Research Article

Photocatalytic Activity of Toluene under UV-LED Light with TiO₂ Thin Films

Thammasak Rojviroon,¹ Apirat Laobuthee,² and Sanya Sirivithayapakorn¹

¹ Department of Environmental Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

² Department of Materials Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

Correspondence should be addressed to Sanya Sirivithayapakorn, fengsys@ku.ac.th

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Titanium dioxide (TiO₂) and ferric-doped TiO₂ (Fe-TiO₂) thin films were synthesized on the surface of 304 stainless steel sheets using a simplified sol-gel preparation method. The Fe-TiO₂ thin films were prepared with weight-to-volume ratios of Fe³⁺/TiO₂ of 0.3%, 0.5%, and 0.7%, respectively. The crystalline phase structures of the prepared TiO₂ and Fe-TiO₂ thin films were entirely anatase. The measured optical band gaps of the TiO₂, 0.3% Fe-TiO₂, 0.5% Fe-TiO₂, and 0.7% Fe-TiO₂ thin films were 3.27, 3.28, 3.22, and 2.82 eV, respectively. The grain sizes and other physical properties of the prepared thin films were also reported. The kinetics of the photocatalytic processes under a UV-LED light source could be explained by the Langmuir-Hinshelwood kinetic model with the specific rates of 2.00×10^{-3} , 4.00×10^{-3} , 5.00×10^{-3} , and $7.00 \times 10^{-3} \text{ min}^{-1} \text{ mW}^{-1}$, for TiO₂, 0.3% Fe-TiO₂, 0.5% Fe-TiO₂, and 0.7% Fe-TiO₂, respectively. An increase in Fe³⁺ dopant concentration could enhance the photocatalytic activity of toluene decomposition as a result of lower optical band gaps, smaller grain size, and higher surface area.

1. Introduction

Titanium dioxide is a photocatalyst that has been used extensively due to its good photocatalytic activity, relatively low toxicity, and low cost. Among the common crystalline forms of TiO₂-anatase, rutile and brookite-anatase are generally recognized as the most active photocatalyst owing to its smaller particle size, high surface area-to-volume ratio, and narrow band gap. Applications of TiO₂ can be found in various practices including sterilization and microorganism disinfection (especially bacteria and viruses), hazardous waste remediation as well as treatment and purification of water and air [1–12]. One of the most widely used methods to fabricate TiO₂ nanoparticles is the sol-gel technique [9, 13–15]. This coating technique has been applied to various materials, such as metal, plastic, silicon, and polymer [6, 16]. In this research, we fabricated both TiO₂ and Fe-TiO₂ thin films using a simplified sol-gel technique modified from Eshaghi et al. [9]. This technique has many advantages such as low processing temperature, the possibility of coating large area substrates, and not requiring complicated equipment.

In this study, we modified this technique by using different solvents for sol-gel preparation, modifying the calcination temperature scheme, adding Fe dopant in the sol-gel process, and reducing the stirring time and dip coating speed. A wide range of physical properties of the thin films were systematically compared and reported. The crystalline phases on the TiO₂ thin films were identified by the X-ray diffraction (XRD) technique. The surface morphology was investigated using atomic force microscopy (AFM). Other physical properties were also investigated including BET surface area as well as adhesion and corrosion testing.

In this research, we selected UV-light emitting diodes (UV-LEDs) with a peak wavelength of 365 nm as the light source. The UV-LED is safer than mercury vapor lamps and UVC germicidal lamps that have been widely used in photocatalytic processes, since the UV-LED does not contain trace amounts of toxic mercury. Moreover, the UV-LED is durable and cheap, consumes less energy, and generates lower heat [17, 18].

The objectives of this research were to develop the technique of TiO₂ thin film preparation and improve

TABLE 1: Surface properties of dip-coated TiO₂ thin films on stainless steel substrates.

