Research Article

TiO₂ Transparent Thin Film for Eliminating Toluene

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TiO₂ nanoparticles undergo a single-phase transition: from amorphous to anatase when calcined at 450°C. It can be noticed from the XRD and AFM results that the particle size of TiO₂ is below 30 nm. Results from viscometer and UV-Vis analysis showed that the film thickness is closely related to the viscosity of dip-coating solutions. It was found that the contact angle for water decreased after being illuminated with UV light at certain periods of time. This indicates that these films exhibit hydrophilic properties that can be used on self-cleaning surfaces and antifogging mirrors. Heterogeneous photocatalytic oxidation allows the oxidation of airborne volatile organic compounds (VOCs) into carbon dioxide and water in the presence of a semiconductor catalyst and UV light source. Titanium dioxide, due to its chemical stability, nontoxicity, and low cost, represents one of the most efficient photocatalysts. Photocatalytic activity of the TiO₂ thin films was evaluated by using toluene and results showed that this film is successful in decomposing toluene.

1. Introduction

“Volatile organic compound” is a blanket term that encompasses many different organic or carbon-based compounds molecules that are used in a broad array of different products with a boiling point range of 50 to 260°C [1]. The low boiling point means that the compound will readily emit gas vapours into the air at ambient temperatures. At high concentrations, some VOCs are toxic or may be carcinogenic. Some common and potentially hazardous VOCs are formaldehydes, benzene, toluene, m-xylene, acetone, and tetrachloroethylene (TeCE) that can be found at home [2]. As these substances possess very serious health hazards, the Environmental Protection Agency (EPA) of most countries considers all of these compounds priority pollutants. The concentration of single VOCs was reviewed to be generally below 15 ppb with most below 1.5 ppb [3]. In any given environment, the concentration of individual VOCs will

be variable and dependent upon the presence of potential emission source.

This research however will be focused on the use and effects of toluene as toluene vapours are more often found in homes like in paint thinners, paint brush cleaners, nail polish, glues, inks, stain removers, and fragrances. Although the primary sources of toluene emissions are crude petroleum and natural gas extraction, petroleum refining, and household furniture manufacturing facilities, it is also emitted from tobacco smoke. Toluene affects the nervous system and high exposure of toluene may affect the kidneys. The US EPA has established a reference concentration of 162 ppb for toluene based on neurological effects in humans and has set a limit of 3×10^{-4} ppm in drinking water [4]. The inhalation of this concentration or less, over a lifetime, would not likely result in the occurrence of chronic noncancer effects.

However, most frequently, these volatile organic compounds are present in dilute form, making the commonly

available abatement technology, such as thermal and catalytic oxidation technologies, energy- and cost-intensive. Therefore, it is imperative to develop alternative technologies that are more economical and energy efficient. Among these alternatives, photocatalysis have shown to be the most promising technology. In order to alleviate these problems, the engineering properties of TiO_2 must be improved and several approaches have been taken by researchers in this field. One of the most widely used techniques is to immobilize the TiO_2 as thin film on various supports including glass, stainless steel, quartz, silica gel, and glass beads. The idea of immobilizing TiO_2 in the form of a thin film was first recognized by Fujishima and Honda 1972 [5]. They found that the thin film photocatalysts had a lower surface area than in the powdered form, resulting in a lower photocatalytic activity. Further research data has shown that TiO_2 in its film form, had a porous structure and exhibited high photoactivity towards organic degradation. Since then, the TiO_2 thin film has emerged as a plausible photocatalyst in environmental applications. TiO_2 , when immobilized on various supports, can be separated from the effluent much easier than its powder form [6] and it can eliminate the problem of shadowing effect.

TiO_2 thin films have been prepared by variety of deposition techniques such as chemical vapor deposition [7], reactive sputtering [8, 9], atomic layer deposition [10], filtered arc deposition [11], pulse laser deposition [12], spray pyrolysis [13, 14], and sol-gel method [15–19]. However, in this study we applied another prominent method that is thermal decomposition that used viscous solvent [20]. By this thermal decomposition method, we can avoid the titanium alkoxide from being hydrolyzed in air since the viscous solvent protects the titanium alkoxide from water in ambient air. In this study, we will discuss the preparation method of transparent TiO_2 thin films and the evaluation of its photocatalytic activity for the elimination of toluene.

