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Dyes and Pigments 73 (2007) 103–110
DYES and PIGMENTS
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The effect of annealing on photocatalytic properties of nanostructured titanium dioxide thin films

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Received 25 February 2005; received in revised form 11 May 2005; accepted 31 October 2005
Available online 5 January 2006

Abstract

The photocatalytic degradation of a non-biodegradable azo dye called (C.I. Direct 80, Red Sulphonyl 3BL) was investigated using TiO_2 thin films in aqueous solution under irradiation of a mercury lamp Philips (UV-C) light source. The effect of operational parameters, i.e., annealing temperature of thin film, substrate nature on which TiO_2 films were deposited, film thickness, pH of the solution, dye concentration, and irradiation time on the degradation rate of azo dye aqueous solutions was examined. Results show that the employment of efficient photocatalyst and the selection of optimal operational parameters lead to complete decolorization. The best conditions for maximum photocatalytic degradation were found to be pH 1 at 5 ppm concentration of dye over TiO_2 thin films deposited on glass substrate coated with indium-tin oxide having 350 nm thicknesses annealed at 550 °C. The samples are all in the complete anatase phase and the particle size is in nanometer scale which is confirmed by XRD pattern analysis.

Keywords: TiO_2; Nanocrystalline; Thin film; Photocatalytic degradation; Azo dye

1. Introduction

Azo dyes constitute the largest class of dyes used in industry. In the textile industry, it is estimated that 10–15% of the dye is lost during the dyeing process and released as effluent. Azo dyes are resistant to aerobic degradation; however, under anaerobic conditions, the azo linkage is reduced to generate aromatic amines that are colorless but can also be toxic and potentially carcinogenic. Azo dyes are synthetic in nature and generally have a complex chemical structure, alien to the natural biotic environment and hence persist in nature. The conventional treatment methods for eliminating dyes from the waste stream generate large amount of solid wastes, which require costly disposal and regeneration methods. This means these methods are not destructive but only transfer the contamination from one phase to another. Therefore, a new and different kind of pollution is faced and further treatments are seemed to be necessary. In recent years an alternative to conventional methods, is ''advanced oxidation processes'' (AOPs), based on the generation of very reactive species such as hydroxyl radicals, that oxidizes a broad range of organic pollutants quickly and non-selectively [1,2]. It was experimentally proved that TiO_2 in aqueous suspension is an efficient photocatalyst for the elimination of biorecalcitrant organic pollutants. Most of organic substances can be transformed since the oxidizing species involved, specially $^{\bullet}OH$, has a very high oxidation potential. Other significant advantages of TiO_2 are the absence of toxicity and its low price. The main disadvantage that limits the development of this method is the need of a difficult and costly step of filtration to eliminate thin particles and recycle the catalyst. Filtration can be eliminated by immobilizing the photocatalyst on a solid support [3].

The aim of the present work is to prepare and characterize an active nanocrystalline anatase TiO_2 thin film, to study

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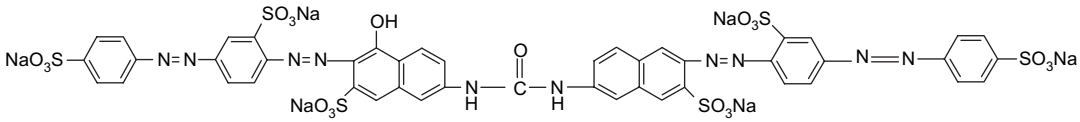
doi:10.1016/j.dyepig.2005.10.016

optical and electrical behaviors of titanium dioxide nanostructure thin films prepared by electron beam evaporation technique and investigate the influence of various parameters on photocatalytic decomposition of an azo dye, called Red Sulphonyl in the presence of this thin film irradiated by the UV-C light. The structure of Red Sulphonyl 3BL (C.I. Direct 80) is as follows:



2. Experimental

2.1. Thin film preparation and characterization

An electron beam evaporation system was used for film deposition. The evaporation conditions were: (1) a vacuum of 4.2×10^{-5} mbar; (2) an accelerating voltage of 1–10 kV; (3) electron beam current 10–12 mA and the rate of evaporation were controlled within the range 0.1–0.25 nm/s. The thickness of TiO_2 thin films was controlled by using a quartz crystal thickness monitor ranging from 50 nm to 500 nm. The TiO_2 thin films were deposited on two substrates including sodaglass and glass coated with indium-tin doped oxide (ITO conducting glass, 28 Ω^{-1}). The target material used was a TiO_2 pellet (purchased from Merck). The substrate temperature during the deposition process was kept at 25 °C. The phase composition of TiO_2 thin films annealed at different temperatures was characterized using XRD technique with a D8 Advanced Bruker X-ray diffractometer at room temperature, with monochromated Cu K_α ($\lambda = 1.54$ Å) in the scan range of 2θ between 10° and 100° with a step size of 0.03 (2θ/s). Measurements were taken under beam-acceleration conditions of 40 kV/35 mA. The UV–visible optical transmission spectra of the thin films were recorded by a double-beam spectrophotometer Cary 500 scan. The sheet resistance of films was measured by four-probe method at room temperature.

