

CHAPTER IV

RESULTS AND DISCUSSION

In this research, preparations of TiO₂ thin film on glass plate using sol-gel technique were investigated. TiO₂ thin films were prepared under different conditions using titanium(IV) butoxide as a precursor, ethanol as a solvent, HCl as a acidic catalyst and acetylacetone as studied additive substance in order to find the role of each parameters and their effects on TiO₂ thin film preparation. The results from this research are shown as follows:

4.1 Role of solvent in preparations of TiO₂ thin film

In this experimental set, the mole ratios of titanium(IV) butoxide : ethanol were varied at 1:10, 1:20, 1:30, 1:40 1:50 and 1:60, respectively. The coated substrates were calcined at 500°C in an electric furnace for 30 min with 3 coating cycles.

4.1.1 Weighing by scale

This weighing method is a primitive step for the evidence of TiO₂ attachment on substrate. The corroboration was examined from the increasing of the amount of TiO₂ that was calculated by weighing substrate before and after coating.

The results show that the weight of TiO₂ thin films obtaining from the different mole ratios of titanium(IV) butoxide : ethanol were increased after coating process as shown in Table 4.1. The result of titanium(IV) butoxide : ethanol at 1:10 contains the highest amount of TiO₂. Furthermore, the amount of TiO₂ attached on glass plate was decreased as the ratio of ethanol increased due to the dilution of TiO₂ with higher amount of ethanol. Therefore, the film with the lowest ratio of ethanol provides the highest amount of TiO₂. Regarding to the study of Vicente *et al* (2001), the layer thickness is strongly dependent on concentration of ethanol. They suggested

that the film thickness could be easily tailored by controlling the titanium and ethanol ratio in the solution. In addition, ethanol, which is an organic solvent, was rapidly evaporated and decomposed during the heat treatment; thus, Table 4.1 presents the remained amount of TiO₂.

Table 4.1 Amount of TiO₂ thin film after coating with different mole ratios of titanium(IV) butoxide : ethanol.

Titanium(IV) butoxide : ethanol	Amount of TiO ₂ per unit of surface area (10 ⁻³ g/cm ²)						
	No.1	No.2	No.3	No.4	No.5	Average	SD
1:10	0.600	0.627	0.733	0.907	0.573	0.688	0.137
1:20	0.227	0.213	0.227	0.227	0.253	0.229	0.015
1:30	0.027	0.120	0.147	0.093	0.053	0.088	0.049
1:40	0.093	0.040	0.120	0.120	0.040	0.083	0.040
1:50	0.067	0.093	0.053	0.067	0.067	0.070	0.015
1:60	0.067	0.040	0.093	0.053	0.053	0.061	0.020

Remark: Amount of TiO₂ was calculated from the film with 3 coating cycles.

The area of glass plate coated with TiO₂ film is about 7.5 cm³.

4.1.2 Adhesive test and corrosive test

Adhesive test (ASTM D3359-95a) was applied to examine the stability, unification and adherence of the films. Corrosive test was employed to investigate the film robustness and corrosive resistance under acidic and basic condition. The results are presented in Table 4.2.

From Table 4.2, TiO₂ thin film derived from the low concentration of ethanol did not pass both adhesive and corrosive tests. At titanium(IV) butoxide : ethanol as 1:10, the film was easily detached from glass substrates by adhesive test and also even dipped into acid and alkali solution. Beside, at 1:20 ratio, the film was not stable from adhesive test as compared to the 1:10 ratio but it exhibited more robustness than the earlier ratio under the aggressive conditions. On the contrary, at the higher ethanol

concentrations as 1:30, 1:40, 1:50 and 1:60 the films were not detached from substrate and their surface were not changed by these two test methods.

Table 4.2 Results of adhesive and corrosive tests of TiO₂ thin film at different ratios of titanium(IV) butoxide : ethanol.

