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Sol–gel preparation and properties study of TiO_2 thin film for photocatalytic reduction of chromium(VI) in photocatalysis process

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Abstract

In this paper, a sol–gel technique with dip coating method is used to prepare photocatalytic TiO_2 thin films immobilized on glass plates. The structure and morphology of thin films are characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The structural characterization of this film shows that the titanium oxide anatase phase is predominant at 400–700 °C. The appearance of the rutile phase depends mainly on the number of coating cycles. For example, the rutile phase appeared at 600 °C with 5 coating cycles, however, it disappeared from TiO_2 crystalline after 8 coating cycles. The obtained thin films from each preparation condition were employed in experiment of photoreduction of chromium. The results show that the Chromium(VI) is successfully removed from aqueous in photocatalysis system using the obtained thin film with high portions of anatase phase. The photoactivity of the prepared TiO_2 thin films exhibits a comparable efficiency with TiO_2 powder, Degussa P-25.

Keywords: Titanium dioxide; Thin film; TiO_2; Photocatalysis; Chromium; Heavy metal; Sol–gel

1. Introduction

Increasing social concerns on the impact, derived from improper handling and management of different types of hazardous wastes on the environment, has drawn attention on development and identification of more practically promising control and abatement methods. One of the potential techniques is application of photocatalytic route to either oxidize or reduce hazardous pollutants [1]. Under favorable conditions, mineralization of organic hazardous waste can occur with production of mineral acids, carbon dioxide, and water. The reduction of highly toxic metal ions to less harmful species can be possible by application of this method. Recently, considerable numbers of study have focused on photocatalytic activity of TiO_2 for organic and inorganic contaminant removals [2–6]. Generally, two forms of TiO_2 in photocatalysis have been widely used including; a highly dispersed fine particles or a suspended particles in liquid medium and thin films on supported materials [6–10]. When suspension TiO_2 is applied in photocatalysis system, the suspended TiO_2 has to be yet separated upon completion of each reaction cycle. However, this problem could be avoided by using the TiO_2 films applied on different types of substrates [11].

The preparation of thin film TiO_2 is one of the major researches in photocatalysis field in order to identify an optimum condition for coating of TiO_2 film on various substrates. A number of methods have been employed to fabricate TiO_2 films, including sputtering, chemical vapor deposition, and sol–gel process [7,10,11]. However, the sol–gel process is one of the most appropriate technologies to prepare thin oxide coating. The interest in application of sol–gel method is due to several advantages including; good homogeneity, ease of composition control, low processing temperature, large area coatings, low equipment cost, and good photocatalytic properties [12].

This paper, aims to investigate effects of the preparation conditions on the surface morphology and photocatalytic properties of TiO_2 catalysts. Sol–gel procedure was used for the preparation of TiO_2. In this work, correlations between photocatalytic activity in the Cr (VI) removal and the properties of TiO_2 samples prepared by various conditions

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in the sol–gel method were studied. The variation of ratio between TiO_2 and alcohol used as well as effect of calcined temperature were investigated. In addition, photocatalytic reduction of Cr (VI) using thin film TiO_2 was included in the scope of work. The result obtained from this research provides useful information to future photocatalysis research works for treatment and removal of contaminants either in water and wastewater applications.

2. Experimental

2.1. Materials

All chemicals used in this experiment were all analytical grades which were used as received. Nanocrystalline titanium dioxide was prepared via sol–gel hydrolysis and condensation of isopropanol solutions (Merck Chemicals) of titanium tetraisopropoxide ($Ti(OC_3H_7)_4$, Aldrich Chemicals) or TTiP. Analytical grade K_2CrO_4 (Merck) together with deionized water was used to prepare the Cr (VI) solutions for photoactivity test. The pH of prepared solution was adjusted to a desired value by use of either NaOH or H_2SO_4 both of which are manufactured by Merck.

2.2. Thin film preparation

Thin film titanium dioxide, for dip coating, were prepared using isopropyl alcohol as solvent with addition of small amounts of water and nitric acid. Two different ratios of sol chemicals, S1and S2, are shown in Table 1. The transparent microscopy glass plates were used as substrates which were dipped into the prepared sol and withdrawn at a constant speed making a gel coating film. The TiO_2 gel films were heated to temperatures ranging from 400 to 700 °C for 30 min in ambient air. The samples were put directly into a furnace, which was maintained at a given temperature.

