

## Structure and Photocatalytic Characteristics of TiO<sub>2</sub> Thin Film Coated on Stainless Steel for Chromium (VI) Removal Application

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### ABSTRACT

*In this work, TiO<sub>2</sub> films with high photocatalytic activities were coated on stainless steel plate by the sol-gel method. Stainless steel plate is a good substrate due to its large surface area, being corrosion-resistant and commercially-available. It was found that TiO<sub>2</sub> films exhibited a uniform surface with high in anatase structure. With increasing of calcination temperature, the higher amount of anatase and the bigger size of nanoparticle in the films were obtained. With multiple coating cycles of the thin film, the increase of thickness can be expected. The photocatalytic activity in chromium(VI) removal of the TiO<sub>2</sub> film coated on stainless steel plate can be related to its crystallization and the thickness. Thicker and better crystallization of TiO<sub>2</sub> film resulted in its higher photocatalytic activity which was evaluated by the photocatalytic reduction of chromium (VI) in a cylindrical photoreactor. Results showed that chromium (VI) was successfully removed from aqueous solution in photocatalysis system using the obtained thin film in which percentage of anatase phase, nanoparticle size, and film thickness were major parameters controlling the photoactivity.*

**Key words:** TiO<sub>2</sub> (Titanium dioxide), Thin film, Photocatalysis, Chromium(VI)

### INTRODUCTION

Photocatalytic process has been of continuous interest in the treatment and purification of air and water since it can complete the reduction of metal ions. Furthermore, organic species can be completely mineralized to carbon dioxide or become nontoxic materials by photocatalytic pathway. Titanium dioxide (TiO<sub>2</sub>) has been widely used as a photocatalyst due to its activity, photostability, non-toxicity and commercial availability (Oppenländer, 2003). As a result of the cost and difficulties in separating the TiO<sub>2</sub> particles from the suspension after completion of the reaction, the powder TiO<sub>2</sub> application is not found to be practical for commercial use (Matthews, 1987; Hilmi et al., 1999; Zhang et al., 2003). In order to overcome these disadvantages, preparations of TiO<sub>2</sub> thin film have been developed by different techniques, for example, chemical vapor deposition, chemical spray pyrolysis, electrodeposition and the sol-gel method. Many researches have focused on preparation by the sol-gel process since this method is very simple, easy to operate and can be applied to complex surfaces or large surface areas. Moreover, this technique is suitable for thin film deposition

on many substrates such as stainless steel, alumina, silica/glass, etc., (Pozzo et al., 1997; Sonawane et al., 2002). By controlling the photocatalytic property, the synthetic TiO<sub>2</sub> thin film can be used in industrial application.

The main objective of this work was to synthesize TiO<sub>2</sub> thin film which was coated on stainless steel, using the sol-gel method for photocatalytic reduction of chromium(VI). In this work, stainless steel was selected as a substrate as it was inexpensive, having large surface area, corrosion-resistant and commercially-available. Besides, it can be modified to any shape that is suitable for photoreactor. For application of the developed thin film TiO<sub>2</sub> on stainless steel, chromium was selected as the tested pollutant as it is frequently found in effluent streams discharging from chrome plating, electronic, metallurgical and leather-tanning industries (Richard, 1998; Schrank et al., 2002). The structure of the TiO<sub>2</sub> coated on stainless steel plate was related to its photocatalytic activity and tested in a photoreactor with chromium (VI) as the model pollutant. The results confirmed that the sol-gel method was a good way to prepare anatase TiO<sub>2</sub> film coated on stainless steel firmly and this film exhibited high photocatalytic activity for the photocatalytic reduction of chromium(VI).

## MATERIALS AND METHODS

### Materials

All chemicals in this research were of analytical grade and were used as received. Titanium tetraisopropoxide (Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>) or TTiP obtained from Aldrich and absolute ethanol supplied by Merck were used as a Ti-precursor and a solvent, respectively. Polyethylene glycol with molecular weight 600 (PEG 600) from Acros and diethylene glycol (DEG) from Unilab were used as organic additives.

### Thin film preparation

The thin nanostructured film of TiO<sub>2</sub> was deposited on stainless steel plate with the surface cleaning prior to use. The synthesis of various sols of TiO<sub>2</sub> was prepared as follows. The TiO<sub>2</sub> precursor solutions were prepared first by stabilizing titanium tetraisopropoxide, dissolved in ethanol, with DEG and PEG 600 as appropriate amount, stirring for 30 min at room temperature. The molar ratios of TTiP to ethanol to PEG 600 and DEG in this study were 1:20:0.5:0.5. The substrates were dipped into the sol and withdrawn at a constant speed to make a gel-coating film. After drying, samples were put directly into a furnace which was maintained at a given temperature in a range of 300–700°C.