Titanium(IV) butoxide : ethanol	Adhesive Test	Corrosive Test	
		Acidic condition	Basic condition
1:10	✗	✗	✗
1:20	✗	✓	✓
1:30	✓	✓	✓
1:40	✓	✓	✓
1:50	✓	✓	✓
1:60	✓	✓	✓

Remark: ✓ means the film was passed the test

✗ means the film was fail in this test

4.1.3 Surface morphology by SEM (Scanning Electron Microscopy)

The SEM images, presented in Figure 4.1, show the different surfaces of sol-gel films resulting from the different prepared sol solutions. As less ethanol presented in the sol (a), the film surface was the separated TiO₂ sheet attached on the glass surface. This thin film surface was plenty of visual cracks along the glass plate. In comparison to the higher amount of applied ethanol (b) and (c), more smoothness of thin film was seen in the latter cases. The TiO₂ attached on the surface of glass plate performed as a thin film with very small cracks. With a higher amount of ethanol in sol solution as shown in Figure 4.1 (d), (e) and (f), surface of the thin film were rugged and had some TiO₂ particles left on its surface. According to the organic components of the unfired coatings were decomposed during the heat treatment, it is contemplated that the particle remaining on the surface of the thin film was the developed TiO₂ (Negishi *et al.*, 1995).

It is clearly represented that role of solvent is not only the dissolvability of precursor but also the smoothness enhancement of the TiO₂ films.