2.2. Photodegradation activity

To evaluate the catalytic activity of the TiO_2 thin films, photocatalytic experiments were carried out in round-bottomed photocatalytic Pyrex glass cells (cut off wavelength: 320 nm) and Red Sulphonyl were the model pollutant for destruction. A TiO_2 thin film of area 14 cm^2 was loaded in 75 ml of the dye solution. Photocatalytic activity was evaluated by measuring the rate of decomposition of dye; the intensity of the absorption spectra at λ_{max} (nm) ranging from 541 to 520 depending on pH corresponding to the color of Sulphonyl decreased with photocatalytic decomposition by TiO_2 thin film (Fig. 1). The irradiation system is equipped with three parallel mercury lamps 8 W (Philips UV-C), which has maximum emission at 350 nm. The distance between the UV source and the thin film was 8 cm. To adjust the solution pH values to the desired levels dilute NaOH and HNO_3 were used. After an appropriate illumination time, the concentration of dye in each degraded sample was determined by a spectrophotometer (UV–vis Spectrophotometer Cary 500 scan) at corresponding λ_{max}.

3. Results and discussion

3.1. Film characterization

3.1.1. XRD pattern

A well-organized crystal structure from titania particles is observed for the films on sodaglass and glass coated with ITO annealed at 450 and 550 °C (Figs. 2 and 3). The initiation of the crystalline anatase phase occurs at a temperature of 450 °C. The XRD peaks at 25.351°, 38.633°, 48.126°, and 55.087° correspond to anatase (101), (112), (200), and (211) crystal planes, respectively [4]. It was also found that anatase (101) is the preferential growth orientation, its intensity increases with annealing temperature. Fig. 3 shows the additional lines at $2\theta = 21.320°$, 30.541°, 37.792° and 51.125° indicating the reflections from the (211), (222), (411) and (440) planes which corresponds to indium oxide and to the

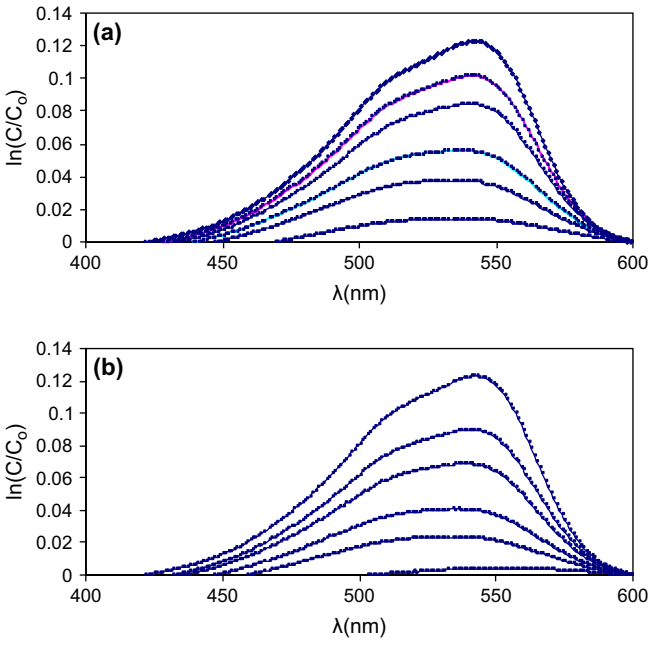


Fig. 1. UV–vis spectra of Red Sulphonyl after photocatalytic reaction using TiO_2 thin film on sodaglass (a) and on ITO conducting glass (b), thickness 350 nm, initial dye concentration 5 ppm, pH 1.

