

# Photoelectrocatalytic activity of ferric oxide nanocatalyst: A synergistic effect of thickness

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## Abstract

The  $\text{Fe}_2\text{O}_3$  thin films have been deposited using ferric trichloride precursor at an optimized substrate temperature and concentration by simple chemical spray pyrolysis technique. Effect of quantity of the spraying solution on physicochemical properties of  $\text{Fe}_2\text{O}_3$  thin films has been studied. Photoelectrochemical technique was used to optimize the quantity of a spraying solution. The PEC study shows that,  $\text{Fe}_2\text{O}_3$  films are photoactive with relatively higher values of  $I_{\text{sc}}=34.2 \mu\text{A}$  and  $V_{\text{oc}}=190 \text{ mV}$  respectively at 50 ml quantity (thickness  $\sim 239 \text{ nm}$ ). Effects of thickness on crystalline structure, morphology and optical properties have been studied. X-ray diffraction study confirms that the films are polycrystalline with rhombohedral crystal structure. The SEM and AFM micrographs depicts that the films are compact and needle shaped grains with grain size  $\sim 160\text{--}250 \text{ nm}$ . The direct band gap energy of  $\text{Fe}_2\text{O}_3$  thin films is found to be in the range of 2.16–2.47 eV. Four characteristic luminescence peaks having near band-edge, violet, blue and green emission are observed in the photoluminescence spectra. Photocatalytic degradation of benzoic acid by using  $\text{Fe}_2\text{O}_3$  photoelectrode under visible light illumination has been investigated. The amount of mineralization is confirmed by COD and TOC analysis.

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**Keywords:**  $\text{Fe}_2\text{O}_3$ ; Thickness; Photocatalysis; COD; TOC

## 1. Introduction

Among the variety of metal oxides, the  $\alpha\text{-Fe}_2\text{O}_3$ , with its wide band gap energy, chemical stability, widespread availability and high absorbance (about 40% of the visible solar spectra) is considered as a potential candidate in photocatalysis [1]. In the group of transition elements, the abundance of iron is tenth in the universe and fourth on the earth. The existence of  $\text{Fe}_2\text{O}_3$  with its four polymorphs ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\epsilon$ ) are well-known [2–3].  $\alpha\text{-Fe}_2\text{O}_3$  has attracted much attention for its applications to water purification. In the last two decades photocatalytic degradation of toxic organic compounds in the presence of semiconductor photoelectrode has been studied extensively. The photoelectrocatalysis could be used for the treating hazardous

and toxic chemical wastes into harmless end-products at ambient temperature. In the photoelectrocatalysis it has been aimed to decolorize and degrade the polluted water by using spray deposited  $\alpha\text{-Fe}_2\text{O}_3$  thin films. Qurashi et al. synthesized  $\alpha\text{-Fe}_2\text{O}_3$  nano-ellipsoids and used for decomposition of methylene blue. It was found that the methylene blue was totally decomposed in 220 min [4]. Maji et al. synthesized the  $\alpha\text{-Fe}_2\text{O}_3$  nano-particles by a simple thermal decomposition technique and photo-catalytic activity of these nano-particles were reported by the complete decomposition of Rose Bengal dye under light irradiation using a 200 W tungsten lamp [5]. Cha et al. prepared  $\alpha\text{-Fe}_2\text{O}_3$  nano-rod thin film by metal organic chemical vapor deposition and photo-catalytic activity of these prepared nanorod films was confirmed through the photo-degradation of Rhodamine B containing nitrogen donor groups under UV irradiation [6]. Kawahara et al. studied photocatalytic decomposition of 2-naphthol using anodic-biased  $\alpha\text{-Fe}_2\text{O}_3$  film under

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visible light and found that  $\alpha\text{-Fe}_2\text{O}_3$  film shows high photocatalytic activity than that of  $\text{TiO}_2$ , for the decomposition of 2-NAP [7]. In our earlier work [8] we have deposited  $\alpha\text{-Fe}_2\text{O}_3$  thin films at various substrate temperatures by the spray pyrolysis method and it was found that photoelectrochemical oxidation of Rhodamine B achieved up to 98% decolorization in 160 min under solar light illumination.

To deposit  $\text{Fe}_2\text{O}_3$  thin films diverse methods have been attempted, including sol–gel [9], atomic layer deposition [10], hydrothermal [11], spray pyrolysis [12], chemical vapor deposition [13] and electrochemical deposition. Among all these methods, spray pyrolysis has several advantages such as low cost, easy doping, conducting or non-conducting substances of any shape and high deposition rate [14].

Present study reports the effect of film thickness onto the structural, optical, morphological and photoluminescence properties of iron oxide thin films prepared by spray pyrolysis technique. The photoelectrocatalytic degradation of benzoic acid using iron oxide thin film as photocatalyst under visible light illumination has been studied.