350 magnification

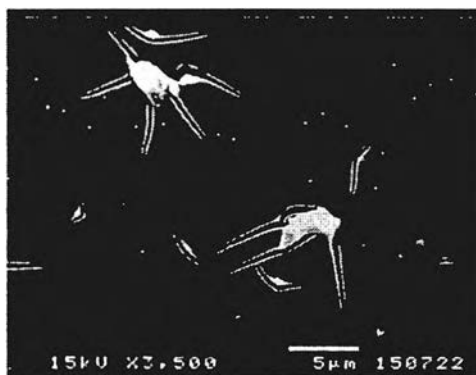


3,500 magnification

(a) titanium(IV) butoxide : ethanol = 1:10



350 magnification

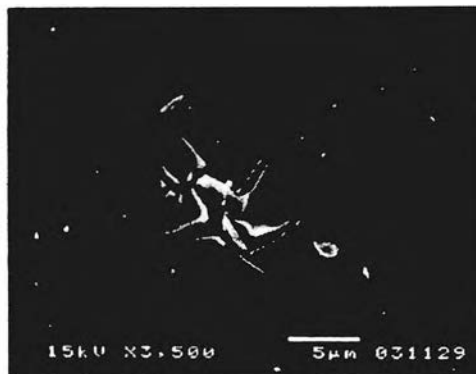


3,500 magnification

(b) titanium(IV) butoxide : ethanol = 1:20

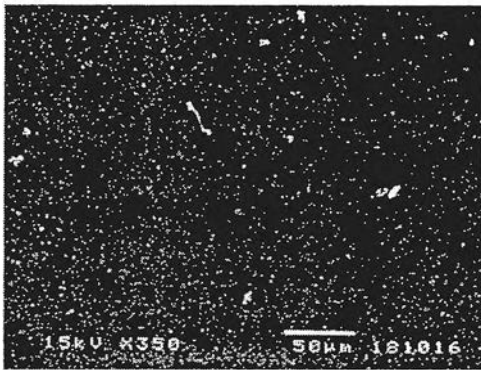


350 magnification



3,500 magnification

(c) titanium(IV) butoxide : ethanol = 1:30

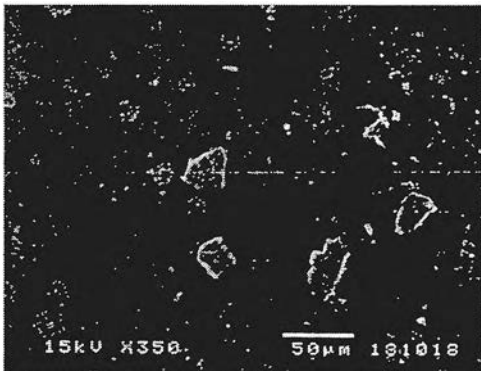


350 magnification

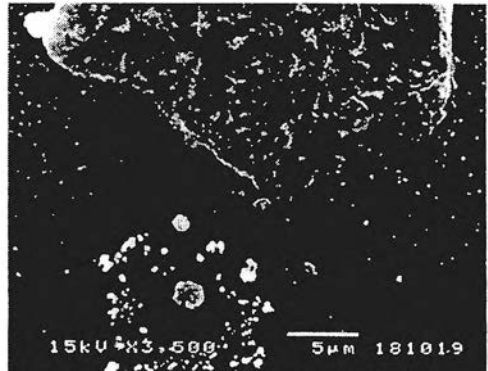


3,500 magnification

(d) titanium(IV) butoxide : ethanol = 1:40

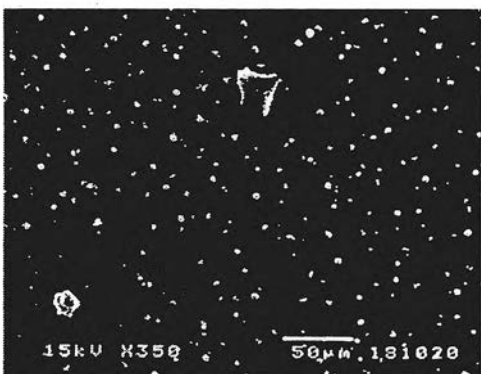


350 magnification



3,500 magnification

(e) titanium(IV) butoxide : ethanol = 1:50



350 magnification



3,500 magnification

(f) titanium(IV) butoxide : ethanol = 1:60

Figure 4.1 (a)-(f) SEM photographs of the TiO_2 coating films derived from different mole ratios of titanium(IV) butoxide : ethanol.

4.1.4 Crystal structures of TiO₂ thin films by XRD (X-ray diffraction)

For XRD analysis, TiO₂ films were coated with 3 coating cycles. Due to the film thickness of 1 coating cycle is too thin to detect the phase of TiO₂ by X-ray process. The X-ray diffraction patterns of the films are shown in Figure 4.2. A major peak corresponding to (1 0 1) reflections of the anatase phase of TiO₂ is shown at the angle 25.3°, while the minor peaks are appeared at 37.8°, 48.05° and 53.90°. The anatase phase was predominant structure for all titanium(IV) butoxide to ethanol ratios. The difference in peak intensity was derived from the variation of sols from less concentration of ethanol (1:10) to the higher amounts (1:20 to 1:30). At titanium(IV) butoxide : ethanol as 1:40, the anatase peak cannot be observed because less amount of TiO₂ on the film exhibit the anatase phase. Thus, the pattern in this case shows no peak as represented that crystal structure of TiO₂ is amorphous. It is worthed to note that the rutile phase does not exist in these conditions.

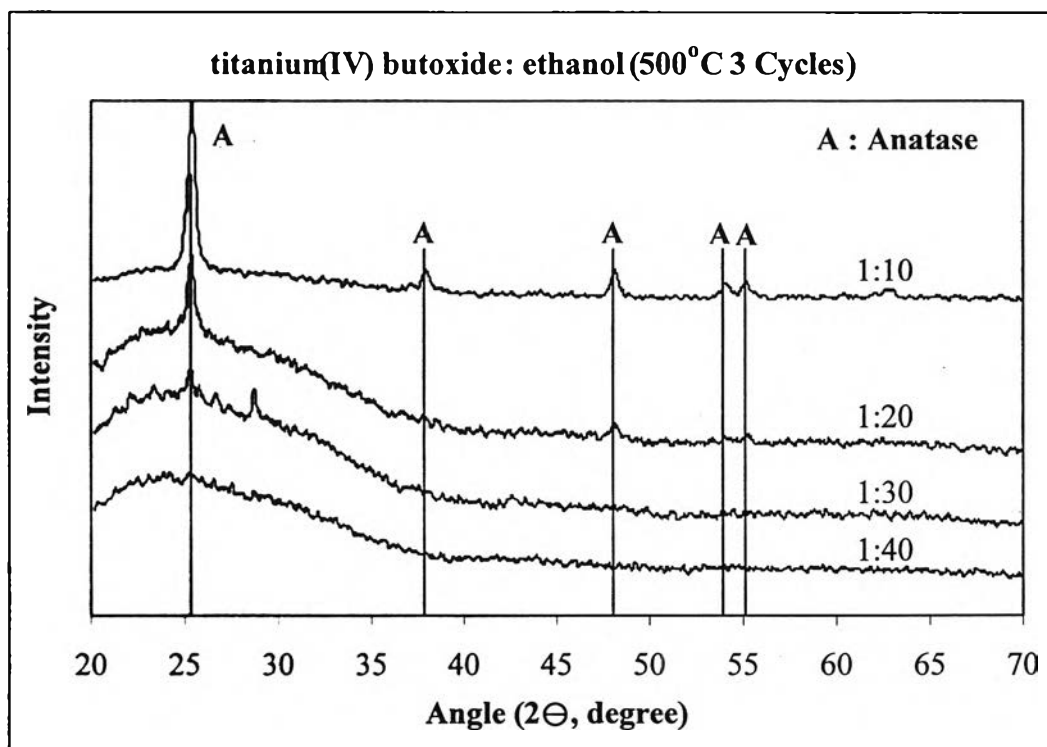


Figure 4.2 XRD patterns of TiO₂ thin films deposited on microscopy glass plates.