### Characterization of TiO<sub>2</sub> thin film

The coating mass of TiO<sub>2</sub> per surface area was determined by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM). The crystal phase of thin film was analyzed by thin film XRD analysis which was recorded on a Philip diffractometer using Cu K $\alpha$  radiation and a step size of 0.02° in the range 10–80°. The step time was 1 second, adequate to obtain a good signal-to-noise ratio in the mean reflections of the two studied TiO<sub>2</sub> crystalline phases, (101) anatase (2 $\theta$  ~ 25.17°) and (110) rutile (2 $\theta$  ~ 27.35°). Scanning Electron Microscope (Philip) was used to examine the smoothness of thin film surface.

### Photocatalytic reaction

The experimental apparatus consisted of a cylindrical quartz reactor (7841–06, Ace Glass; Vineland, NJ), a double-walled quartz cooling water jacket and a 450 W medium-pressure Hg lamp (7825–34, Ace Glass) with a nominal wavelength range of 220–1400 nm. The cooling water jacket was set up inside the reactor to maintain the temperature within a

range of 25–31°C, preventing excessive heating of the reaction. A lamp was placed inside the cooling water jacket. The volume of aqueous in all experiments conducted was 500 ml. A total of six stainless steel plates of thin film TiO<sub>2</sub> were placed in the reactor to perform photoactivity experiments. The reaction solution was stirred with a magnetic stirrer at a constant speed to keep it well-mixed during the experiments.

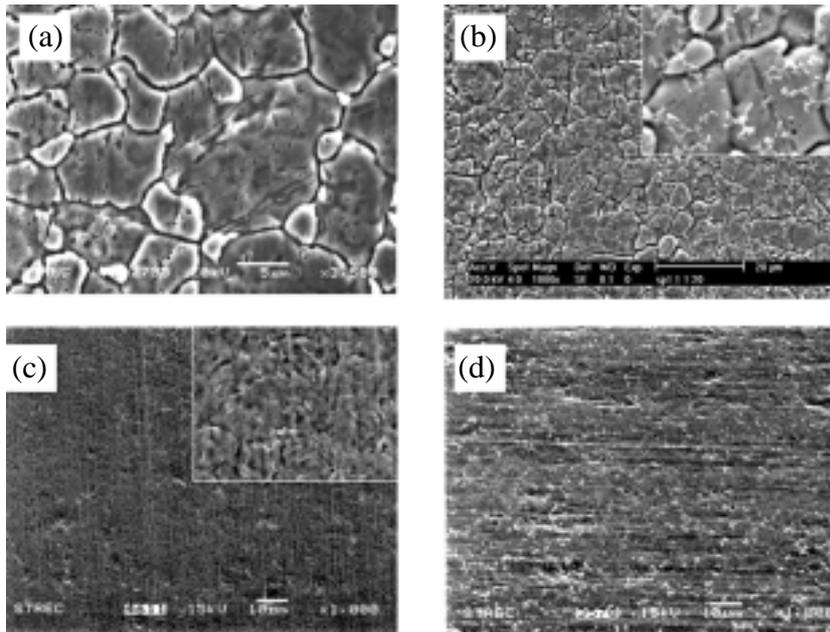
Before turning on the UV lamp, the solution was adjusted to a pH of 3. The solution was placed in the dark, covered with aluminum foil and kept stirring for a certain time until the pH was stable, indicative of adsorption equilibrium. After dark adsorption, the UV light was turned on and samples were retrieved from the reactor for analysis at different time intervals. The residual concentrations of chromium (VI) in the solution were analyzed by UV/Vis spectrophotometer (JASCO V-530) at 540 nm, using diphenylcarbazide as the color reagent.

