Photocatalytic oxidation of Rhodamine B with ferric oxide thin films under solar illumination

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A B S T R A C T

Thin films of iron oxide are synthesized by spray pyrolysis technique using ferric chloride as precursor in non-aqueous medium. The effect of solution concentration onto photochemical, structural, morphological, optical, luminescence and thermal properties has been investigated. Structural analysis confirms the rhombohedral crystal structure with strong (1 1 0) orientation. Raman spectrum reveals that the deposited films contain α-phase of Fe_2O_3 (hematite). The SEM images of optimized Fe_2O_3 thin films show microneedle like structure with varying grain size from 75 to 120 nm. The observed direct band gap is about 2.0 eV for Fe_2O_3 thin film. Room temperature photoluminescencespectra showed three pronounced emission peaks for all concentrations. The photocatalytic oxidation of Rhodamine B with hematite Fe_2O_3 thin films under solar illumination is investigated. The first order rate constants for this heterogeneousphotocatalysis are evaluated as a function of the initial concentration of Rhodamine B (RhB). The extent of mineralization of degraded sample is confirmed by total organic carbon (TOC) andchemical oxygen demand (COD)analysis. This work suggests that prepared iron oxide photoelectrodes demonstrate an excellent ability to remove toxic dyes from industrial wastewater.

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1. Introduction

The large amount of dyes are produced annually and applied in different industries including textile, cosmetic, paper, leather, pharmaceutical and nutrition industries, out of which 15% is lost during the dyeing process [1]. The presence of even trace concentration of dyes in effluent is highly visible and undesirable which causes some serious problems to aquatic life and human health disorders [2]. For removal of dyes from water various methods such as biodegradation, coagulation, adsorption, advanced oxidation processes (AOP's) and the membrane process have been suggested. These processes have some advantages and disadvantages over the other methods. Out of these methods we needed to look into the worth on choosing an appropriate method which can be used to degrade the dye in the solution. From the last decade the researchers found the photo-assisted catalytic decomposition using semiconductors as photocatalysts has been a promising method for the elimination of organic pollutants in water and in the atmosphere [3]. The material used for driving the reactions involved in the photocatalysis of water is required to satisfy several requirements i.e. suitable bandgap, favorable positioning of the band edge stability in aqueous environment,

abundance and ease of fabrication are considered to be the most important [4,5]. There are various semiconductor photocatalysts have been used in the field of photodegradation of pollutants. Among these, TiO_2 and ZnO are known to be good photocatalysts for the degradation of several environmental pollutants [6]. However, TiO_2 and ZnO mainly absorbs UV light with wavelengths <380 nm (which covers only less than 4% of the solar spectrum) due to its wide band-gap of 3.2 eV. Therefore, it is of great interest to develop new visible light photocatalyst to enlarge the absorption wavelength range into the visible region. The hematite (α-Fe_2O_3) is considered to be an attractive semiconductor material, having desired property of narrow band gap (approximately 2.2 eV), which in principle allows utilization of a larger fraction of the solar spectrum, low cost, electrochemical stability and low toxicity [7]. The iron oxide is of scientific and technological importance because of its usage in photochemical catalyst, pigments, magnetic materials, gas sensors, and lithium-ion batteries [8,9].

The iron oxide thin films have been prepared by a variety of techniques, such as thermal oxidation [10], sputtering [11], atomic layer deposition [12], spray pyrolysis [13], chemical and metal organic deposition [14], sol–gel deposition [15], ion-beam deposition [16] and molecular beam epitaxy [17]. Among these methods, the SPD has many advantages as simplicity, low cost and large area depositions and easily adjusting the various deposition parameters to prepare homogeneous thin films using various spray

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solutions [18]. Bandara et al. [19] reported the degradation of 4-chlorophenol and orange II by Fe_2O_3 composite photocatalyst under daylight irradiation. Also Karunakaran et al. [20] reported the photocatalytic property of Fe_2O_3 and they discussed its mechanism using a kinetic model. Zhou et al. [21] reported the photocatalytic degradation of Rh B dye by iron oxide nanoparticles. Yu et al. synthesized hydrothermally ferric oxide hollow spheres at optimized concentration of $FeCl_3 \cdot 6H_2O$ and evaluated visible-light photocatalytic activity by decolorization of Rhodamine B (RhB) aqueous solution under visible-light illumination in the presence of H_2O_2 at ambient temperature. While increasing the $FeCl_3$ concentration it was found that the average crystallite size, shell thickness, and pore size slightly increase and photocatalytic activity slightly decrease, this might be due to its low specific surface area and bandgap [22]. Zhou et al. first time reported the α-Fe_2O_3 nanocatalysts with well-defined architectures and certain amount of this, as prepared α-Fe_2O_3 photocatalyst was used for degradation RhB with constant magnetic stirring under visible light [23]. But the degradation of Rh B under solar light illumination by immobilized iron oxide thin films had not been investigated so far.

In the present work, we report the effect of solution concentration onto the physical properties (structural, optical, morphological and photoluminescence) of iron oxide thin films by spray pyrolysis. Solar light induced photoelectrocatalytic degradation activity with Rhodamine B (Rh B) under iron oxide thin film as photocatalyst has been studied.