2. Experimental

2.1. Sample Preparation. For the preparation of TiO_2 thin films, tetrapropoxy (ortho) titanate (TPOT) (Wako Chemical) (as a TiO_2 precursor), α -terpineol (Wako Chemical) and 2-propanol (Wako Chemical) (as a solvent), (2-(2-ethoxyethoxy) ethanol) (EEE) (Wako Chemical), (as ligand for TiO_2), while hydroxypropyl cellulose (HPC) Mw 80 K and 370 K (Aldrich), and polyethylene imine (PEI) Mw 600, and 1800 (Wako Chemical) were used as polymer additives. Silica-coated glass plates ($100 \times 150 \times 1.1 \text{ mm}^3$) was used as a substrate. The withdrawing speed of the glass plate from the dip-coating solution was 1.5 mm/s. The dip-coated glass plates were treated at 450°C for 1 hour, through 10 dip coating cycles.

2.2. Characterization. The viscosity of the dip coating solution was measured by using a Brookfield DV-I viscometer. The thermal analysis was carried out using a Shimadzu TG/DTA 50 thermal analyser between room temperature and 800°C under flowing air (20 mL/min). The transmittance

spectrum was measured using a Shimadzu UV 3600 UV-Vis double-beam spectrometer. The contact angle on each film was determined with a Drop Master 300 (Kyowa Interface Sci. Co.). The surface texture of the film was observed by atomic force microscopy (AFM; Shimadzu SPM 9300 J). The film crystal structure was observed by using a Rotaflex RU 300. The surface area of the thin film was measured by using Quantachrome AS-1 with N_2 adsorption.

2.3. Photocatalytic Measurement. The photocatalytic activities of TiO_2 thin film were tested using 1 ppm of toluene in air using the device shown in Figure 1. Dry air was mixed with water saturated air to obtain a relative humidity (RH) of 50% taking into account a low flow rate of dry N_2 containing the organic pollutant. The RH was checked with humidity sensor (CHINO MR 6661). The size of the TiO_2 thin film coated placed into the photocatalytic reactor was $100 \times 50 \times 1.1 \text{ mm}^3$. A 10 W black light lamp ($\lambda = 358 \text{ nm}$) was used. The irradiance at the surface of the photocatalyst was 1 mW/cm^2 . Each sample was pretreated under UV irradiation for 16 h in order to clean the photocatalyst surface. Air contaminated with toluene was then flowed at 0.5 L/min in the dark for 30 minutes to reach absorption equilibrium. After that the sample was UV-irradiated for 180 minutes. Changes in toluene concentration were measured with a FID Shimadzu GC-14A gas chromatograph. The evaluation for this photocatalytic activity is following to Japanese Industrial Standard (JIS R 1701-3) [21].

3. Result and Discussion

3.1. Thermal Analysis. The thermal stability and phase transformation of the prepared TiO_2 gel was investigated by obtaining the first derivative of the DTA and TG curves. The results are shown in Figure 2. The initial weight loss occurs at temperature below 100°C , indicating that propanol and water started to evaporate from the gel. Another weight loss occurs in stages as temperature reached 200°C until 420°C which could be attributed to decomposition of various organic compound used during preparation of TiO_2 gel that may include nonhydrolyzed tetrapropoxy (ortho) titanate, terpineol, and hydroxypropyl cellulose. Beyond that, there is no more weight loss as all volatile organic compounds have been removed. From the DTA curves, a sharp exothermic reaction peak appears at temperature of about 420°C , indicating phase transformation occurred as gel started to transform from amorphous phase to crystalline anatase. This finding suggested, the optimum calcination temperature for the gel can be carried out from 420°C to 500°C . Hence, for the purpose of this research, 450°C was selected as the appropriate calcination temperature for the preparation of the TiO_2 films.