2.3. Characterization of TiO_2 thin film

A coating mass of TiO_2 per surface area was determined by X-ray diffraction (XRD) and scanning electron microscope (SEM). X-ray diffraction patterns of the samples were recorded on a Philip diffractometer using Cu Kα radiation and a step size of 0.02° in the range of 10–80°. The step time was 1 s which is adequate to obtain a good signal-to-noise ratio in the mean reflections of the two studied TiO_2 crystalline phases (1 0 1) including anatase ($2\theta \sim 25.17°$) and (1 1 0) rutile ($2\theta \sim 27.35°$). Scanning electron microscope (Philip) was used to examine the smoothness of thin film surface.

Table 1
Compositions of starting solutions

Sol	Composition (molar)			
	$Ti(OC_3H^i_7)_4$	C_3H_7OH	HNO_3	H_2O
S1	0.50	20	0.10	0.50
S2	0.50	25	0.10	0.50

2.4. Photocatalysis experiment

The experimental apparatus consisted of a cylindrical pyrex glass 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 to be 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 glass plates of thin film TiO_2 were placed in the reactor to perform photoactivity experiments. The reaction solution was stirred with a magnetic stirrer at a constant speed to maintain a 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, which is an 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.

All the solutions were analyzed for the residual concentrations of metals ions by using colorimetric method. UV–Visible spectra for Cr (VI) measurements were recorded on a Hewlett-Packard model diode array spectrometer.

3. Results and discussion

3.1. Characteristics and microstructure of TiO_2 films

The use of sol–gel process in this research, led to a production of transparent TiO_2 thin films with reproducibility, scratch, acid and alkali corrosive resistance, and capability of adherence on glass substrates. The film characteristics are strongly dependent on the molar ratios of alkoxide to solvent. The SEM images, presented in Fig. 1, show that the sol–gel films exhibit different surfaces resulting from the prepared sol solutions. The thin film surface obtained from S1 sol preparation appeared as a thin sheet attached on the glass surface of which the film surface was observed with visual cracks along the glass plate. In comparison to the higher amount of applied solvent (S2), more smoothness of thin film was seen in this case. The TiO_2 attached on the surface of glass plate in this case exhibited as the thin film with considerably small cracks. It is clearly represented that role of solvent is not only the dissolvability of alkoxide but also the smoothness enhancement of the TiO_2 films.

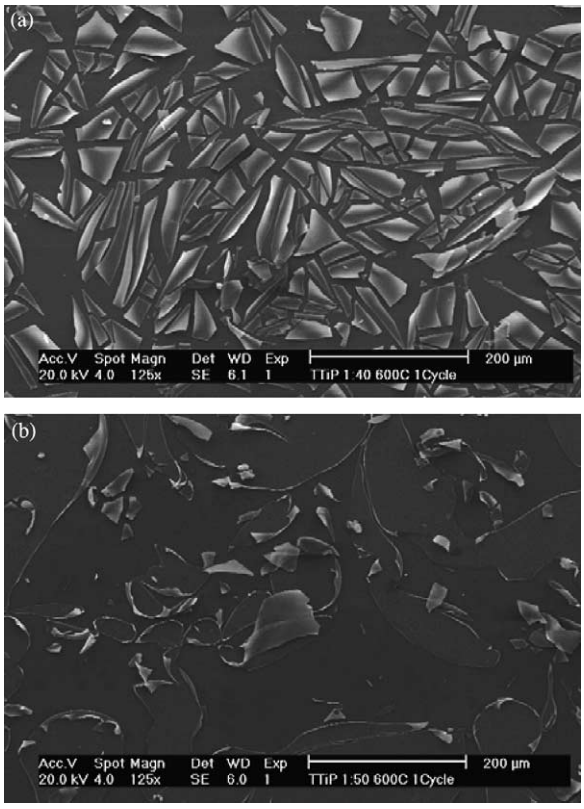

Fig. 1. SEM photographs of the TiO_2 coating films calcined at 600 °C for 30 min and 1 cycle coating (a) S1 sample and (b) S2 sample.