2. Experimental

Initially, the soda lime glass substrates (SLG) supplied by Blue Star, Mumbai, were washed with labolene detergent and again washed with double distilled water, followed by ultrasonic cleaning for 10 min. The chemical spray pyrolysis process, which consists of a solution that is sprayed onto a preheated substrate, where the solution reacts to form the oxide thin films. The Fe_2O_3 thin films were synthesized onto the ultrasonically cleaned bare and FTO coated glass substrates. The ethonolic solution of $FeCl_3 \cdot 6H_2O$ was sprayed for different solution concentrations ranging from 0.05 to 0.15 M keeping interval of 0.025 M. The optimized values of important process parameters are shown in bracket viz. airflow rate (1.5 kg/cm^2), spray rate (5 mL/min), distance between substrate to nozzle (32 cm), deposition temperature (400 °C) and quantity of the spraying solution (50 mL) were kept constant for all experiments. The PEC cell was fabricated using Fe_2O_3 thin films as photoelectrode and 1 M NaOH solution as electrolyte with graphite as counter electrode. This cell was illuminated under visible light for the measurement of short circuit current (I_{sc}) and open circuit voltage (V_{oc}).

The structural characterization of thin films was carried out, by analyzing the X-ray diffraction patterns obtained using Bruker powder diffractometer (AXS), Analytical Instruments Pvt. Ltd. Germany, Model:D2 Phaser ($\lambda = 1.5406$ Å for Cu-Kα). Surface morphology of spray deposited films on glass substrate was studied using JEOL JSM-6360 scanning electron microscope (SEM). The optical absorption study was carried out using Shimadzu UV-1800 spectrometer, Germany. The thickness was measured by optical reflectance using a StellerNetInc USA reflectometer having UV–vis light source with CCD detector. The room-temperature photoluminescence (PL) spectra were recorded using Horiba Instrument, Luminescence Spectrometer (Model: Fluromax-4). Raman scattering spectrum was recorded in air at room temperature with micro Raman system from JobinYvonHoribra LABRAM-HR visible within 100–1400 cm^{-1}. The Raman spectra were excited using the He–Ne 632 nm laser source with 600 and 1800 lines/mm gratings and CCD detector.

In order to study photocatalytic experiments the Fe_2O_3 thin films electrode was deposited by spray onto large area (100 cm^2) FTO coated glass with sheet resistance of 10–20 Ω. The Fe_2O_3 films are used as photoanode and stainless steel disk as a cathode at a distance of 0.1 cm facing the photoanode. The photoelectrode was illuminated from backside using solar light. The active surface area of the electrode in contact with the pollutant species was 64 cm^2. The external bias voltage of about 0.4 V was applied in order to increase the rate of reaction. The Rhodamine B was used as a model organic species which was obtained from s.d. fine chem. Ltd. Mumbai to make electrolyte in double distilled water and was re-circulated through the single PEC reactor with a constant flow rate using a Gilson MINIPLUS peristaltic pump, France with silicon tubing. Using required amount of samples withdrawn from the recirculated solution at specific interval of time, the concentration of Rh B in the solutions were determined by measuring the extinction spectra by Shimadzu UV-1800 spectrometer, Germany. These samples were also used for determining chemical oxygen demand (COD) using the standard method of oxidation with an excess of dichromate in concentrated sulphuric acid by digestion at 140 °C and 2 h. The concentration of the organic solute was calculated from the dichromate extinction at various wavelengths.

3. Results and discussion

3.1. Photoelectrochemical (PEC) characterization

The optimization of solution concentration of deposited α-Fe_2O_3 thin films is studied with the help of PEC technique by measuring short circuit current (I_{sc}) and open circuit voltage (V_{oc}). Fig. 1(a) shows the variation of I_{sc} and V_{oc} w.r.t. solution concentration. It is observed that in dark cell gives some dark voltage, due to difference between two half-cell potentials between Fe_2O_3 thin film and graphite electrodes. It is observed that, the values of I_{sc} and V_{oc} gradually increases with the increase in spray solution concentration up to 0.1 M ($I_{sc} = 34.7$ μA and $V_{oc} = 0.192$ V) and decreases for the higher concentrations. After illumination of junction, the magnitude of V_{oc} increases with negative polarity toward the Fe_2O_3 thin films, indicating cathodic behavior of photovoltage which confirms the films are n-type in nature [24]. Fig. 1(b) shows the I–V graph of typical optimized iron oxide thin film under visible light illumination by W/I 100 W lamp in 1 M NaOH electrolyte. From this curve it is clear that the dark current increases after 1.6 V, so one can apply bias voltage upto 1.6 V without electrode damage.

3.2. X-ray diffraction studies

Fig. 2 presents the XRD patterns of the α-Fe_2O_3 thin films deposited using different solution concentrations. The XRD reveals that the sharp and strong diffraction peaks are in agreement with those for rhombohedral α-Fe_2O_3 powder (Hematite, JCPDS 33-0664). The X-ray diffraction peaks are well indexed to α-Fe_2O_3 (Hematite) crystalline phase (space group: R3c (167), $a = 0.5036$ Å, $b = 0.5036$ Å, $c = 1.3749$ Å). It indicates that no impurity peaks are present in the deposited films. The average crystallite size is estimated from the Scherer equation [25];

$$D_{hkl} = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where D_{hkl} is the crystallite size (nm) perpendicular to the normal line of (h k l) plane, β is the full width at half maximum, θ is the Bragg angle, and λ is the wavelength of X-ray ($\lambda = 0.15406$ nm). The average crystallite size of Fe_2O_3 films according to the Scherer