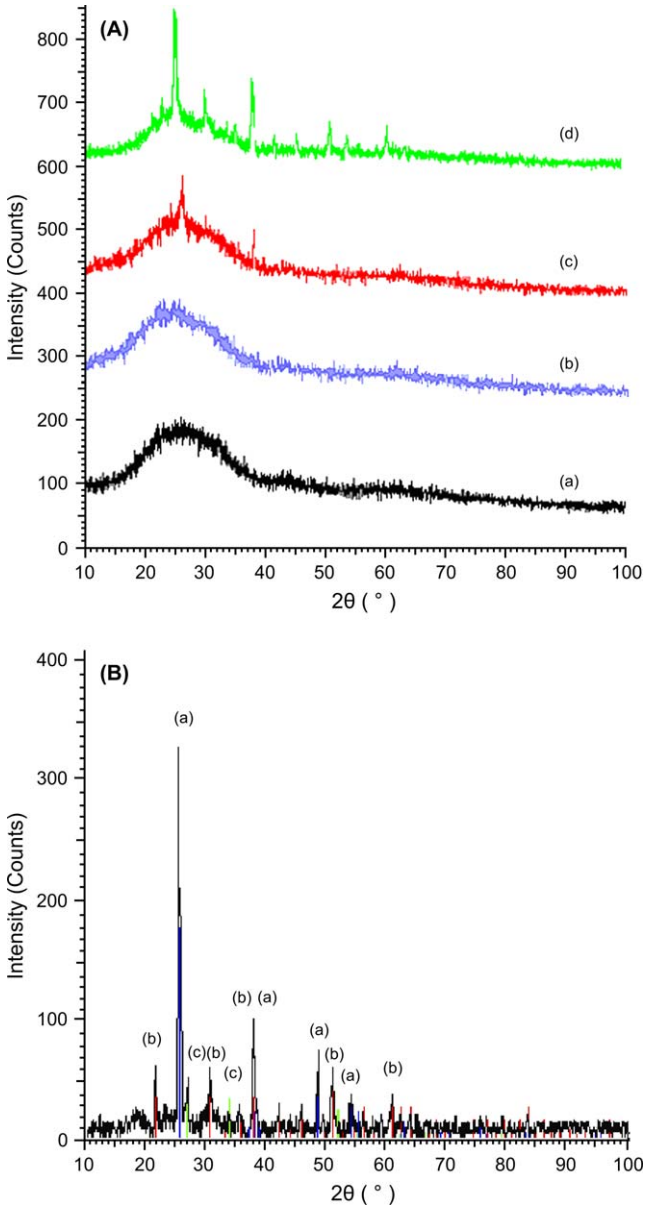


Fig. 2. (A). XRD patterns for TiO_2 thin films on ITO conducting during annealing, thickness 350 nm: (a) 250 °C, (b) 350 °C, (c) 450 °C, and (d) 550 °C. (B) XRD pattern for TiO_2 thin film annealed at 550 °C on sodaglass coated with indium-tin oxide, thickness 350 nm. In_2O_3 (a), TiO_2 (b), SnO_2 (c).

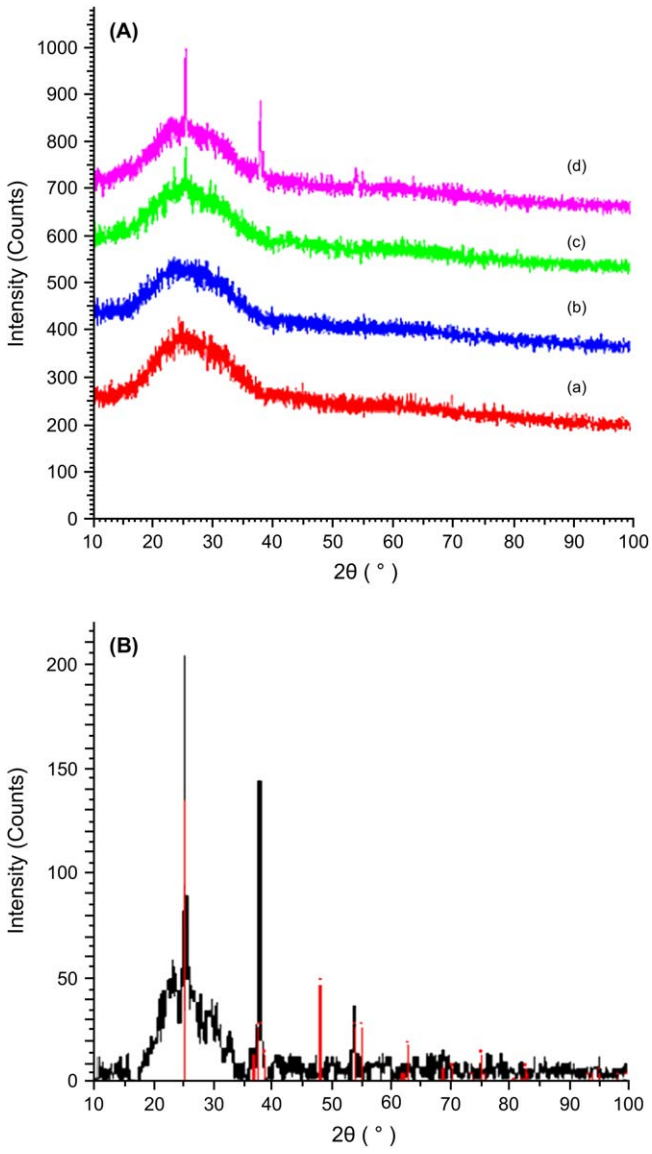


Fig. 3. (A) XRD patterns for TiO_2 thin films on sodaglass during annealing, thickness 350 nm: (a) 250 °C, (b) 350 °C, (c) 450 °C, and (d) 550 °C. (B) XRD pattern for TiO_2 thin film on sodaglass coated with indium-tin oxide annealed at 550 °C, thickness 350 nm.

characteristic peak of SnO_2 at $2\theta = 26.325°$. By applying the Scherer formula [5], the TiO_2 crystallites size can be estimated from FWHM of line at $2\theta = 25.351$ to be ca. 45 nm and 23 nm, for the films on sodaglass and ITO conducting glass, respectively.

