.0122	This West-
10	α -Fe ₂ O ₃	KhB	225	0.0133	I his work

Table	3:	
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Sl. No.	Composition of the electrode material	Sensitivity	References
1	Pt-CeO ₂	0.45 mA/cm^2	57
	10% Pt/TiO ₂ -NFs	0.110 mA/cm ²	
	16% Pt/TiO ₂ -NFs	0.161 mA/cm ²	
2	21% Pt/TiO ₂ -NFs	0.336 mA/cm^2	58
	27% Pt/TiO2-NFs	0.277 mA/cm^2	
	Pt/C	0.259 mA/cm^2	
3	Pt-CePO ₄	0.1 mA/cm^2	59
5	Pt-Fe ₂ O ₃	0.748 mA/cm ²	This Work





Figure 2



Figure 3







Figure 5



Figure 6



Figure 7



Figure 8



Figure 9



Figure 10







Figure 12



Figure 13







Polycrystalline α -Fe₂O₃ thin films with hematite (hexagonal) phase were deposited on FTO coated glass substrates by a modified electrochemical technique. Such films were found to efficiently degrade toxic dyes, viz. Indigo Carmine and Rhodamine B in presence of visible light. The degradation followed pseudo first order kinetics and the measured rate coefficient has been found to be 0.0188 min⁻¹ for Indigo Carmine and 0.0133 min⁻¹ for Rhodamine B. After activating the surface of the FTO/ α -Fe₂O₃ electrodes with Pt nanoparticles, significant enhancement in methanol oxidation has been observed. This indicates that the deposited films can act as a good photocatalyst for the degradation of Indigo Carmine and Rhodamine B, as well as it could be a good candidate for the methanol detection and electro-oxidation.