3.2. Viscosity and Film Thickness. The relationship between solution viscosity and film thickness was seen as linear, although we used different polymer additives with and without additions of viscous solvent (alpha terpineol) while keeping the dip-coating withdrawal speed (approximately

FIGURE 1: Schematic diagram of reactor for flat test pieces (a) full diagram, (b) cross-sectional view of photoreactor.

1.5 mm/s) as shown in Figure 3. From this linear graph, we obtained the following:

$$t = \frac{\eta}{13.96}, \quad (1)$$

where t indicates the film thickness, η is the solution viscosity. Using this equation we can calculate the required film thickness for certain solution viscosity. This suggests that the film thickness is dependent on the solution viscosity. These results concur with the work of Menaa et al. [22], Negishi and Takeuchi [23], and Akbarzadeh et al. [24] as they observed that, as the viscosity of the solution increased, the film thickness also increased. As expected, as the solution viscosity increased from 19.02 cP to 59.01 cP, the thickness also increases from 1.6 μm (1600 nm) to 4.0 μm (4000 nm). All of these films had a very good adhesion and scratch resistance as well.

As all the prepared films are transparent, the film thickness was calculated from the transmittance spectra of TiO_2 films using this equation [23]:

$$d = \frac{\lambda_1 \lambda_2}{2n(\lambda_2 - \lambda_1)}, \quad (2)$$

whereby d represents film thickness, λ_1 and λ_2 are the wavelengths of adjacent pairs of minima or maxima, and $n = 2.1$ is the refractive index of TiO_2 thin films. The n value obtained was lower than that of anatase TiO_2 ($n = 2.52$) and could be related to the porous nature of the film produced. The refractive indexes of porous TiO_2 thin films were known to be lower than those of fine TiO_2 thin films. Our results indicated that the TiO_2 thin films developed in this work, with a maximum thickness of 4 μm , were transparent and porous in structure.

As can be seen, the film thicknesses for all the solutions that consist of alpha-terpineol were much higher compared to the solutions without the addition of alpha-terpineol. In

TABLE 1: Contact angle of the TiO₂ thin films for the 10 numbers of coatings.

Contact angle	HPC 80 K with alpha-terpineol	HPC 370 K with alpha-terpineol	PEI 600 wo alpha-terpineol	PEI 600 with alpha-terpineol	PEI 1800 wo alpha-terpineol	PEI 1800 with alpha-terpineol
Before UV irradiation	14.7	17.6	14.9	16.8	18.2	21.3
After a 30 mins UV irradiation	7.3	8.6	7.1	7.9	10.1	12.5
After a 60 mins UV irradiation	3.5	4.5	4.2	5.9	5.0	6.3

FIGURE 2: Thermal gravimetric (TG) and differential thermal analysis (DTA) curves for a TiO₂ gel.

FIGURE 3: Relationship between the solution viscosity and the film thickness under a withdrawing speed of 1.5 mm/s for the 10 number of coatings.

this case alpha terpeneol acts as a viscous solvent, hence, the number of coatings can be reduced. Figure 4 shows the optical properties of the TiO₂ thin film for a 10-layer coating of HPC 80 k and PEI 1800 with terpeneol samples. Results indicate that the average percentage of light transmission in visible range regions (above 400 nm), are different for both samples. As for HPC samples, light transmitted is above 90% compared to other PEI samples. This result suggests that the film thickness of HPC samples is much thinner compared to

(a)

(b)

FIGURE 4: Optical properties of the TiO₂ films for the 10 numbers of coatings (a) HPC 80 K and (b) PEI 1800 with alpha terpeneol samples.

the PEI samples, hence its capability to transmit light is more effective.