3.1.2. Optical properties

UV–vis spectroscopy has been utilized to characterize the bulk structure of crystalline and amorphous titania. Fig. 4 (A–D) shows the UV–vis spectra of TiO_2 thin films on two substrates annealed at different temperatures having thickness 50 nm and 350 nm in wavelength range of 300–800 nm. The band fluctuation is due to the interference color of the film and increases with film thickness. The amplitude of interference spectra also increases with increasing annealing temperature and film thickness, due to the increase in the refractive index of TiO_2 thin films. Optical transmittance higher than 90% in the visible region of spectrum is obtained for all films. However, the transmittance of TiO_2 films decreases with increasing thickness. The fast decrease below 380 nm is due to absorption of light caused by excitation of electrons from the valence band to the conduction band of TiO_2. The UV–vis absorption band edge is a strong function of titania cluster size, which can be attributed to well-known quantum size effect for semiconductors [6]. Compared with the transmittance spectra of TiO_2 films on sodaglass substrate, the absorption of those films on ITO conducting glass shows a slight pseudo-blue shift. This is ascribed to the fact that the latter films

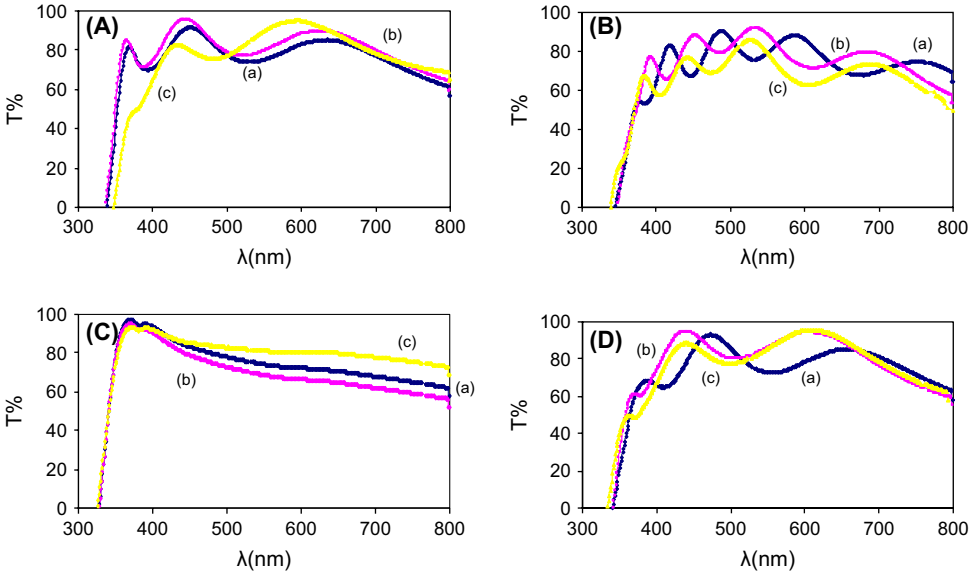


Fig. 4. UV–vis spectra of TiO_2 films having different thickness at different temperatures annealing: (a) 350 °C, (b) 450 °C, and (c) 550 °C. (A, B): 350 nm and (C, D): 50 nm thickness; TiO_2 film on sodaglass (A, C) and on ITO conducting glass (B, D).

contain smaller TiO_2 particles, and a quantum size effect appears, resulting in a pseudo-blue shift of the absorption edge. The difference in the transmittance between the TiO_2 films was attributed to the difference in film thickness and absorption of light.

3.1.3. Refractive index and porosity

The refractive index of prepared TiO_2 films was calculated from the measured transmittance spectrum. The evaluation method used is based on the analysis of the transmittance spectrum of a weakly absorbing film deposited on a non-absorbing substrate [7]. The refractive index $n(\lambda)$ over the spectral range is calculated by using the envelopes that are fitted to the measured extreme.