In addition, crystallite sizes of TiO₂ can also be estimated from the broadening of corresponding X-ray spectral peaks by Debye-Scherrer equation as shown in Table

4.3. As previous study reported that the higher amount of sol concentration influences thickness and crystallite size (Legrand-Buscema *et al.*, 2002), in this work, we found that the crystallite sizes of anatase phase are in the same range of 12.59-26.86 nm. Consequently, from this study the concentration of ethanol did not exert the pronounce effect on crystallite size of TiO₂.

Table 4.3 Crystallite size of TiO₂ films prepared from different mole ratios of titanium(IV) butoxide : ethanol.

Titanium(IV) butoxide : ethanol	Crystallite Size (nm)
1:10	19.19
1:20	26.86
1:30	12.59

4.1.5 Photocatalytic activity

To study the photocatalytic activity of prepared thin films, films with titanium(IV) butoxide to ethanol ratios equal to 1:20 and 1:30 were engaged for Cr(VI) removal. The results from these experiments were shown in Figure 4.3.

To compare the photocatalytic activity of prepared TiO₂ thin films, the efficiency and reaction rate constant (k) of Cr(VI) removal were determined by fitting statistically with the experimental data. The photocatalytic reaction with respect to initial concentration can be explained as the reaction rate with an apparent equation:

$$\frac{d[C]}{dt} = -k [C]^n \quad (4.1)$$

Where k is the apparent rate constant, n is the reaction order.

When n = 0, the reaction is *zero order*, and upon integrating, the rate constant (k) can be obtained from;

$$[C] = [C]_0 - kt \quad (4.2)$$

When $n = 1$, the reaction is *first order*, both with respect to C and overall, the rate constant (k) can be obtained from;

$$[C] = [C]_0 e^{-kt} \quad (4.3)$$

If the reaction is greater than first order ($n = 2$), the reaction is *second order*, the rate constant (k) can be obtained from;

$$\frac{1}{[C]} = \frac{1}{[C]_0} + kt \quad (4.4)$$

The reaction rates of these experiments were found to follow the zero order kinetic models. The calculated reaction rate constants were shown in Table 4.4. These results indicate that the photocatalytic activity of the thin film TiO_2 prepared at 1:20 leads to achieve the highest photoactivity of Cr(VI) removal. It is can be explained from the amount of anatase presented in each thin film TiO_2 as described earlier via the XRD pattern.