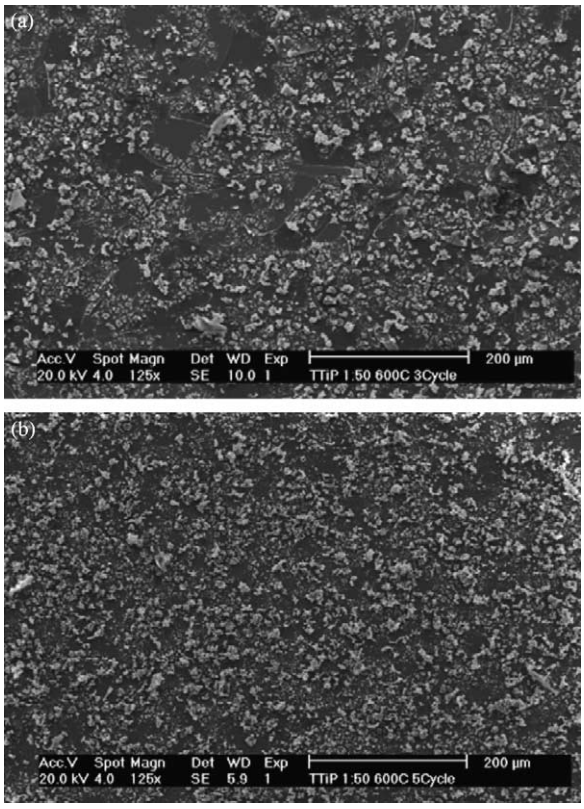

Fig. 2. SEM photographs of TiO_2 thin film with multi-step coating cycles (a) 3 cycles and (b) 5 cycles.

The use of multi-step coating process led to higher quality of thin films compared to the one step coating. This multi-step can be performed by dipping the substrates for 3 and 5 times into S2 sol and heating at 600 °C for 30 min after each coating cycle. It is found that the multi-step preparation of TiO_2 thin films (Fig. 2) enhanced high homogeneity and adherence ability on glass substrates as well as increasing thickness of TiO_2 thin films. The average thickness of the thin films was changed from 30 nm to be 1 and 3 µm for 1, 3, and 5 coating cycles, respectively.

The X-ray diffraction patterns of the S1 and S2 are shown in Fig. 3. A peak at 25.116° is corresponding to (1 0 1) reflections of the anatase phase of TiO_2. The anatase phase was predominant structure of the thin films obtained from S1 and S2 sols. The difference in peak intensity was derived from the alteration of sols from less concentration of solvent to the higher extents. The rutile phase does not exist in these conditions. In comparison, with the increasing of coating cycles, the rutile was shown in Fig. 4 and high amounts of anatase crystalline were also obtained. This may be attributed to the high content of titanium dioxide with several coating cycles resulting in the obvious peaks of anatase [13].

As a thin film sample in this study, contained only anatase and rutile phases, the mass fraction of rutile (χ) can be calculated from the following equation [14]:

$$\chi = \frac{I_R}{0.8I_A + I_R} \quad (1)$$

where, I_A and I_R represent the integrated intensity of the anatase (1 0 1) and rutile (1 1 0) peaks, respectively.

The percentages of anatase and rutile were calculated from Eq. (1) as shown in Fig. 5. The percentage of rutile was not appeared in thin films prepared with 1 and 3 coating

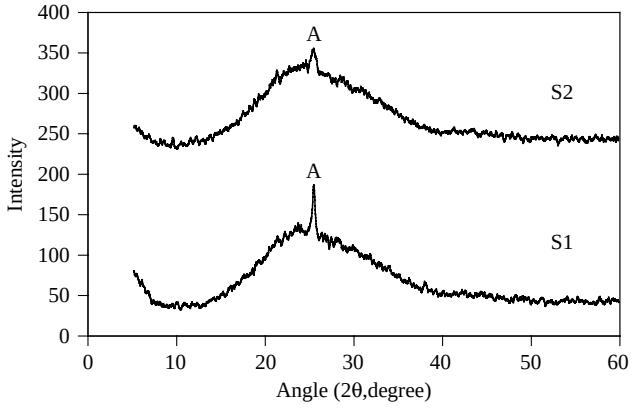

Fig. 3. XRD patterns of TiO_2 thin films deposited on microscopy glass plates.