3.3. Water Contact Angle. The water contact angle for films were measured following the Japanese Industrial Standard method (JIS R-1703-1) [24]. Results are shown in Figure 5 and tabulated in Table 1. In this study, samples were not coated with oleic acid to keep the UV irradiation time frame

FIGURE 5: Diagram of water contact angle experiment for TiO₂ thin films after 10 numbers of coatings.

below 60 minutes. It was observed that the water contact angle of each prepared film decreased after being irradiated under ultraviolet light for specific durations. Before UV irradiation, the contact angle of the water droplets on the surface increased (Table 1). After irradiation at 365 nm for 60 mins with 1 mW/cm², the contact angle decreased to around 3–7°. On a side note observation, these measurements indicate the TiO₂ films possess self-cleaning and superhydrophilic properties.

3.4. Phase Identification. All prepared samples were subjected to XRD analysis to determine the phases present in each samples along with the crystallite sample sizes. The crystallite size is determined from the broadening of corresponding X-ray spectral peaks by Scherrer's equation [25]:

$$L = \frac{K\lambda}{\beta \cos \theta}, \quad (3)$$

where L is the crystallite size, λ is the wavelength of the X-ray radiation ($\text{CuK}\alpha = 0.15418$). K is taken as 0.89 and β is the line width at half maximum height. This is a generally accepted method to estimate the mean crystallite size of nanoparticle.

Figure 6 shows the XRD patterns of transparent TiO₂ thin films calcined at 450°C. The XRD spectrum shows that all samples are well crystallized. Five distinctive TiO₂ peaks can be found at 2θ of 25.25°, 37.8°, 48.0°, 53.9°, and 55.1° corresponding to anatase (101), (004), (200), (105) and (211) crystal planes (JCPDF 21-1272), respectively, which indicate that the TiO₂ exists in the form of anatase phase after calcined at 450°C. Similar observations were found with works done by Chan et al. [26]. There were no observable rutile phases in all samples. Hence, we conclude that 100% of anatase phase were formed in each of our prepared samples. Thus, the diffraction spectrum of nanoparticles becomes broader and weaker. The average crystallite size of nanoparticle TiO₂ films were calculated to be around 13–15 nm (XRD) and 6–15 nm (AFM) (refer to Table 2).

FIGURE 6: XRD profile of the transparent TiO₂ thin films at calcinations temperature 450°C.

TABLE 2: Crystallite size of TiO₂ thin films after 10 numbers of coatings.

TiO ₂ thin films	Crystallite size (nm)	
	XRD	AFM (refer Figure 6)
HPC 80 K with alpha-terpineol	15.55	14.54
HPC 370 K with alpha-terpineol	15.25	13.96
PEI 600 with alpha-terpineol	13.70	6.39
PEI 1800 with alpha-terpineol	13.16	7.99

3.5. Surface Structure and Areas. Figure 7 shows the AFM images of the TiO₂ thin film surface after 10 coatings. The images reveal that all these films consist of smoothly aggregated nano-TiO₂ particles with average diameter 6–15 nm, which are in agreement with the crystallite sizes calculated by XRD patterns. However, it was observed that the particle and surface structure of films prepared by HPC system are slightly larger and rough compared to

FIGURE 7: AFM images of the TiO_2 thin films after 10 numbers of coatings (a) HPC 80 K, (b) HPC 370 K, (c) PEI 600, and (d) PEI 1800 with α -terpineol.

the films prepared by PEI system. This striking difference in the surface structure can be explained by the different size of molecular polymers. Larger polymers will affect the interaction between ligand (EEE) and alkoxide (TPOT) to

become loose and weak [22]. Hence, the large particles grew and accumulated on the surface. The result of BET surface area measurements are presented in Table 3. The surface area of all of these films is around $78\text{--}86\text{ m}^2/\text{g}$.

TABLE 3: Surface area of TiO_2 thin films after 10 numbers of coatings.

TiO_2 thin film Photocatalysts	Surface area, m^2/g
HPC 80 K with alpha-terpineol	78.92
HPC 370 K with alpha-terpineol	80.23
PEI 600 with alpha-terpineol	85.78
PEI 600 without alpha-terpineol	82.12
PEI 1800 with alpha-terpineol	86.90
PEI 1800 without alpha-terpineol	81.09

FIGURE 8: Film thickness and percentage removal of toluene in the presence of TiO_2 thin films photocatalysts.