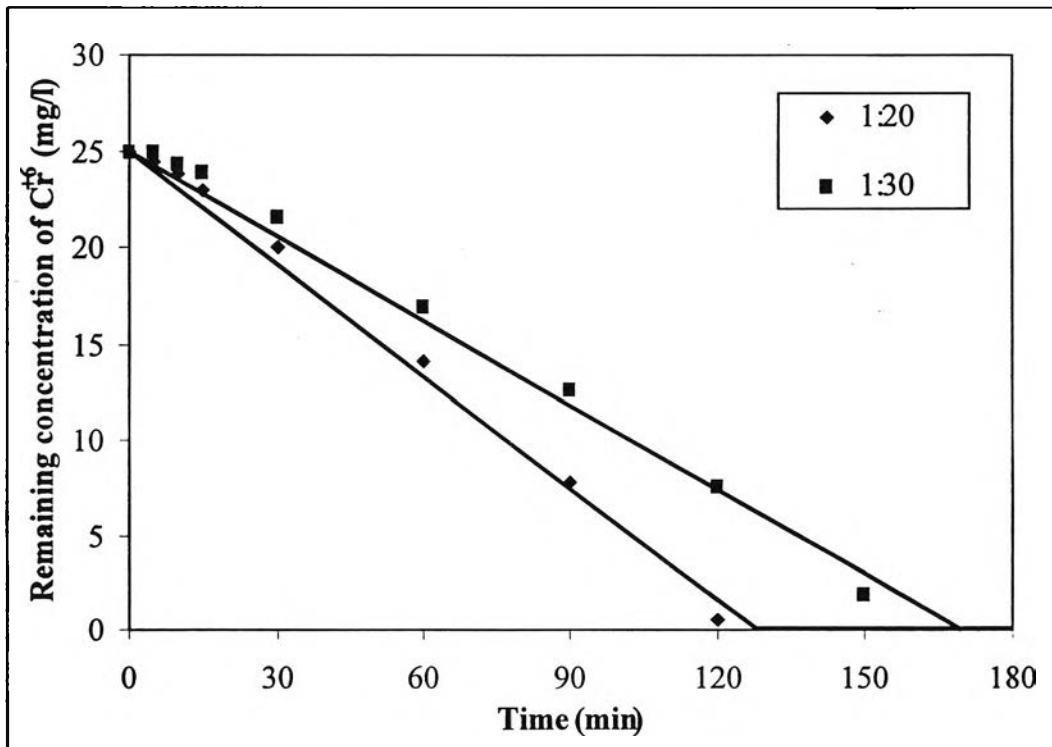


Figure 4.3 Photocatalytic reduction of Cr(VI) on TiO_2 thin film derived from different mole ratios of titanium(IV) butoxide : ethanol.

Table 4.4 Reaction rate constants for chromium(VI) photocatalytic removal using different thin film TiO₂.

Titanium(IV) butoxide : ethanol	Rate constant (k, mg/l-min)	r²
1:20	0.1951	0.9925
1:30	0.1461	0.9903

Nevertheless, the films prepared at the ratio of 1:20 exhibit the highest photoactivity they were not suitable for the applications as elucidated in the previous information. Therefore, the films with the ratio of 1:30 were taken to study for the further experiments.

4.2 Role of acidic catalyst in preparations of TiO₂ thin film

In this investigation, the mole ratios of titanium(IV) butoxide : ethanol : HCl were varied at 1:30:0, 1:30:0.5, 1:30:1 and 1:30:2, respectively. The coated substrates were calcined at 500°C in an electric furnace for 30 min with 3 coating cycles.

4.2.1 Weighing by scale

The results show that as the increasing of HCl concentration, amount of TiO₂ attached on glass plates was slightly decreased as shown in Table 4.5. It could be concluded that HCl had no effect on the adherence of TiO₂ films. Since little amount of HCl were added into sol solutions comparing with ethanol concentration. Therefore, the influence of HCl on increasing in amount of TiO₂ can be ignored.

Table 4.5 Amount of TiO₂ thin film after coating with different mole ratios of titanium(IV) butoxide : ethanol : HCl.

Titanium(IV) butoxide : ethanol : HCl	Amount of TiO ₂ per unit of surface area (10 ⁻³ g/cm ²)						
	No.1	No.2	No.3	No.4	No.5	Average	SD
1:30:0	0.027	0.120	0.147	0.093	0.053	0.088	0.049
1:30:0.5	0.053	0.093	0.120	0.147	0.013	0.085	0.053
1:30:1	0.053	0.093	0.043	0.093	0.067	0.070	0.023
1:30:2	0.040	0.053	0.080	0.093	0.066	0.066	0.021

Remark: Amount of TiO₂ was calculated from the film with 3 coating cycles.

The area of glass plate coated with TiO₂ film is about 7.5 cm³.

4.2.2 Adhesive test and corrosive test

The results of adhesive and corrosive test were presented in Table 4.6. It was shown that in the present of HCl in every prepared conditions, all samples were passed both adhesive and corrosive tests.

Table 4.6 Results of adhesive and corrosive tests of TiO₂ thin film at different ratios of titanium(IV) butoxide : ethanol : HCl.

Titanium(IV) butoxide : ethanol : HCl	Adhesive Test	Corrosive Test	
		Acidic condition	Basic condition
1:30:0	✓	✓	✓
1:30:0.5	✓	✓	✓
1:30:1	✓	✓	✓
1:30:2	✓	✓	✓

Remark: ✓ means the film was passed the test

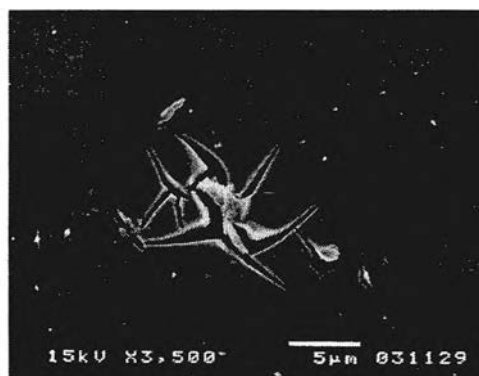
✗ means the film was fail in this test

4.2.3 Surface morphology by SEM (Scanning Electron Microscopy)

Surface morphologies of TiO_2 thin films obtaining from different amount of HCl were shown in Figure 4.4. The result shows that surfaces of all samples were quite smooth and less cracks. As the observation of sol preparation, HCl enhances the dissolvable of precursor. From the previous study, it was indicated that acids such as HCl, HNO_3 and H_2SO_4 are commonly used as acidic catalyst which accelerates the hydrolysis reaction. Furthermore, more smoothness and fewer cracks of TiO_2 films were acquired as the amount of acid increased. However, utilization of HCl more than is proper, properties of the film surface tends to be inferior. It might be refer to the dilution of content TiO_2 with higher amount of HCl. From this study, TiO_2 film prepared with titanium(IV) butoxide : ethanol : HCl ratio of 1:30:0.5 provide good surface morphology. When concentration of HCl which higher than 0.5 mol/l were employed, the quality of TiO_2 films surface were not different from the others.