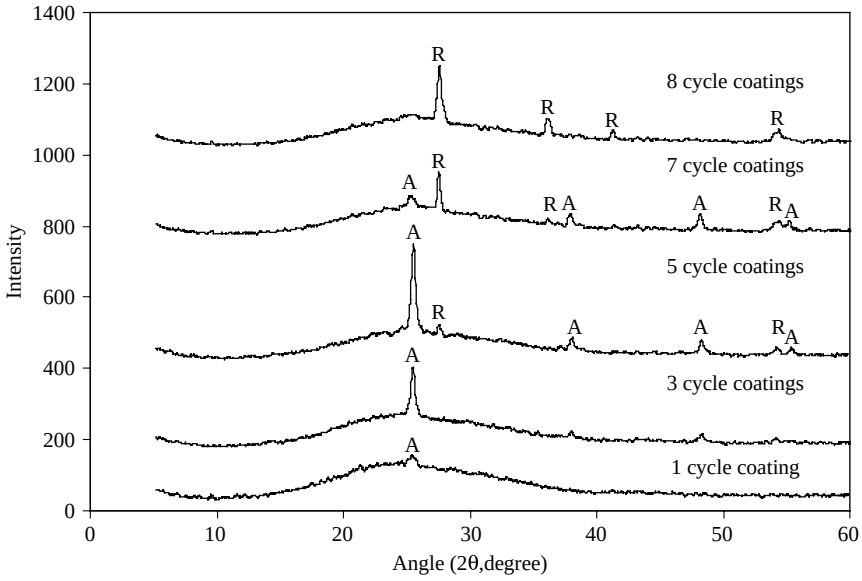

Fig. 4. XRD patterns of several coating cycles of TiO_2 thin films.

cycles. At 5 coating cycle of TiO_2 thin film, percentage of anatase was 81.34% whereas remainders of 18.66%, was rutile. As represented by XRD patterns, the anatase was disappeared in thin films prepared with 8 coating cycles. This information suggests that the transformation from anatase to rutile was more pronounced with increasing numbers of coating cycles. In addition, the rutile tends to increase with the numbers of coating cycle of TiO_2 whereas the anatase tends to decrease with the number of coating after 3 cycles.

3.2. Crystallization behavior

XRD patterns of TiO_2 thin films (from S2 sol) on glass annealed at different temperatures from 400 to 700 °C are presented in Fig. 6 with (a) for 1 coating cycle and (b) for 3 coating cycles. Results from both conditions exhibited the same finding. As the temperature increased from 300 to 700 °C, the intensities of the anatase peaks were increased implying an improvement in crystallinity. At 300 °C the anatase did not formed, as no peak is presented in both 1 and 3 coating cycles. The obtained results are consistent with the previous work [15] such that, with the isopropanol as solvent, the films annealed at temperature less than 400 °C were amorphous and the anatase phase precipitated at 350–400 °C. For the rutile transformation, we found that the anatase crystal structure did not get transformed into the rutile even at 700 °C. Previous study [15] reported that the anatase-to-rutile phase transformation took place at temperatures of 600–800 °C, while Kim et al. [16] reported that the phase formation occurred at 1000 °C. The discrepancy of this transformation may be due to the differences in crystallite structure and thickness of TiO_2 films.

3.3. Photocatalytic activity

The photocatalytic activity of the thin film TiO_2 was determined by applying in chromium removal. The thin film TiO_2 with 1 coating cycle and calcined temperature of 600 °C was used in photocatalytic test to compare with powder TiO_2 (Degussa P-25). The latter is the most widely used, as studied titania catalyst due to its high activity which is taken as point of reference in many photocatalytic processes.

The quantity of sample used was adjusted to achieve equal TiO_2 concentration (1 g/l) for the purposes of comparing the activity of the different catalysts. As seen in Fig. 7, the amount of Chromium(VI) ions decreased with increasing irradiation time in the presence of each catalyst. It is clearly showed that the Chromium(VI) ions underwent photoreduction process in which many of previous works reported about the process mechanism [17]. It is remarkable the activity of the obtained thin film TiO_2 is closed to that obtained from Degussa P-25.

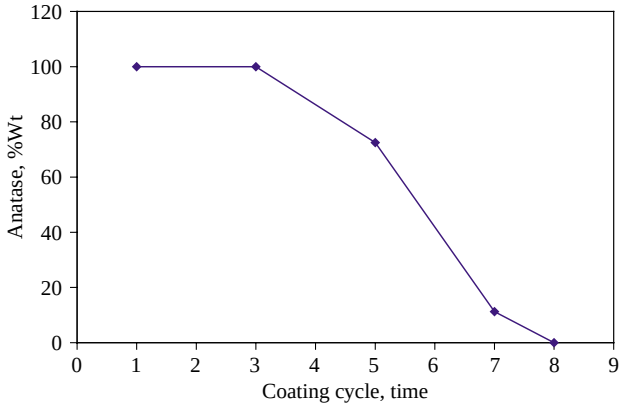

Fig. 5. Percentage of anatase phase of TiO_2 thin films with several coating cycles.