$$n(\lambda) = \sqrt{S + \sqrt{S^2 - n_o^2(\lambda)_s^2(\lambda)}} \quad (1)$$

$$S = (1/2)n_o^2(\lambda) + n_s^2(\lambda) + 2n_o n_s(T_{max}(\lambda) - T_{min}(\lambda))/(T_{max}(\lambda) \times T_{min}(\lambda))$$

where n_o and n_s are the refractive indices of air and substrate, respectively, T_{max} is the maximum envelope, and T_{min} is the minimum envelope. The porosity of the TiO_2 thin films was calculated using the following equation. [8]:

$$\text{Porosity} = \left[1 - \left(n^2 - 1\right)/\left(n_d^2 - 1\right)\right] \times 100(\%) \quad (3)$$

where n_d is pore-free TiO_2 to be 2.52 [9]. The resultant refractive index and porosity of TiO_2 thin films annealed at different temperatures are listed in Table 1. The results showed that the refractive index increased with annealing temperature up to 550 °C. On the other hand, the porosity showed opposite trend. This is due to film densification and pore destruction in films during annealing. However, the porosity of TiO_2 films deposited on sodaglass showed more reduction than that of TiO_2 films deposited on ITO conducting glass. Accordingly, the former TiO_2 films are less porous than the latter ones by 20% at 550 °C.

3.1.4. Estimation of TiO_2 band gap

A given semiconductor can exhibit direct or indirect band to band transitions depending on its crystal structure. It was found in the literature [10,11] that a TiO_2 thin film has direct and indirect band gaps changing from 3.58 to 3.79 eV and from 3.05 to 3.4 eV, respectively depending on deposition parameters and conditions. These transitions are all in the UV region [12]. The catalyst with band gap more than 3.2 eV exhibits high selectivity.

The absorption coefficient ($\alpha = d^{-1}\ln(1/T)$, d is the thickness of film and T is the transmittance) values have been computed at different annealing temperatures and are found to be in the order of 100 cm^{-1} at the band edge. Subsequently, the optical band gaps have been determined by plotting the $(\alpha h\nu)^n$ vs. $h\nu$ ($n = 2$ for allowed direct, $n = 1/2$ for allowed indirect, $n = 1/3$ for forbidden indirect and $n = 2/3$ for forbidden direct optical transitions) and extrapolating the linear region of the plot toward low energies. The linear nature of the plots of $(\alpha h\nu)^2$ above the absorption edge indicates that the

Table 1
The calculated refractive index and porosity of TiO_2 thin films annealed at different temperatures

Annealing temperature (°C)	TiO_2 film on glass		TiO_2 film ITO conducting glass	
	n	p (%)	n	p (%)
350	1.58	71	1.84	55
450	1.64	68	1.65	49
550	1.72	63	2.01	43

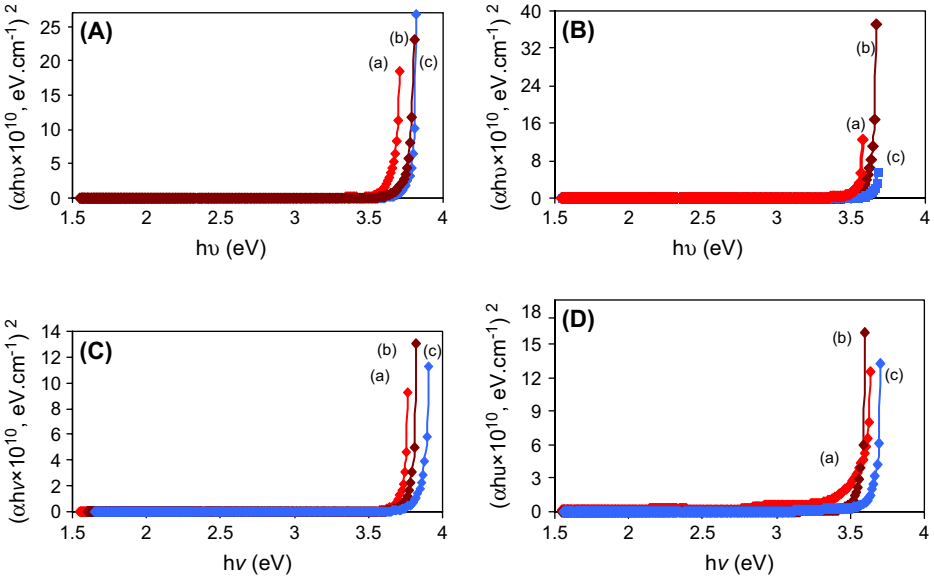


Fig. 5. The band gap determination of TiO_2 films having different thickness at different temperatures annealing: (a) 350 °C, (b) 450 °C, and (c) 550 °C. (A, B): 350 nm and (C, D): 50 nm thickness. TiO_2 film on ITO conducting glass (A, C) and on sodaglass (B, D).

fundamental optical transition in these films is direct. Plots of $(\alpha h\upsilon)^{1/2}$ vs. $h\upsilon$ did not show linearity. The evaluated band gap for TiO_2 thin films is shown in Fig. 5. As seen in Fig. 5, band gap for TiO_2 thin film with 350 nm thicknesses on ITO conducting glass and on glass at 550 °C was 3.68 and 3.59 eV, respectively. The optical results showed that by increasing of annealing temperature and the film thickness, the direct band gap was increased for both TiO_2 films.