## RESULTS AND DISCUSSION

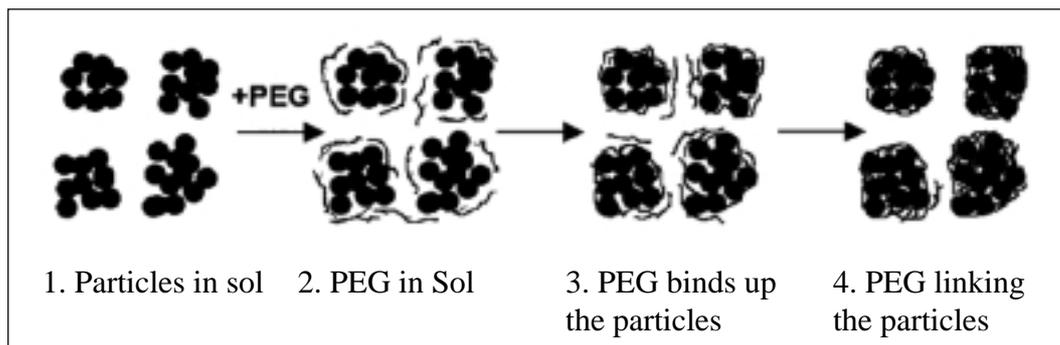
### Texture of TiO<sub>2</sub> films coated on stainless steel plate

Figure 1 (a) shows the original macroscopic morphology of stainless steel without any deposition of TiO<sub>2</sub> on the surface. The grain boundary of stainless steel is clearly seen. The macroscopic morphology of TiO<sub>2</sub> thin film deposited on stainless steel plate in the absence of any additive is shown in Figure 1 (b) with 1000x magnifications. It is noteworthy that the morphology is similar to the original stainless steel plate. With a higher magnification, inset picture in Figure 1(b), there are some particles left on the surface of the thin film. Due to the organic components of the unfired, coatings were decomposed during the heat treatment (Negishi et al., 1995). It is anticipated that the nanoparticles remaining on the surface of the thin film were the developed TiO<sub>2</sub>. These particles disappeared in the presence of either PEG 600 or DEG in the sol solution. The flatness and smoothness of TiO<sub>2</sub> thin films on stainless steel as shown in Figure 1 (c) for PEG 600 addition and Figure 1 (d) for DEG were obtained.

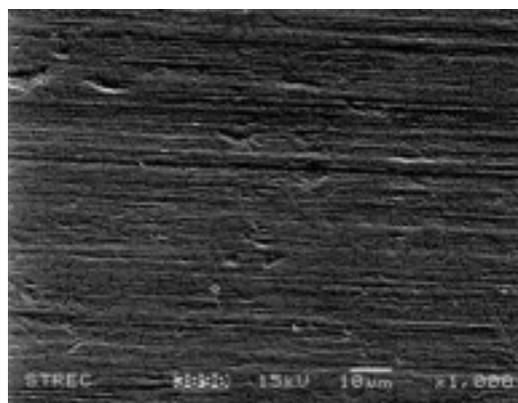
Results from SEM clearly represented that addition of PEG600 yielded the high surface areas with many pores produced during the heat treatment. Zhang et al., (2003) elucidated the effect of PEG as the structure-directing agent. Ti-precursor was first hydrolyzed by water to form sol particles. The particles can be covered by the PEG chain to form “particles-PEG” complexes. The resulting complexes then self-assemble through cross-linking and polymerization to form mesoscopically-ordered inorganic/polymer composites. Schematic presentation to illustrate the tentative structure-directing process of PEG in the precursor sol in this experiment is shown in Figure 2. During heating, PEG was oxidized and decomposed to carbon dioxide. Pores were generated by the elimination of the gas phase from the coating (Kato et al., 1996). When adding only DEG to the sol solution, the film was flat and smooth but some cracks were observed. Effect of DEG on the thin film TiO<sub>2</sub> was possibly similar to that of PEG600. With the small chain of DEG, the short cross-linkages of inorganic/polymer composites were formed and the small cracks along the stainless steel plate could be expected. The coating solution which contained both PEG600 and DEG also gave the film smoothness without any cracks. The coating solution containing both PEG600 and DEG provided the film smoothness without any cracks as seen in Figure 3.



**Figure 1.** SEM images of (A) stainless steel plate without TiO<sub>2</sub>; (B) thin film TiO<sub>2</sub> on stainless steel plate; (C) thin film TiO<sub>2</sub> with PEG 600 deposited on stainless steel plate and (D) thin film TiO<sub>2</sub> with DEG deposited on stainless steel plate.