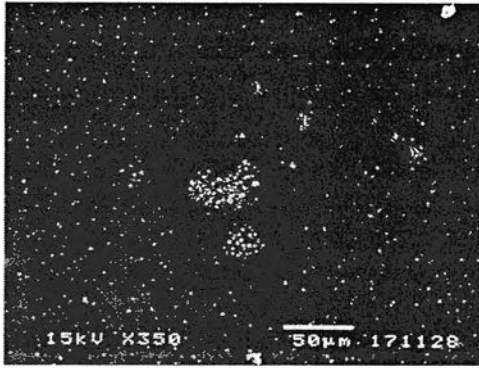


350 magnification

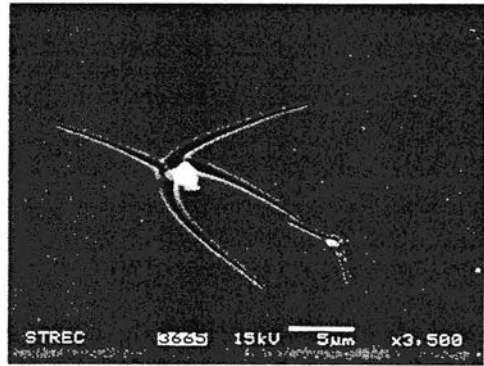


3,500 magnification

(a) titanium(IV) butoxide : ethanol : HCl = 1:30:0

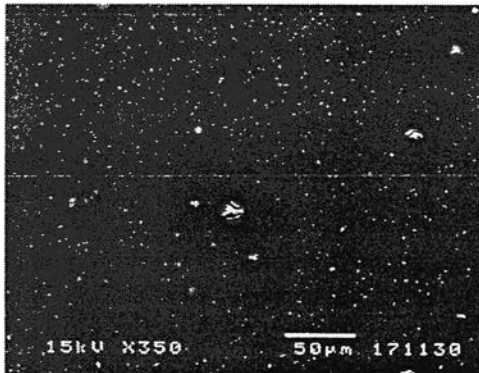


350 magnification



3,500 magnification

(b) titanium(IV) butoxide : ethanol : HCl = 1:30:0.5

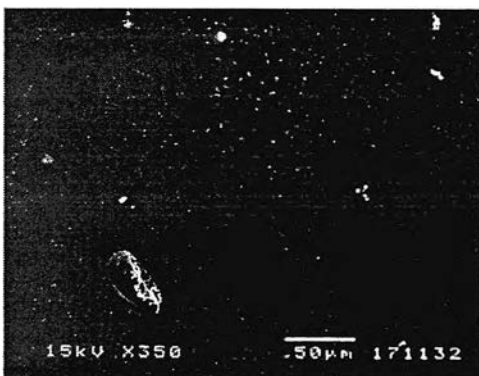


350 magnification



3,500 magnification

(c) titanium(IV) butoxide : ethanol : HCl = 1:30:1



350 magnification



3,500 magnification

(d) titanium(IV) butoxide : ethanol : HCl = 1:30:2

Figure 4.4 (a)-(d) SEM photographs of the TiO₂ coating films derived from different mole ratios of titanium(IV) butoxide : ethanol : HCl.