3.1.5. TiO_2 thin film resistivity measurement

The resistivity of the TiO_2 thin films is calculated by the formula

$$\rho = \frac{2\pi L}{C}\frac{V}{I} \tag{4}$$

where ρ represents the resistivity of samples (Ω^{-1}), L is the space of the adjacent probe, V is the measured voltage, I is the measured current of surface and C is the amendment factor which have relation to the figure, size and thickness of sample and position of the probe. It was observed that the resistivity of TiO_2 thin films on ITO conducting glass enhances with the increase of the annealing temperature (Table 2). The TiO_2 thin films deposited on glass are insulators. TiO_2 block materials are nonconductor, but the TiO_2 thin films become conductor or semiconductor due to electrons transfer at interface. Since the depth of the transfer of electron is determined by the difference of work function, the conductivity of TiO_2 thin films depends on the thickness of the film and the substrate material.

Table 2
The resistivity[a] of TiO_2 thin films as a function of annealing temperature and film thickness

Annealing temperature (°C)	Resistivity of TiO_2 film on glass coated with ITO (Ω^{-1})[a]				
250	23	46	72	89	105
350	51	61	90	126	139
450	98	110	132	154	166
550	123	156	175	198	253

[a] The thickness of films: 50 nm, 100 nm, 200 nm, 350 nm, and 500 nm for values reported, respectively.

3.2. Effect of operational parameters on photocatalytic activity

There are many factors affecting the photocatalytic process by TiO_2 thin films, for example surface acidity, annealing temperature, film thickness and dye concentration [13–16].

3.2.1. Solution pH

The semiconductor oxide particles are generally amphoteric in nature and the photocatalytic process takes place on the surface of TiO_2. The pH of the solution shows strong influence on the surface properties of TiO_2 particle. Since the surface charge of the titanium dioxide thin film is influenced by the pH of solution and Red Sulphonyl 3BL dye has a negative charge, experiments were performed at different pH to investigate the effect of pH on the adsorption of Red Sulphonyl over TiO_2 thin films. It was observed that the percent adsorption increases in acidic medium and decreases in basic pH. The same trend was observed for both TiO_2 thin films on sodaglass and ITO conducting glass. A study of photoactivity shows a similar behavior between adsorption and degradation, so it can be suggested that the influence of pH on photocatalysis is due to the amount of dye adsorbed on TiO_2 surface. It is worth to note for all pH values and all dye concentrations, the dye photodegradation fits first-order kinetics. Fig. 6 shows the pH dependence of photodegradation of Red Sulphonyl 3BL dye over TiO_2 thin films deposited on ITO conducting glass. These results show

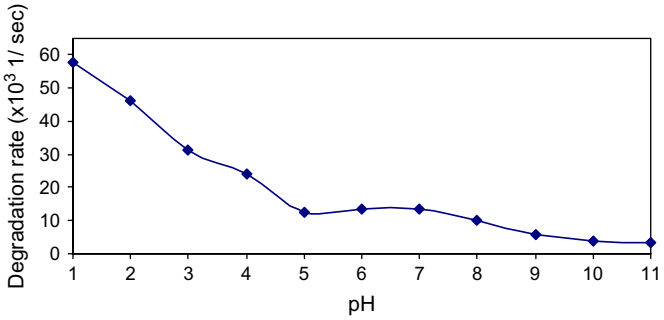


Fig. 6. Influence of pH on the rate of degradation of Red Sulphonyl 3BL, initial concentration 5 ppm, on TiO_2 thin films deposited on ITO conducting glass with thickness of 350 nm.

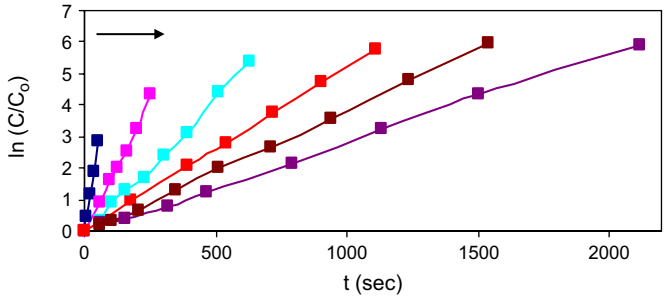


Fig. 7. The plot of photodegradation rate of Red Sulphonyl 3BL on ITO conducting glass at different dye concentration (5–40 ppm) vs. irradiation time.

that color removal is to a great extent faster at acidic medium (the best result at pH 1). For a practical photocatalytic reactor, the adhesion strength between the film and the substrate must be strong enough to prevent the film brushing off the substrates during the utilization. So the adhesion strength is an important property of film. The studied TiO_2 thin films in this work were not washed off at wide pH range.