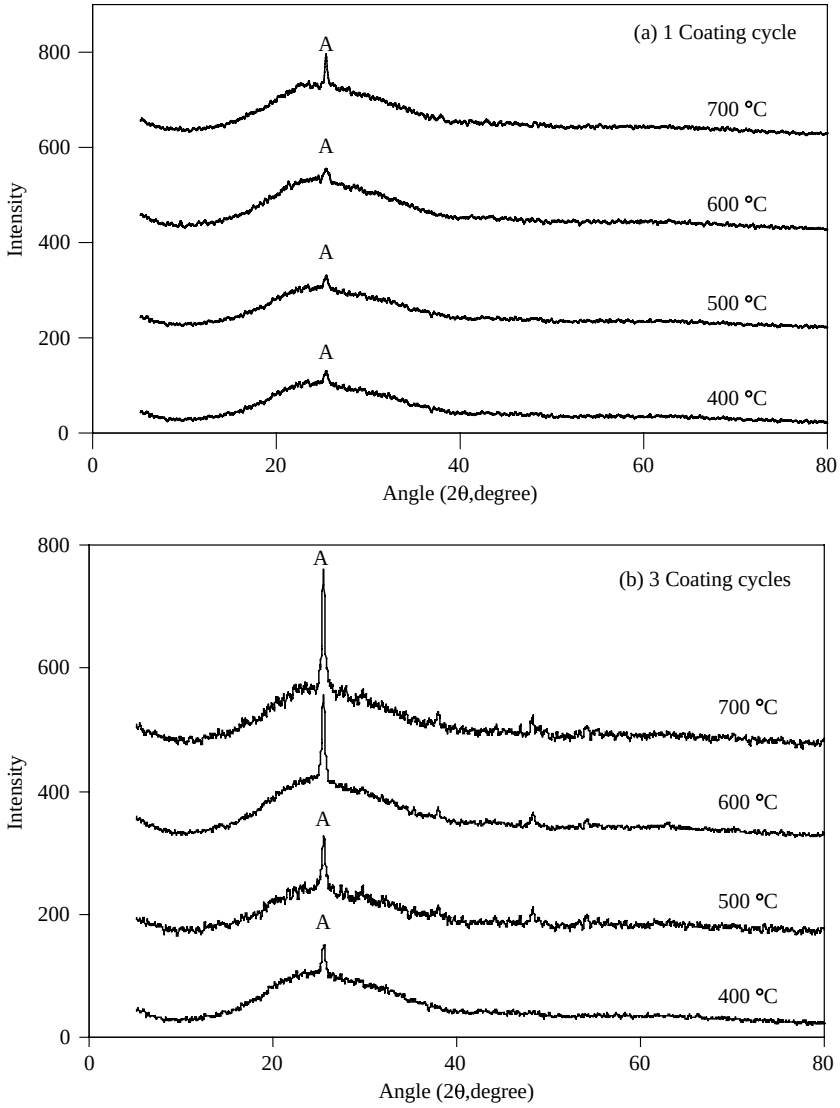

Fig. 6. XRD patterns of thin film TiO_2 from S2 solution using different calcinations temperature; (a) 1 coating cycle and (b) 3 coating cycles.

On the basis of thin film photoactivity studies, further investigations were conducted to understand effect of different thin film preparation conditions on the photocatalytic performance. Fig. 8 shows the effect of calcination temperatures in thin film preparation on the fraction of Chromium(VI) remaining in the water as a function of time. The reaction rates were statistically found following zero order kinetic model, of which the reaction rate of constants were determined by statistically fitting with the experimental data. The calculated reaction rate of constants, as shown in Table 2, were 0.0656, 0.0894, 0.0895, and 0.097 for the thin film obtained from the different calcination temperatures of 300, 400, 500, and 600 °C, respectively. These results indicate that the photocatalytic activity of the thin film TiO_2 prepared at 600 °C was the highest among all thin films tested. It can be rationalized from the amount of anatase found in each thin film TiO_2 that with 600 °C calcinations temperature, the highest amount of anatase yielded the highest photoactivity of chromium reduction.