**Figure 2.** Tentative structure-directing process of PEG in the precursor sol.

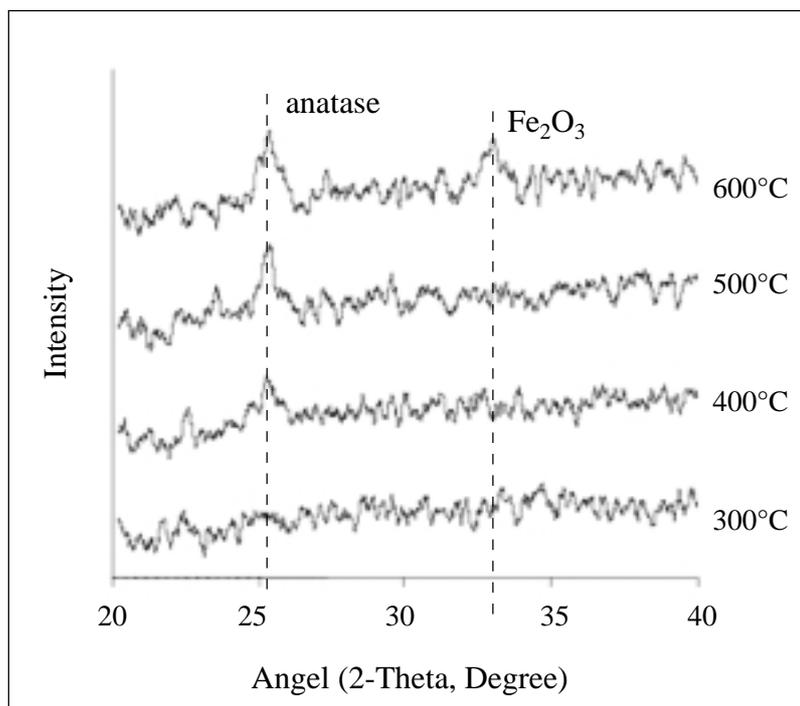


**Figure 3.** Smooth surface of thin film TiO<sub>2</sub> with addition of PEG 600 and DEG.

### Crystallization of TiO<sub>2</sub> films

X-ray diffraction was used to investigate the crystallization of the TiO<sub>2</sub> films on the stainless steel plate. Figure 4 illustrates the XRD diffraction patterns with the peaks in the range of  $2\theta = 20\text{--}40$  degree of the TiO<sub>2</sub> thin film coated on the stainless steel, which were prepared by calcining at different temperatures in the range of  $300\text{--}600^\circ\text{C}$ . A good signal-to-noise ratio in the main reflections of the studied TiO<sub>2</sub> crystalline anatase phase (101) at  $2\theta = 25.17$  degree was clearly shown in each XRD pattern.

Calcination is a common treatment that can be used to improve the crystallinity of TiO<sub>2</sub> particles. The XRD results from this work indicated that TiO<sub>2</sub> thin film calcined at  $300^\circ\text{C}$  was amorphous. The anatase peak appeared at  $400^\circ\text{C}$ , resulting from a phase transition from amorphous phase to the anatase phase. The increase of anatase peak implied the improvement in crystallinity. In addition, no phase transformation from anatase to rutile occurred at calcined temperature as high as  $600^\circ\text{C}$ . From the previous work (Liu et al., 2003), the retardation of the phase transition temperature might come from types of supporting material. For example, the rutile phase of TiO<sub>2</sub> films coated on NiTi alloy existed simultaneously at temperature of  $600\text{--}750^\circ\text{C}$ , while the phase transition from anatase to rutile began to appear at  $600^\circ\text{C}$  when coated TiO<sub>2</sub> on titanium plate (Liqiang et al., 2003) and at  $1000^\circ\text{C}$  when coated TiO<sub>2</sub> on quartz glass (Kim et al., 2001). Findings from this work suggested that at the studied calcination temperature at  $600^\circ\text{C}$ , the transformation of anatase to rutile phase on stainless steel plate did not occur. In addition, it is worth to note that the oxidation transformation of Fe to Fe<sub>2</sub>O<sub>3</sub> was detected at the studied calcination temperature at  $600^\circ\text{C}$ , as shown in  $2\theta = 33.21$  degree in Figure 4.