3.2.2. Dye concentration

The relation between photodegradation efficiency of Red Sulphonyl and its concentration is presented in Table 3. The observed results reveal that the initial dye concentration influences the rate of degradation of the dye. As the initial concentration of dye increases, the degradation rate decreases which is attributed to decrease in the path length of photons entering the solution, and in low concentration the reverse effect is observed [17]. Hence it is concluded that as the initial concentration of dye increases, the requirement of catalyst surface needed for the degradation also increases. The major portion of degradation occurs in the region (termed as reaction zone) nearer to the irradiated side since the irradiation intensity in this region is much higher than the other side [18]. At higher dye concentration degradation decreases at sufficiently long distances from the light source or reaction zone due to retardation in the penetration of light [19]. This means that the rate of photodegradation decreases considerably with increase in dye concentration. However, complete degradation of Red Sulphonyl takes place in the order of minutes even at higher concentration. Under the experimental conditions used, the photocatalytic curves follow first-order reaction kinetics. It is

Table 3
The dye concentration effect on photodegradation rate on TiO_2 thin films with 350 nm thickness annealed at 550 °C, solution pH 1

Dye concentration (ppm)	TiO_2 film on ITO conducting glass	R^2	TiO_2 film on glass	R^2
5	0.0583	0.99	0.0391	0.99
10	0.0340	0.98	0.0261	0.99
15	0.0138	0.98	0.0085	0.97
20	0.0097	0.97	0.0054	0.96
30	0.0047	0.98	0.0025	0.98
40	0.0028	0.97	0.0017	0.98

well established that photocatalysis experiments follow the Langmuir–Hinshelwood model [20–22],

$$R = \frac{dc}{dt} = k_r\theta = k_rKC/(1+KC) \quad (5)$$

where the reaction rate R is proportional to the surface coverage θ, k_r is the reaction rate constant, K is the adsorption coefficient of the reactant, and C is the reactant concentration.

As seen in Fig. 7 more irradiation time was required with increasing dye concentration.

3.2.3. Annealing temperature of thin film

As seen before, XRD patterns of TiO_2 films deposited on two substrates show no peaks of anatase up to 450 °C. Because of the lack of the heat resistance of sodaglass plates used, the annealing temperature more than 550 °C was not attainable. Therefore, the TiO_2 films of rutile crystal were not used as a photocatalyst in the present study. The results indicated that the heat treatment temperature and its duration can influence the rate of photodegradation. The samples were all in the complete anatase phase at 550 °C and showed the best rate of degradation. It has been found reportedly the photocatalytic activity of TiO_2 varies with its structural form and is higher in the anatase form compared to the rutile form [23,24]. Since TiO_2 is an n-type semiconductor, the concentration of Ti^{3+} in TiO_2 films forms a donor level between the band gap of TiO_2 which results in the reduction of recombination of photogenerated electrons and holes. The increase in photocatalytic activity of TiO_2 films with the heat treatment time may be due to an increase in Ti^{3+} concentration during annealing [25]. However, the long heating in air results in a decrease in the specific surface area, which also limits the photocatalytic activity of TiO_2 films. Table 4 shows the effect of heat treatment time on photocatalytic activity.

3.2.4. Nature of substrate

According to reports [6,26], the photocatalytic activity of TiO_2 thin film on sodaglass decreased remarkably because alkali ions diffused from the glass substrate provided recombination centers for electron–hole pairs. To exclude this effect, the deposition of thin ITO layers has been common practice. We have examined these phenomena using two different substrates i.e., sodaglass, for which a sodium ion effect might be

Table 4
Effect of heat treatment time on photocatalytic activity[a]

Time (min)	15	30	45	60	90	120	180
k (s^{-1})	0.0392	0.0420	0.0456	0.0491	0.0583	0.0567	0.0543

[a] Heat treatment temperature 550 °C, film thickness 350 nm on ITO conducting glass, solution pH 1 and TiO_2 thin.

expected; and other one of which has a coating of indium-tin oxide on the surface which may be expected to act as a barrier to sodium migration. As the XRD results show that there is no detectable "sodium ion effect" with these films, since the TiO_2 phase for all films reported here are exclusively anatase, the sodium ion effect would appear to be a consequence of a change in phase from anatase to brookite [6]. As represented in Table 3 the films deposited on ITO conducting glass showed more photoactivity than the films deposited on glass. These results can be due to higher porosity (Table 1) and higher direct band gap of the former films (Fig. 5).