Surface properties	Catalysts			
	TiO ₂	0.3% Fe-TiO ₂	0.5% Fe-TiO ₂	0.7% Fe-TiO ₂
Crystalline phase	Anatase	Anatase	Anatase	Anatase
Optical band gap (eV)	3.27	3.28	3.22	2.82
Grain size (nm)	20–250	20–150	50–180	30–100
RMS average roughnesses (nm)	18.30	11.92	18.40	12.92
Apparent surface area (m ² m ⁻²) ⁽¹⁾	1.08	1.06	1.11	1.09
Total weight of TiO ₂ on substrate (g m ⁻²) ⁽²⁾	0.15	0.15	0.15	0.14
Total apparent surface area per total weight of TiO ₂ (m ² g ⁻¹) ⁽³⁾ = ⁽¹⁾ / ⁽²⁾	7.13	7.07	7.66	7.81
BET surface area (m ² g ⁻¹)	36.98	21.61	32.57	42.73
Adherence				
Classification	4B	4B	4B	4B
Rank	Good	Good	Good	Good
Corrosion test	✓	✓	✓	✓

✓: no visible damage.

FIGURE 1: Schematic diagram of the photoreactor used for the degradation of toluene. 1: sampling port, 2: glass reactor, 3: coated stainless steel impeller, 4: UV-LED light source, 5: motor, 6: power supply.

TABLE 2: L-H parameters obtained in the photocatalytic degradation of toluene.

Catalyst	k (mol·m ⁻³ ·min ⁻¹)	K (m ³ ·mol ⁻¹)	kK (min ⁻¹)
TiO ₂	1.83×10^{-4}	109.29	0.02
0.3% Fe-TiO ₂	2.00×10^{-4}	200.00	0.04
0.5% Fe-TiO ₂	2.02×10^{-4}	247.52	0.05
0.7% Fe-TiO ₂	2.57×10^{-4}	272.37	0.07

the photocatalytic efficiency of TiO₂ thin films by adding Fe dopant. Using the prepared TiO₂ thin films and UV-LED as

FIGURE 2: XRD patterns of crystalline TiO₂.

the light source, the degradation efficiencies and kinetics of toluene in the photocatalytic process in a batch reactor are reported.

2. Experimental

2.1. Preparation of TiO₂ and Fe-TiO₂ Thin Films. The TiO₂ and Fe-TiO₂ thin films were prepared with an acid-catalyzed sol-gel dip-coating on the surface of 304 stainless steel sheets (40.0 × 85.0 × 0.3 mm) using titanium tetraisopropoxide (Ti [OCH(CH₃)₂]₄, TTIP) as a precursor. For the preparation of the TiO₂ thin films, the sol-gel solution was prepared by mixing TTIP with isopropanol with a volume ratio of 1:15. For the preparation of the Fe-TiO₂ thin films, iron (III) nitrate (Fe(NO₃)₃·9H₂O) was added to the TTIP and isopropanol solution with weight-to-volume ratios of

FIGURE 3: XRF spectrum of 0.3% Fe-TiO₂ on a glass slide.

Fe³⁺/TiO₂ of 0%, 0.3%, 0.5%, and 0.7%. Afterwards, the pH of the solutions was adjusted to between 2 and 3 using concentrated hydrochloric acid. The solutions were stirred at room temperature in a closed chamber with constant flow of N₂ gas for 1 h and left to dry at room temperature for 24 h before being ready to use. The thin films were developed on the surfaces by dip-coating the sol-gel solutions at a rate of 9 mm/min in a sealed chamber. During this dip-coating process, the chamber was continuously flushed with nitrogen gas to minimize contact with air. The first layer of coating was heated at 100°C to prepare the surface for coating the next layer. After coating the first layer, the same dip-coating processes were carried out layer by layer for the subsequent layers. The second and third layers were heat-treated in an oven at 250 and 500°C for 1 h, respectively. After the heat treatment, the coated substrates were gradually cooled down in the oven for 1 h before being taken out and left to cool down at normal room temperature. All of the stainless steel sheets were weighed before and after coating each layer.

2.2. Characterization of the Thin Films. The nanostructure and optical band gap of the thin films were determined by XRD (Bruker model D8 Advance) and UV-Vis spectrometer in the wavelength range 290–800 nm (Lambda 650 Perkin-Elmer), respectively. The surface morphology of the thin films was investigated by AFM (Asylum Research MFP-3D-BIO). The grain size was measured directly from cross-sectional AFM images at the base of each grain. The apparent surface areas of the thin films were determined with Gwyddion software, version 2.22 (<http://gwyddion.net/>). To confirm the composition of thin films, elemental analysis was performed using X-ray Fluorescence (Horiba XGT-2000 W). The X-ray tube and current parameters were set to 50 kV and 1 mA. Since the substrates for thin films were 304 stainless steel sheets, we measured Fe-TiO₂ glass slides coated by the same procedure.