## 2. Experimental

The  $\text{Fe}_2\text{O}_3$  thin films were synthesized using a chemical spray pyrolysis technique onto the ultrasonically cleaned bare and FTO coated glass substrates. The 0.1 M Ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) Himedia, 99.99%, A.R. grade is dissolved in A.R. grade ethanol. Films were deposited by spraying different quantities of solution ranging from 30 to 70 ml at an interval of 10 ml. Other preparative parameters viz., solution concentration (0.1 M), substrate temperature ( $400^\circ\text{C}$ ), spray rate (4 cc/min), and nozzle to substrate distance (32 cm) were kept constant and compressed air was used as a carrier gas. All deposited films were annealed at  $500^\circ\text{C}$  for 2 h in an ambient atmosphere. In order to optimize the quantity of solution, the PEC cell was tested in 0.1 M NaOH as an electrolyte and a two-electrode configuration which comprising  $\alpha\text{-Fe}_2\text{O}_3$  thin film as a photoanode and graphite as a counter electrode. The PEC cell was illuminated by 100 W (tungsten lamp) visible light for the measurement of short circuit current ( $I_{\text{sc}}$ ) and open circuit voltage ( $V_{\text{oc}}$ ). The structural characterization of deposited thin films was carried out from X-ray diffraction patterns obtained under  $\text{Cu-K}_\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation from Bruker X-ray diffractometer model D2 Phaser and surface morphology was studied using JEOL JSM-6360 scanning electron microscope (SEM) and atomic force microscope model Bruker Innova 1B3BE with contact operating mode. The optical absorption and transmission study were carried out using Shimadzu UV-1800 spectrometer, Germany. The thickness was recorded using a Steller Net. Inc., USA Reflectometer having UV–vis light source with a CCD detector. The room-temperature photoluminescence (PL) spectra was recorded using Horiba Instrument, Luminescence Spectrometer (Model: Fluoramax-4) with a Xenon flash lamp and a grating to select the source of excitation (wavelength is 325 nm). Photocatalytic activity has been studied with the help of photoelectrocatalytic reactor with  $\text{Fe}_2\text{O}_3$  thin film electrode as a photocatalyst. The  $\text{Fe}_2\text{O}_3$

electrode used in this study was deposited onto conducting glass substrates (spray deposited fluorine doped tin oxide on the glass, FTO, with sheet resistance of  $10\text{--}20 \Omega \text{ cm}^{-2}$ ) by spray pyrolysis. The Single photoelectrochemical cell comprises of  $\text{Fe}_2\text{O}_3/\text{FTO}$  electrode ( $10 \text{ cm} \times 10 \text{ cm} \times 0.125 \text{ cm}$ ) as photoanode and stainless steel disc as a cathode at a distance of 1 mm facing the photoanode. During the experiment illuminated surface area of the photoelectrode in contact with the liquid circulated through the reactor was  $64 \text{ cm}^2$ . The external bias voltage of about 0.6 V was applied for enhancing the rate of degradation efficiency. Benzoic acid was obtained from SD Fine Chem. Ltd. and used as model organic species without further purification to make electrolyte in double distilled water. The electrolyte was circulated through the PEC reactor with a constant flow rate of  $12.4 \text{ l h}^{-1}$  using a Gilson MINIPUS peristaltic pump, France with silicon tubing. The liquid samples are collected from the reaction mixture at some intervals and the concentrations of impurities in the solutions were determined by measuring the extinction spectra using Shimadzu UV-1800 spectrometer, Germany. The COD and TOC measurements were carried out by standard method of oxidation. The samples withdrawn at various intervals during the degradation reaction were added to the excess of dichromate in concentrated sulfuric acid by digestion at  $140^\circ\text{C}$  was used. The concentration of the organic solute was calculated from the dichromate extinction at various wavelengths.

## 3. Results and discussion

### 3.1. Photoelectrochemical performance

Fig. 1 shows the variation of short circuit current ( $I_{\text{sc}}$ ) and open circuit voltage ( $V_{\text{oc}}$ ) with respect to solution quantity (films thickness) for  $\text{Fe}_2\text{O}_3$  photoelectrodes under visible light illumination. Both  $I_{\text{sc}}$  and  $V_{\text{oc}}$  increase gradually with spraying solution quantity and attains a maximum values ( $I_{\text{sc}} = 34.2 \mu\text{A}$  and  $V_{\text{oc}} = 0.190 \text{ V}$  respectively) at 50 ml and then decreases for higher quantity of solution. This might be due to formation of

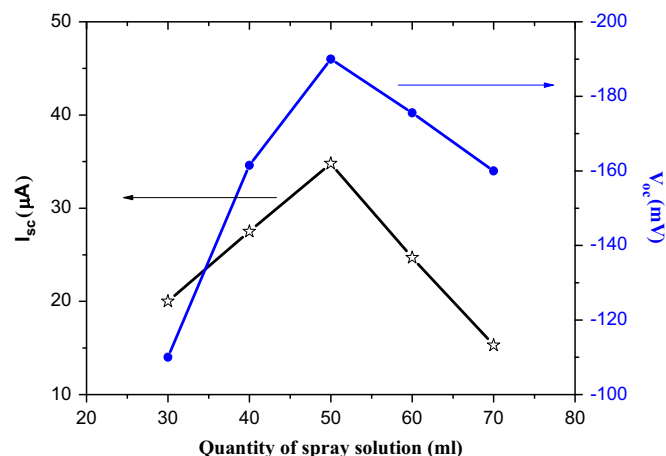


Fig. 1. Variation of  $I_{\text{sc}}$  and  $V_{\text{oc}}$  for  $\text{Fe}_2\text{O}_3$  film deposited from non-aqueous medium at various solution quantities.

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