Fig. 9 shows effect of coating cycles in thin film preparation on photocatalytic process. The reaction rate constants of each sample were also represented in Table 2. It is found that the thin film TiO_2 with 3 coating cycles

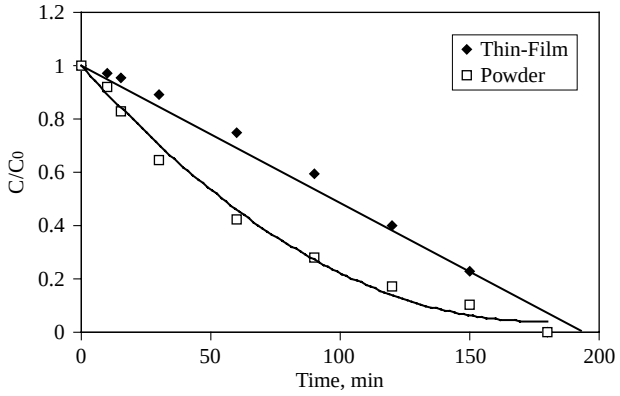

Fig. 7. Comparison of photocatalytic reduction of Chromium(VI) using thin film TiO_2 and Degussa P-25.

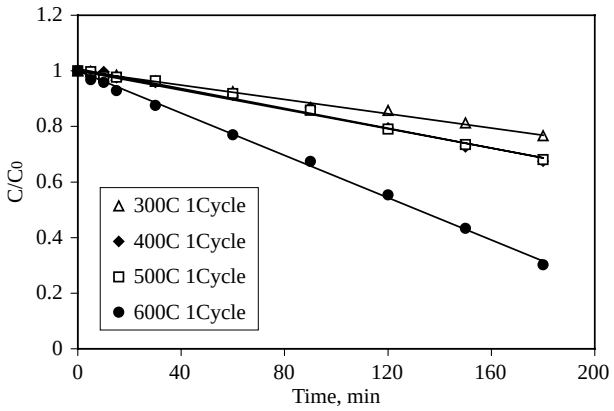

Fig. 8. Photocatalytic reduction of chromium on TiO_2 thin film derived from different calcinations temperatures.

Table 2
The reaction rate constants for Chromium(VI) photocatalytic removal using different thin film TiO_2

Sample no.	Calcination temperature (°C)	Coating cycle	k (min^{-1})	R^2
1	300	1	0.0656	0.988
2	400	1	0.0894	0.9921
3	500	1	0.0895	0.9936
4	600	1	0.097	0.9984
5	600	3	0.1463	0.9902
5	600	5	0.1426	0.9866

exhibited the highest photoactivity in Chromium(VI) removal with the value of reaction rate constant at 0.1463. As the coating cycle increased, the amount of deposited titanium dioxide and its anatase was increased resulting in high activity of photocatalytic process, as can be seen from the illustration when the coating cycle was increased from 1 to 3 cycles. However, the photocatalytic efficiency was reduced with the application of 5 cycle coatings of thin film TiO_2. The weak photoactivity of this film possibly can be explained by the formation of rutile crystalline, which has the small band gap for photocatalytic reaction [1].

Results from these experiments substantiate that the photocatalytic process is considerably affected by the thin film preparation conditions of which its importance can be related to the structural morphology of TiO_2.

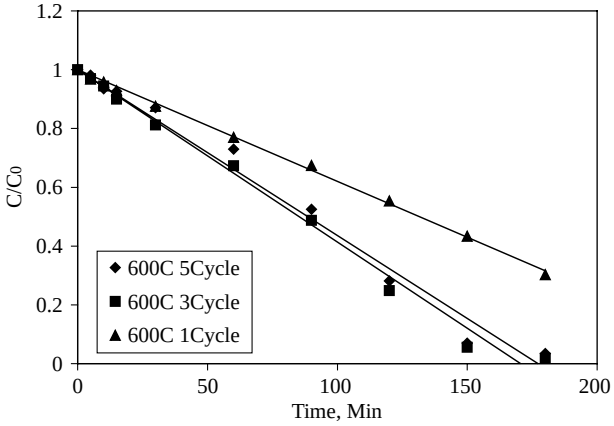

Fig. 9. Photocatalytic reduction of chromium on TiO_2 thin film derived from different coating cycles.