3.6. Photocatalytic Activity. Photocatalytic degradation of toluene using substrate coated with TiO_2 film developed in this work was conducted under UV irradiation emitted from a 10 W black light lamp ($\lambda = 358 \text{ nm}$) that produced a UV intensity of $1 \text{ mW}/\text{cm}^2$. The plots indicating toluene degradation are presented in Figure 9. It was found that thicker films degraded faster compared to thinner films. A higher rate of toluene removal with an increase in film thickness, could be attributed to the increased amount of TiO_2 involved in photocatalytic reactions.

It can be noticed that with the PEI 1800 thin films, TiO_2 prepared with alpha-terpineol showed the highest percentage of toluene removal when compared to other films. This is due to the fact that TiO_2 films produced from this route had smaller particles and a larger surface area that results in the efficient removal of toluene. This smaller particle size is responsible for forming more charge carriers at the photocatalyst surface that resulted in enhanced photocatalytic efficiency. PEI 1800 films also displayed a higher UV light transmittance. Hence, light can efficiently irradiate to the interior regions of the film. This characteristic contributes to the increase in electrons and holes generated in TiO_2 films and results in an increased rate of photochemical reactions. As PEI 1800 films have a larger surface area, it enables more reactants (toluene) on its contact surface.

FIGURE 9: Photodegradation of toluene in the presence of TiO_2 thin films photocatalysts.

It is important to underline that reaction kinetic studies are only started after completion of dark experiments (30 mins) to allow the equilibrium of adsorption/desorption of toluene gas on the TiO_2 thin film surface. In the absence of light, no important variation in the relative concentration is observed (Figure 9), suggesting that toluene does not degrade and it is under dynamic equilibrium at the catalyst or thin film surface (adsorbs and desorbs at the same rate).

Reduction of toluene concentration is observed when reaction occurs under UV-Vis light (Figure 9). For all samples, the most intense decrease in toluene concentrations are observed 5 minutes after UV-irradiation begins followed by a slow degradation process. However, the most intense decreases in toluene concentrations are shown in PEI 1800 and PEI 600, that is, samples with additions of alpha-terpineol. For these samples, almost 50% of the toluene were removed during the first 5 minutes of UV-irradiation. The high efficiency of these particular samples were due to the fact that samples prepared with addition of alpha-terpineol not only led to smaller crystallite size of anatase nanocrystal that formed during calcination, but it also acquired higher specific surface area, that is, $87 \text{ m}^2/\text{g}$ and $86 \text{ m}^2/\text{g}$ for PEI 1800 and PEI 600, respectively. In comparison, samples prepared without addition of alpha-terpineol, resulted in surface areas of $81 \text{ m}^2/\text{g}$ and $82 \text{ m}^2/\text{g}$ for PEI 1800 and PEI 600, respectively. Samples with higher surface areas can effectively adsorb more molecules and receive more UV light as well as offer more reaction sites. Therefore it is believed that the thicker film may play a role as an adsorbent layer. The summary of the physical, optical, and photocatalytic properties for all the prepared photocatalysts is shown in Table 4.

TABLE 4: Summary of the Physical and Photocatalytic Properties for all the prepared Photocatalysts.

Photocatalysts	Film thickness μm	Surface area m^2/g	Concentration toluene ppm	Amount of toluene removed $\mu\text{mol/hr}$	Percentage of toluene remove %
HPC 80 K with alpha terpineol	2.06	78.92	0.99	0.48	35.46
HPC 370 K with alpha terpineol	2.56	80.23	0.98	0.52	38.84
PEI 600 with alpha terpineol	3.45	85.78	0.98	0.61	45.97
PEI 600 without alpha terpineol	2.96	82.12	1.00	0.57	42.22
PEI 1800 with alpha terpineol	3.95	86.90	0.99	0.77	57.10
PEI 1800 without alpha terpineol	3.25	81.09	1.00	0.58	43.10