Both TiO₂ and Fe-TiO₂ nanoparticle powders for the BET surface area analyses were prepared by heating the sol-gel solutions at 100°C for 1 h and then at 500°C for 1 h. The BET surface area of the powders was calculated from the N₂ adsorption isotherm (BELSORP-max). The cross-hatch adhesion between the thin films and the substrates was examined using the ASTM method D3359B-08 [21]. Using a method modified from Shankar et al. [22], the corrosion

resistance of the thin films was tested by dipping the coated substrates in nitric acid and sodium hydroxide at concentrations of 1, 5, and 10 molar percent, respectively, for 5 min.

2.3. Photocatalytic Activity Test. The photocatalytic activities of the thin films were evaluated by the degradation of toluene. A cylindrical glass batch reactor of 1100 mL capacity was used as a reaction vessel (photoreactor). The reactor was placed in a UV-LED light source chamber that contained 500 UV-LED light bulbs. The average intensity in the photoreactor was 1000 mW·m⁻². The top cover plates of the reactor were made from stainless steel. Two coated stainless steel sheets were mounted onto the stainless steel shaft that was powered by the motor (Figure 1) to provide both mixing and photoreactions. The concentration of toluene vapor was measured with a gas chromatograph (Model Shimadzu GC-2014). The gas chromatograph was equipped with an Intercap-1 capillary column of 30 m length, 0.25 mm inner diameter, and 0.4 μm film thickness. The operating conditions of the GC were as follows: injector temperature 120°C, detector temperature 200°C, column temperature 150°C, and a sample volume of 40 μL.

The desired amount of toluene was injected as gas phase into the reactor. A sample of the initial concentration of toluene was taken for measurement just before the UV-LED light sources were turned on. The concentration of toluene was recorded with reaction time throughout the photocatalytic activity test. The measured concentrations of toluene from the photocatalytic activity test were corrected using the results from control experiments carried out in the dark (with catalyst) and those carried out under UV-LED light only (without catalyst) before the kinetics calculations.

3. Results and Discussion

3.1. Characterization of TiO₂ Thin Films. The XRD pattern showed prominent peaks occurring at $2\theta = 25.2^\circ$ (Figure 2). The strong peaks confirm the presence of only anatase phase in the TiO₂ thin films [23–25]. From the XRD pattern, increasing the Fe³⁺ dopant concentration in TiO₂ thin films does not affect the phase of TiO₂. Similar to the finding of Yu et al. [26], other Fe_xTiO_y phases were not found in the XRD pattern mainly because of the low Fe-doping concentration and the similar radius of Fe³⁺ (0.64 Å) and Ti⁴⁺ (0.68 Å). Thus, the Fe³⁺ ions can enter into the crystal structure of titania and locate at interstices or replace some of the lattice sites of TiO₂, forming an iron-titanium solid solution [26, 27]. A similar finding was also reported previously in several studies, which prepared the thin films by the sol-gel, chemical vapor deposition (CVD) and electrophoretic deposition (EPD) techniques, and where the films were annealed at temperatures ranging from 400 to 600°C [9, 24, 25, 28].

Owing to the limitations of the XRD technique, XRF was used to analyze the composition of the thin films qualitatively. The XRF spectrum of 0.3% Fe-TiO₂ coated on a glass slide is shown in Figure 3. The appearance of the Fe peak implies that Fe was successfully doped in the TiO₂ thin films.

FIGURE 4: 2D AFM images of TiO_2 thin films on stainless steel substrate: (a) TiO_2 ; (b) 0.3% Fe- TiO_2 ; (c) 0.5% Fe- TiO_2 ; (d) 0.7% Fe- TiO_2 .

TABLE 3: Specific rate comparisons with other studies for the photocatalytic degradation of toluene.