4. Conclusion

This paper, shows that the properties of TiO_2 thin film are considerably influenced by their preparation conditions. The molar ratio of alkoxide to alcohol, calcination temperature, and coating cycles were the major parameters, which are yet to be controlled. The photocatalytic reactivity of the obtained thin film was studied of which the obtained results can be compared with that of the powder TiO_2 (Degussa P-25). It was found that differences in photocatalytic reduction of Chromium(VI) could be correlated with the structural morphology of the thin film. For example, the thin film obtained from 600 °C calcinations temperature provided the highest efficiency in Chromium(VI) removal due to the highest amount of anatase in the thin film composition. Coating cycle also showed an important effect on the film properties. The presence of rutile in the higher coating cycle causes the decreasing of photocatalytic activity. Findings from this research can be the fundamental information of TiO_2 thin film preparation for other environmental pollution control applications.

Acknowledgements

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References

[1] A. Fujishima, T.N. Rao, D. Tryk, Titanium dioxide photocatalysis, J. Photochem. Photobiol. A: Chem. 1 (2000) 1–21.
[2] M. Schiavello (Ed.), Heterogeneous Photocatalysis, Wiley, New York, 1997.
[3] D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993.
[4] S. Devipriya, S. Yesodharan, Photocatalytic degradation of pesticide contaminants in water, Sol. Energy Mater. Sol. Cells 86 (2005) 309–348.
[5] D. Bahnemann, Photocatalytic water treatment: solar energy applications, Solar Energy 77 (2004) 445–459.
[6] M. Lindner, D.W. Bahnemann, B. Hirthe, W. Griebler, Solar water detoxification: novel TiO_2 powders as highly active photocatalysts, Solar Eng. 1 (1995) 399–408.
[7] Z. Ding, X. Hu, P.L. Yue, G.Q. Lu, P.F. Greenfield, Synthesis of anatase TiO_2 supported on porous solids by chemical vapor deposition, Catal. Today 68 (2001) 173–182.

[8] P. Kaitvichyanukul, C.R. Chenthamarakshan, K. Rajeshwar, S.R. Qasim, Photo-catalytic reactivity of thallium(I) species in aqueous suspensions of titania, J. Electroanal. Chem. 519 (2002) 25–32.
[9] D.S. Bhatkhande, V.G. Pangarkar, A. Beenackers, Photocatalytic degradation for environmental applications—a review, J. Chem. Technol. Biotechnol. 77 (2001) 102–116.
[10] G. Pecchi, P. Reyes, P. Sanhueza, J. Villasenor, Photocatalytic degradation of pentachlorophenol on TiO_2 sol–gel catalysts, Chemosphere 43 (2001) 141–146.
[11] R.S. Sonawane, S.G. Hegde, M.K. Dongare, Preparation of titanium (IV) oxide thin film photocatalyst by sol–gel dip coating, Mater. Chem. Phys. 77 (2002) 744–750.
[12] S. Sakka, T. Yoko, in: J.C. Jørgenson, R. Reisfield (Eds.), Chemistry, Spectroscopy, and Application of Sol–Gel Glasses, Springer, Heidelberg, 1991, pp. 89–91.
[13] J. Yu, X. Zhao, Effect of substrates on the photocatalytic activity of nanometer TiO_2 thin films, Mater. Res. Bull. 35 (2000) 1293–1301.
[14] Y. Bessekhouad, D. Robert, J.V. Weber, Synthesis of photocatalytic TiO_2 nanoparticles: optimization of the preparation conditions, J. Photochem. Photobiol. A: Chem. 6286 (2003) 1–7.
[15] L. Hu, T. Yoko, H. Kozuka, S. Sakko, Effects of solvent on properties of sol–gel derived TiO_2 coating films, Thin Solid Films 219 (1992) 18–23.
[16] D.J. Kim, S.H. Hahn, S.H. Oh, E.J. Kim, Influence of calcination temperature on structural and optical properties of TiO_2 thin films prepared by sol–gel dip coating, Mater. Lett. 57 (2000) 355–360.
[17] J. Gimenz, M.A. Aguado, S. Cervera-March, Photocatalytic reduction of chromium(VI) with titania powders in a flow system, kinetics and catalyst activity, J. Mol. Catal. A: Chem. 105 (1996) 67–78.