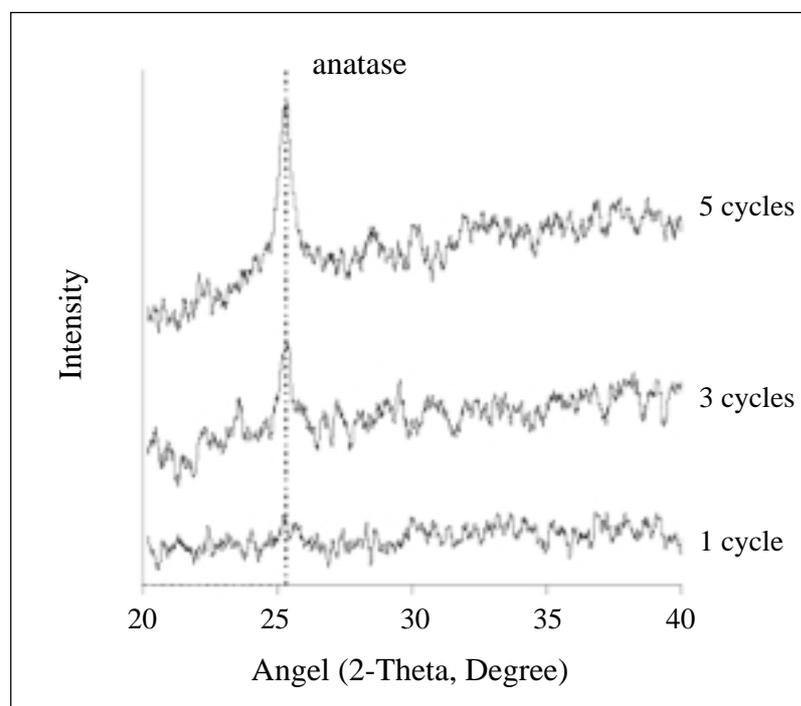
**Figure 4.** X-ray diffraction pattern of TiO<sub>2</sub> thin film calcined at  $300^\circ\text{C}$  to  $600^\circ\text{C}$ .

The average crystallite sizes of TiO<sub>2</sub> thin film were calculated as shown in Table 1. The crystallite size of the anatase phase was increased from 39.9 to 46.1 nm as the calcination temperature increased from  $400$  to  $600^\circ\text{C}$ . This is in good agreement with the early results reported by Kim et al., (2001) and Liqiang et al., (2003) that the particle growth was enhanced by increasing of calcination temperature.

**Table 1.** Crystallite size of TiO<sub>2</sub> thin film prepared with various calcined temperatures.

Calcination temperature (°C)	Crystallite Size (nm)
400	39.9
500	45.0
600	46.1

Structures of a TiO<sub>2</sub> thin film calcinated at 500°C with multiple coating numbers of 1-, 3- and 5- times were analyzed by XRD as shown in Figure 5. For one-coating film, the XRD pattern shows the lowest intensity of anatase due to an insufficient content of TiO<sub>2</sub>. With the increase of coating cycles, higher amount of anatase was obtained. The five-coating cycle film shows the highest intensity of anatase with no rutile phase.

**Figure 5.** X-ray diffraction pattern of TiO<sub>2</sub> thin film with multiple coating cycles.

Crystallite sizes of TiO<sub>2</sub> thin film prepared with different coating cycles are shown in Table 2. It was found that crystallite size of anatase decreased at higher coating cycle from 60.9 to 40.2 nm with 1- to 5-coating time.

**Table 2.** Crystallite size of TiO<sub>2</sub> thin film prepared with different coating cycles.

Coating cycle	Crystallite Size (nm)
1	60.9
3	45.0
5	40.2

**Photocatalytic activity**

The photocatalytic reduction of chromium(VI) using 1-, 3- and 5-coating cycles and calculated reaction rates are shown in Table 3. The total chromium in the aqueous solution was removed from the water within 180 minutes with different reaction rates of each thin film condition. It was found that TiO<sub>2</sub> thin film with 5-coating cycles performed the highest photoactivity in chromium(VI) removal with the reaction rate constant at 0.0505 mg/(L.min). As the coating cycle increased, the amount of deposited titanium dioxide and its anatase was increased, resulting in high activity of photocatalytic process. This behavior can be seen clearly from the reaction rates when the coating cycle was increased from 1 cycle to 5 cycles. Moreover, with the smaller nanoparticle sizes obtained from multiple coating, for example, 40.2 nm with 5 coating cycles and 60.9 nm with 1 coating cycle, the high surface area of active size for photocatalytic process could be expected.

Other factor that might play a role here is the thickness of the film. The thin film obtained from 5 coating cycles was relatively thicker than that obtained from 1 coating cycle. Yu et al., (2001) found that the rate constant increased with increasing film thickness and approached a limiting value at thick film. The latter mainly resulted from the two factors: (a) aggregation of TiO<sub>2</sub> particles in the interior region of thick film during heat treatment, causing a decrease in the number of surface active sites, and (b) the increase in opacity and light scattering of TiO<sub>2</sub> thick films, leading to decrease in the passage of irradiation through the film. Findings from this work suggested that percentage of anatase crystallite, nanoparticle size and thickness of thin film TiO<sub>2</sub> deposited on stainless steel plate are the major factors which play an important role in photocatalytic reduction of chromium (VI).