4. Conclusion

Transparent TiO_2 thin films are prepared by thermal decomposition methods. Results indicate a linear relationship between solution viscosity and film thickness. The rate of increase in the film thickness is dependent on the solution viscosity. We also conclude that 450°C is the most appropriate calcination temperature for the preparation of TiO_2 thin films while considering the main factors such as properties of TiO_2 nanoparticles and the adhesion of nanoparticle TiO_2 film to SiO_2 glass (substrate). The crystallite structure obtained was TiO_2 anatase alone and the size of the crystallite of TiO_2 anatase were around 13–15 nm (XRD) and 6–15 nm (AFM). The optical properties of the TiO_2 thin film for 10 coatings showed that as for HPC samples, light transmittance is above 90% as compared to other PEI samples. It shows the change of water contact angles on these films after 60 mins of UV irradiation is around 3.5–6.5 degree. The surface area of all of these films is around 78–86 m^2/g . Lastly, it can be seen that from the photocatalytic activity, the toluene removal by the catalyst increases with the increase in film thickness. This also indicates a possible increase in the amount of nanoparticle TiO_2 participating in the photocatalytic reaction.

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References

- [1] A. P. Jones, "Indoor air quality and health," *Atmospheric Environment*, vol. 33, no. 28, pp. 4535–4564, 1999.
- [2] WHO, "Indoor air quality: organic pollutants," Report on a WHO meeting, EURO Report and Studies, 1989.
- [3] P. Wolkoff and G. D. Nielsen, "Organic compounds in indoor air-their relevance for perceived indoor air quality?" *Atmospheric Environment*, vol. 35, no. 26, pp. 4407–4417, 2001.
- [4] ATSDR, Agency for Toxic Substances and Disease Registry. Toxicological Profile for toluene. Atlanta, Ga, USA: U.S. Department of Health and Human Services, Public Health Service, 2000.
- [5] A. Fujishima and K. Honda, "Electrochemical photolysis of water at a semiconductor electrode," *Nature*, vol. 238, no. 5358, pp. 37–38, 1972.
- [6] C. Anderson and A. J. Bard, "An improved photocatalyst of $\text{TiO}_2/\text{SiO}_2$ prepared by a sol-gel synthesis," *Journal of Physical Chemistry*, vol. 99, no. 24, pp. 9882–9885, 1995.
- [7] P. Babelon, A. S. Dequiedt, H. Mostéfa-Sba, S. Bourgeois, P. Sibillot, and M. Sacilotti, "SEM and XPS studies of titanium dioxide thin films grown by MOCVD," *Thin Solid Films*, vol. 322, no. 1-2, pp. 63–67, 1998.
- [8] D. Mardare, M. Tasca, M. Delibas, and G. I. Rusu, "On the structural properties and optical transmittance of TiO_2 r.f. sputtered thin films," *Applied Surface Science*, vol. 156, no. 1, pp. 200–206, 2000.
- [9] F. M. Liu and T. M. Wang, "Surface and optical properties of nanocrystalline anatase titania films grown by radio frequency reactive magnetron sputtering," *Applied Surface Science*, vol. 195, no. 1–4, pp. 284–290, 2002.
- [10] J. Aarik, A. Aidla, T. Uustare, M. Ritala, and M. Leskelä, "Titanium isopropoxide as a precursor for atomic layer deposition: characterization of titanium dioxide growth process," *Applied Surface Science*, vol. 161, no. 3, pp. 385–395, 2000.
- [11] A. Bendavid, P. J. Martin, and H. Takikawa, "Deposition and modification of titanium dioxide thin films by filtered arc deposition," *Thin Solid Films*, vol. 360, no. 1-2, pp. 241–249, 2000.
- [12] T. Sumita, T. Yamaki, S. Yamamoto, and A. Miyashita, "Photo-induced surface charge separation of highly oriented TiO_2 anatase and rutile thin films," *Applied Surface Science*, vol. 200, no. 1–4, pp. 21–26, 2002.
- [13] M. O. Abou-Helal and W. T. Seeber, "Preparation of TiO_2 thin films by spray pyrolysis to be used as a photocatalyst," *Applied Surface Science*, vol. 195, no. 1–4, pp. 53–62, 2002.
- [14] L. Castaneda, J. C. Alonso, A. Ortiz, E. Andrade, J. M. Saniger, and J. G. Banuelos, "Spray pyrolysis deposition and characterization of titanium oxide thin films," *Materials Chemistry and Physics*, vol. 77, no. 3, pp. 938–944, 2002.
- [15] M. C. Blount and J. L. Falconer, "Characterization of adsorbed species on TiO_2 after photocatalytic oxidation of toluene," *Journal of Catalysis*, vol. 200, no. 1, pp. 21–33, 2001.
- [16] T. Noguchi, A. Fujishima, P. Sawunyama, and K. Hashimoto, "Photocatalytic degradation of gaseous formaldehyde using TiO_2 film," *Environmental Science and Technology*, vol. 32, no. 23, pp. 3831–3833, 1998.
- [17] I. Sopyan, M. Watanabe, S. Murasawa, K. Hashimoto, and A. Fujishima, "An efficient TiO_2 thin-film photocatalyst: photocatalytic properties in gas-phase acetaldehyde degradation," *Journal of Photochemistry and Photobiology A*, vol. 98, no. 1-2, pp. 79–86, 1996.
- [18] Y. Xu, W. Zheng, and W. Liu, "Enhanced photocatalytic activity of supported TiO_2 : dispersing effect of SiO_2 ," *Journal of*