Catalyst	kK (min^{-1}) (¹)	Coated area (m^2) (²)	Intensity ($\text{mW} \cdot \text{m}^{-2}$) (³)	Specific rate ($\text{min}^{-1} \cdot \text{mW}^{-1}$) (¹)/(²) $\times$ (³)	Reference
Ag/ TiO_2	0.04	0.12	5800	5.74×10^{-5}	[19]
TiO_2	0.15	0.03	20,950	2.39×10^{-4}	[20]
TiO_2	0.02			2.00×10^{-3}	
0.3% Fe- TiO_2	0.04	0.01	1000	4.00×10^{-3}	This study
0.5% Fe- TiO_2	0.05			5.00×10^{-3}	
0.7% Fe- TiO_2	0.07			7.00×10^{-3}	

The optical band gaps for the thin films are listed in Table 1. To estimate the band gap energies, the absorption onsets of the samples were determined by linear extrapolation from the inflection point of the curve to the baseline [29, 30]. The band gap, E_g , was obtained from a linear regression of $(\alpha h\nu)^{1/2}$ against $h\nu$ with extrapolation to zero (Equation (1), often called a Tauc plot) [1, 29–32]:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g), \quad (1)$$

where α is the absorbance, arbitrary units; $h\nu$ is photon energy, eV; A is an independent parameter of the photon's energy for the respective transitions, eV; E_g is the band

gap, eV. Since the band gap of anatase was 3.2 eV, the results indicated that the structure of TiO_2 in the thin film was indeed anatase. Increasing Fe^{3+} dopant concentration in TiO_2 thin films greatly enhanced their absorption band and clearly narrowed the band gap from 3.27 eV to 2.82 eV and which was suitable for application as a catalyst in the photocatalytic process. A similar effect on the band gap has also been reported by several researchers, for example, Zhang et al. [33].

The 2D AFM images of the TiO_2 and Fe- TiO_2 thin films on stainless steel substrate are shown in Figure 4. The data for surface morphology are summarized in Table 1. The grain sizes, the root mean square (rms) average roughness,

FIGURE 5: Photocatalytic degradation of toluene with various Fe-TiO₂ catalysts using UV-LED light source. (a) TiO₂, (b) 0.3% Fe-TiO₂, (c) 0.5% Fe-TiO₂, and (d) 0.7% Fe-TiO₂.

and the apparent surface areas of all thin films were in the same range. However, the total apparent surface area per unit weight of TiO₂ and the BET surface area tended to increase with the amount of Fe³⁺ added. The data indicated that the coating process used in this study could achieve a particle size of 30 nm, a suggested optimum size for light absorption and scattering efficiencies [34].

Adhesion testing of all of the TiO₂ thin films yielded a classification in class 4B (good adhesion) [21]. The results imply that the calcination temperature used in this study (500°C) was sufficiently high to create good adhesion of TiO₂ films on surfaces [35]. The corrosion-resistance test indicated that the TiO₂ thin films could resist corrosion without any visible damage (Table 1).

3.2. Photocatalytic Activity of Toluene. A series of tests of photocatalytic degradation for various initial concentrations of toluene vapor with different catalysts evaluated the

decomposition efficiency (η) of toluene. The value of η was calculated from

$$\eta = \frac{(C_0 - C)}{C_0} \times 100\%, \quad (2)$$

where C_0 is the initial concentration of toluene (ppmv) and C is the concentration of toluene at time t (ppmv). The photocatalytic degradation of toluene according to the initial concentration is shown in Figure 5.

The data showed that the Fe-TiO₂ catalyst was more active than TiO₂ alone. It indicated that this modification could promote the activity of the TiO₂ catalyst to a certain extent, since the Fe³⁺ ions created more chance to generate electron-hole pairs. Consequently, the amount of hydroxyl radicals ($\cdot\text{OH}$), which are highly oxidative species in the photocatalytic oxidation reaction, would increase [11, 36]. Therefore, the photocatalytic activity could be improved by increasing the Fe³⁺ dopant concentration [33, 37]. The improvement in the photoactivity could be caused by

FIGURE 6: L-H plots of r_0^{-1} versus C_0^{-1} for toluene with various Fe-TiO₂ catalysts using a UV-LED light source. (a) TiO₂, (b) 0.3% Fe-TiO₂, (c) 0.5% Fe-TiO₂, and (d) 0.7% Fe-TiO₂.

the combined effects of the crystalline structure, the optical band gap, grain size, and the surface area of the catalyst [38–42]. The photocatalytic degradation efficiency of Fe-TiO₂ thin films increased and reached a maximum when the Fe³⁺ dopant concentration was 0.7%. Piera et al. [38] and Khan et al. [43] showed that the Fe³⁺ ions in TiO₂ thin films were responsible for a reduction in the photogenerated hole-electron recombination rate. This corresponded to the reduction in the optical band gaps of the Fe-TiO₂ thin films. The active sites in the Fe-TiO₂ thin film could effectively capture the electrons and prolong the lifetime of photogenerated charges, thereby increasing the efficiency of charge separation and transfer of Fe-TiO₂ [44]. It is believed that the efficiency of a photocatalyst depends on quantum efficiency of the photo generation of the electron-hole pair [33, 44]. Moreover, the degradation rate of toluene by the Fe-TiO₂ films can be enhanced due to increased surface area [36]. In this study, the maximum concentration of Fe³⁺ dopant of 0.7% showed the highest photocatalytic activity.