4.2.4 Crystal structures of TiO₂ thin films by XRD (X-ray diffraction)

Figure 4.5 indicates X-ray diffraction patterns of the synthesized TiO₂ from the catalysis in HCl. In the HCl system, with increasing amount of HCl, anatase crystals grow rapidly until they start to convert into amorphous at ratio of 1:30:1. Kim *et al.* (2002) reported that rutile peaks appeared at 1000°C when HCl was used a catalyst. Therefore, the crystallite structure in rutile form can not be observed by calcining TiO₂ film at 500°C. Additional, they also indicated that the phase transformation temperature turned out to rely upon the concentration of catalyst HCl. Since both H⁺ and Cl⁻ of HCl simultaneously react with TiO₂. From literature review (Yamazaki *et al.*, 2001), the present of HNO₃ and H₂SO₄ in sol-gel process, NO₃⁻ and SO₄²⁻ involve in phase transformation of TiO₂. These anions extend the crystal form growing and converting to rutile phase at high temperature. In the HCl system, as large amount of HCl was included, Cl⁻ was supposed to extend the emergence of anatase phase. Thus, proper amount of HCl should be applied since H⁺ can accelerate the hydrolysis of sol; otherwise, Cl⁻ can conspicuously react with TiO₂ over H⁺. In this study, the highest intensity of anatase peak was achieved at 1:30:0.5 ratio that is expected to be the proper condition for Cr(VI) removal. Beside, crystallite size of TiO₂ was not dependence on amount of HCl. The crystallite sizes of TiO₂ films with variation ratios of HCl were shown in Table 4.7.

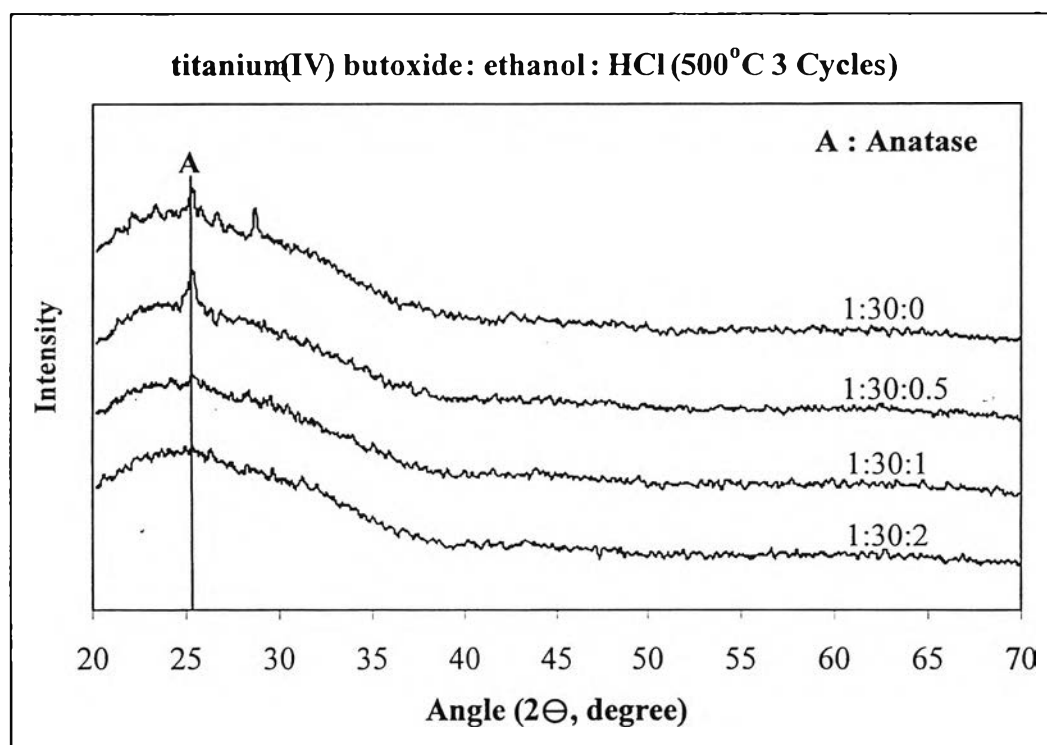


Figure 4.5 XRD patterns of TiO_2 thin films derived from different mole ratios of titanium(IV) butoxide : ethanol : HCl.

Table 4.7 Crystallite size of TiO_2 films prepared from different mole ratios of titanium(IV) butoxide : ethanol : HCl.

Titanium(IV) butoxide : ethanol : HCl	Crystallite Size (nm)
1:30:0	12.59
1:30:0.5	12.59
1:30:1	13.00

4.2.5 Photocatalytic activity

The photoreduction experiments of Cr(VI) were performed to examine the photocatalytic activity of the obtained TiO_2 thin films. The photoreduction of Cr(VI) were attained corresponding with intensity of anatase peak. It was seen that the photocatalytic activity of the TiO_2 thin film prepared at 1:30:0.5 also leads to achieve

the highest photoactivity of Cr(VI) removal. Figure 4.6 and Table 4.8 present the photoactivity of TiO₂ films.