- Photochemistry and Photobiology A*, vol. 122, no. 1, pp. 57–60, 1999.
- [19] M. E. Zorn, D. T. Tompkins, W. Zeltner, and M. A. Anderson, “Catalytic and photocatalytic oxidation of ethylene on titania-based thin-films,” *Environmental Science and Technology*, vol. 34, no. 24, pp. 5206–5210, 2000.
- [20] N. Negishi, S. Matsuzawa, K. Takeuchi, and P. Pichat, “Transparent micrometer-thick TiO_2 films on SiO_2 -coated glass prepared by repeated dip-coating/calcination: characteristics and photocatalytic activities for removing acetaldehyde or toluene in air,” *Chemistry of Materials*, vol. 19, no. 15, pp. 3808–3814, 2007.
- [21] JIS R 1701-3, “Fine ceramics (advanced ceramics, advanced technical ceramics),” in *Test Method for Air Purification Performance of Photocatalytic Materials*, Removal of Toluene.
- [22] B. Mena, M. Takahashi, Y. Tokuda, and T. Yoko, “Preparation and properties of polyphenylsiloxane-based hybrid glass films obtained from a non-aqueous coating sol via a single-step dip-coating,” *Optical Materials*, vol. 29, no. 7, pp. 806–813, 2007.
- [23] N. Negishi and K. Takeuchi, “Preparation of a transparent thin-film photocatalyst for elimination of VOC,” *Research on Chemical Intermediates*, vol. 29, no. 7–9, pp. 861–879, 2003.
- [24] R. Akbarzadeh, S. B. Umbarkar, R. S. Sonawane, S. Takle, and M. K. Dongare, “Vanadia-titania thin films for photocatalytic degradation of formaldehyde in sunlight,” *Applied Catalysis A*, vol. 374, no. 1-2, pp. 103–109, 2010.
- [25] B. R. York, “New X-ray diffraction line profile function based on crystallite size and strain distributions determined from mean field theory and statistical mechanics,” in *Advances in X-ray Diffraction*, 1997.
- [26] C. C. Chan, C. C. Chang, W. C. Hsu, S. K. Wang, and J. Lin, “Photocatalytic activities of Pd-loaded mesoporous TiO_2 thin films,” *Chemical Engineering Journal*, vol. 152, no. 2-3, pp. 492–497, 2009.