The kinetic modeling of the photocatalytic process followed the Langmuir-Hinshelwood model (L-H model), which can be expressed as [45]

$$r = \frac{kKC}{(1 + KC)}, \quad (3)$$

where k is the reaction rate constant ($\text{mol} \cdot \text{m}^{-3} \cdot \text{min}^{-1}$), K is the adsorption equilibrium constant ($\text{m}^3 \cdot \text{mol}^{-1}$), and C is the concentration of toluene ($\text{mol} \cdot \text{m}^{-3}$). This model usually analyzed the initial rate of photocatalytic degradation. The initial photocatalytic degradation rate, r_0 ($\text{mol} \cdot \text{m}^{-3} \cdot \text{min}^{-1}$) is observed to be a function of the initial concentration of toluene (C_0). According to (4), a linear L-H plot of r_0^{-1} versus C_0^{-1} is obtained and the L-H rate constant, k , and the Langmuir adsorption constant, K , of toluene in the photocatalytic degradation reaction can be calculated:

$$\frac{1}{r_0} = \frac{1}{kKC_0} + \frac{1}{k}. \quad (4)$$

The L-H plots of r_0^{-1} versus C_0^{-1} for toluene with various Fe-TiO₂ catalysts using a UV-LED light source are shown in Figure 6. The kinetic parameters k and K of the photocatalytic degradation reaction are summarized in Table 2.

The effect of toluene concentration on toluene degradation with a UV-LED light source and TiO₂ thin films could be well defined by the L-H kinetic equation. The results of the overall photocatalytic degradation efficiency of this study are quite low, between 13.56% and 36.51% within 60 min. This could be mainly due to the UV-LED light source

used in our experiments providing a UV-light intensity of only $1000 \text{ mW} \cdot \text{m}^{-2}$. In terms of the photocatalytic kinetic constants, both the reaction rate constant (k) and the adsorption equilibrium constant (K) increased with increasing concentration of Fe^{3+} dopant (Table 2). When comparing the kinetics results from this study to those of other studies using different light intensities and a similar catalyst for toluene degradation, we found that the values of the overall reaction rate constants, kK , from this study were lower than those of Kim and Hong [20] for TiO_2 catalyst, but were comparable to those of Shie and Pai [19] for Ag/TiO_2 catalyst (Table 3). However, the specific rates calculated in this study were around $10^{-3} \text{ min}^{-1} \cdot \text{mW}^{-1}$, which is about one to two orders of magnitude higher than those in the other studies (Table 3). The results indicated that the enhanced activity of the photocatalytic process using Fe^{3+} could potentially be applied for photocatalytic degradation of VOCs using a UV-LED light source. This indicated that, in further applications, the degradation efficiency can be improved by increasing the surface area coating of the photocatalyst, increasing the intensity of the UV-LED light source, and reducing the distance between the light source and catalyst.

4. Conclusions

The prepared TiO_2 and $\text{Fe}-\text{TiO}_2$ thin films had desirable physical properties including anatase crystalline structure, nano-sized grains, good mechanical stability, and good corrosion resistance and could be suitable catalysts in various photocatalytic processes. Increasing the Fe-doping amount in TiO_2 thin films decreased the optical band gaps and enhanced the performance of the photocatalytic process under UV-LED light irradiation. The photocatalytic degradation efficiency of toluene increased as the amount of Fe^{3+} dopant increased and reached its maximum efficiency at 0.7%. The values of the reaction rate constants from this study are in the order of $10^{-3} \text{ min}^{-1} \cdot \text{mW}^{-1}$ with specific rates in the range of $2.00 \times 10^{-3} - 7.00 \times 10^{-3} \text{ min}^{-1} \cdot \text{mW}^{-1}$.

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