3.2.5. Time of irradiation

Results presented in Fig. 7 clearly showed that the time required for complete decolorization of aqueous solutions of Red Sulphonyl strongly depends on the initial concentration of the dye. It is important to note that for dye concentrations between 5 ppm and 40 ppm, which are typically observed at wastewaters of dye houses, complete degradation of Red Sulphonyl takes place in the order of minutes (Table 5). However, the time required for complete decolorization of Red Sulphonyl solutions increases with increasing initial dye concentration. This dependence could again be related to the formation of several monolayers of adsorbed dye on the TiO_2 surface, which is favored at high dye concentrations. At higher dye concentrations, larger amounts of the dye adsorb on the photocatalyst and inhibit the reaction of adsorbed molecules with the photoinduced positive holes or hydroxyl radicals, since there is not a direct contact of the semiconductor with them. This results in the observed decrease in the apparent reaction rate. In addition, it should be taken into account that the incident photons can be absorbed either by the TiO_2 or by dye molecules present in the solution. Increasing dye concentration leads to an increase of the amount of photons which are absorbed by the dye molecules and never reach the photocatalyst surface. Photodegradation efficiency of dye was small when photolysis was carried out in the absence of TiO_2 thin film and negligible in the absence of the UV light.

Table 5
Photodegradation efficiency of Red Sulphonyl 3BL vs. irradiation time[a]

Irradiation time (min)	TiO_2 on ITO conducting glass	TiO_2 on glass
3	64.94	54.78
6	78.16	63.44
9	84.43	75.63
12	96.66	84.29
15	97.02	91.70
18	100	95.59
21		100

[a] Red Sulphonyl 3BL concentration = 40 ppm, pH 1, TiO_2 film thickness = 350 nm on ITO conducting glass, annealing temperature 550 °C.

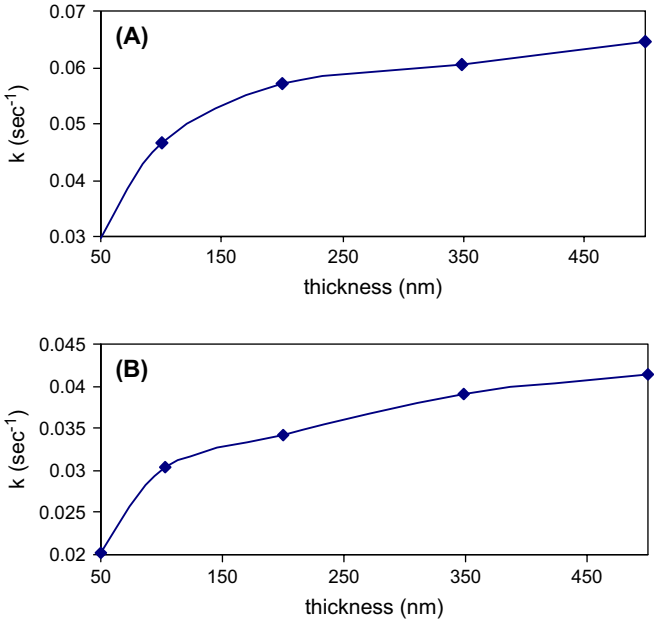


Fig. 8. The photodegradation rate variation with TiO_2 film thickness: (a) on ITO conducting glass, and (b) on sodaglass.

3.2.6. Film thickness

It is seen from Fig. 8 that decomposition rate constants depend on the film thickness. As expected the rate constants increase with increasing film thickness which is attributed to two factors: (a) increase in amount of titanium dioxide to participate in the photocatalytic reaction, and (b) increase in the charge carrier concentrations of TiO_2 thin films. However, a limiting value can be observed at thick films due to: (a) aggregation of TiO_2 particles in the interior region of thick films, causing a decrease in the number of surface active sites and (b) increase in opacity and light scattering leading to a decrease in the passage of irradiation through the film.

4. Conclusion

Photocatalytically active, robust and transparent TiO_2 thin films have been prepared on glass and ITO conducting glass by electron beam evaporation method. The results of our study showed that the use of TiO_2 thin film prepared by electron beam evaporation can be a powerful and efficient alternative to conventional treatment methods used for the discoloration of the azo family dyes at low concentrations.

The results also indicated that the degree of photodegradation of dye was obviously affected by the initial dye concentration, pH of solution, substrate nature on which thin films deposited, the thickness of thin films, annealing temperature and its duration. The higher porosity in TiO_2 thin films on ITO conducting glass is beneficial to rapid diffusion of various reactants and products during UV illumination and enhances the speed of photocatalytic reaction. Secondly, UV–vis spectra

show that the absorption edge of these films is at a shorter wavelength range than that of TiO_2 films on sodaglass. This is because former films contain smaller crystallites. The best conditions for maximum photocatalytic degradation were found to be pH 1 at 5 ppm concentration of dye over TiO_2 thin films deposited on glass substrate coated with indium-tin oxide having 350 nm thicknesses and annealed at 550 °C. The samples are all in the complete anatase phase and the particle size is in nanometer scale which is confirmed by XRD pattern analysis.

Acknowledgments

The authors wish to thank the University of Isfahan for financially supporting this work.

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