**Table 3.** Reaction rate constants for chromium(VI) removal of TiO<sub>2</sub> films prepared with different coating cycles.

Coating cycle	Rate constant (k, am/L.min)	Correlation Determination (r <sup>2</sup> )
1	0.0347	0.9876
3	0.0377	0.9924
5	0.0505	0.9898

**CONCLUSION**

A good morphology and crystalline phase of TiO<sub>2</sub> film (40–60 nm) with a high photocatalytic activity can be obtained by sol-gel method coated on stainless steel plate. The addition of polyethylene glycol (PEG600) and diethylene glycol (DEG) drastically improved the quality of the thin film TiO<sub>2</sub> deposited on stainless steel plate. Calcination temperatures and multiple coating were important operating factors in controlling the nanoparticle size and the percentage of anatase of thin film TiO<sub>2</sub>. The obtained thin film TiO<sub>2</sub> coated on stainless steel exhibited high photoactivity in chromium (VI) removal. Major factors controlling the photoactivity of the films included percentage of anatase crystallite, nanoparticle size and thickness of thin film TiO<sub>2</sub> deposited on stainless steel.

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## REFERENCES

- Hilmi, A., J. H. T. Luong, and A. L. Nguyen. 1999. Utilization of TiO<sub>2</sub> deposited on glass plates for removal of metals from aqueous wastes. *Chemosphere* 38: 865–874.
- Kato, K., A. Tsuge, and K. Niihara. 1996. Microstructure and crystallographic orientation of anatase coating produced from chemically modified titanium tetraisopropoxide. *Journal of the American Ceramic Society* 79: 1483–1488.
- Kim, D. J., S. H. Hahn, S. H. Oh, and E. J. Kim. 2001. Influence of calcinations temperature on structural and optical properties of TiO<sub>2</sub> thin films prepared by sol-gel dip coating. *Materials Letters* 57: 355–360.
- Liqiang, J., S. Xiaojun, C. Weimin, X. Zili, D. Yaoguo, and H. Honggang. 2003. The preparation and characterization of nanoparticle TiO<sub>2</sub>/Ti films and their photocatalytic activity. *Journal of Physics and Chemistry of Solids* 64: 615–623.
- Liu, J. X., D. Z. Yang, F. Shi, and Y. J. Cai. 2003. Sol-gel deposited TiO<sub>2</sub> film on NiTi surgical alloy for biocompatibility improvement. *Thin Solid Films* 429: 225–230.
- Matthews, R. W. 1987. Photooxidation of organic impurities in water using thin films of titanium dioxide. *The Journal of Physical Chemistry* 91: 3328–3333.
- Negishi, N., T. Iyoda, K. Hashimoto, and A. Fujishima. 1995. Preparation of transparent TiO<sub>2</sub> thin film photocatalyst and its photocatalytic activity. *Chemistry Letter* 9: 841–842.
- Oppenländer, T. 2003. Photochemical purification of water and air. Weinheim: WILEY-VCH.
- Pozzo, R. L., M. A. Baltanás, and A. E. Cassano. 1997. Supported titanium oxide as photocatalyst in water decontamination: State of the art. *Catalysis Today* 39: 219–231.
- Richard, J. W. 1998. Hazardous wastes: Sources pathways receptors. New York: John Wiley&Sons.
- Schrank, S. G., H.J. José, and R. F. P. M. Moreira. 2002. Simultaneous photocatalytic Cr(VI) reduction and dye oxidation in a TiO<sub>2</sub> slurry reactor. *Journal of Photochemistry and Photobiology A: Chemistry* 147: 71–76.
- Sonawane, R. S., S. G. Hegde, and M. K. Dongare. 2002. Preparation of titanium(IV) oxide thin film photocatalyst by sol-gel dip coating. *Materials Chemistry and Physics* 77: 744–750.
- Yu, J., X. Zhao, and Q. Zhao. 2001. Photocatalytic activity of nanometer TiO<sub>2</sub> thin films prepared by the sol-gel method. *Materials Chemistry and Physics* 69: 25–29.
- Zhang, L., Y. Zhu, Y. He, and H. Sun. 2003. Preparation and performances of mesoporous TiO<sub>2</sub> film photocatalyst supported on stainless steel. *Applied Catalysis B: Environmental* 40: 287–292.