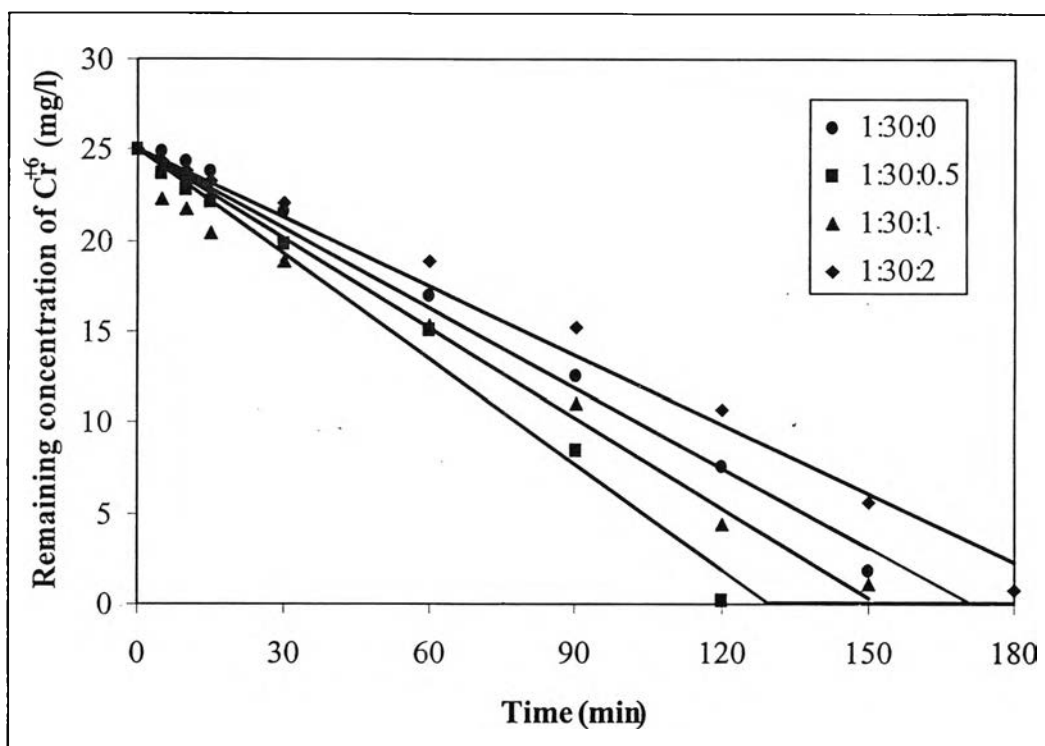


Figure 4.6 Photocatalytic reduction of Cr(VI) on TiO₂ thin film derived from different mole ratios of titanium(IV) butoxide : ethanol : HCl.

Table 4.8 Reaction rate constants for chromium(VI) photocatalytic removal using thin film TiO₂ derived from different mole ratios of titanium(IV) butoxide : ethanol : HCl.

Titanium(IV) butoxide : ethanol : HCl	Rate constant (k, mg/l-min)	r ²
1:30:0	0.1461	0.9903
1:30:0.5	0.1930	0.9877
1:30:1	0.1644	0.9744
1:30:2	0.1259	0.9877

It can be noted that TiO₂ thin films prepared at ratio of 1:30:0.5 were taken to investigate for the later experiments.

4.3 Role of additive substance in preparations of TiO₂ thin film

In this experiment, coating solutions were prepared by varying mole ratios of titanium(IV) butoxide : ethanol : HCl : acetylacetone at the value of 1:30:0.5:0, 1:30:0.5:1, 1:30:0.5:2 and 1:30:0.5:3, respectively. The coated substrates were calcined at 500°C in an electric furnace for 30 min with 3 coating cycles. The results from this experiment not only showed the roles of acetylacetone but the optimum ratio in sol preparation was also obtained.

4.3.1 Weighing by scale

The results in Table 4.9 show the remained amount of TiO₂ attached on glass plates. It was found that amounts of TiO₂ of each titanium(IV) butoxide : ethanol : HCl : acetylacetone ratio were not different. As the amount of acetylacetone increase amounts of TiO₂ attached on substrates were slightly decreased. It could be implied that adding acetylacetone into sol did not affect on the change of amount of TiO₂. Due to acetylacetone is an organic substance as same as ethanol which is easily evaporated during heat treatment.

Table 4.9 Amount of TiO₂ thin film after coating with different mole ratios of titanium(IV) butoxide : ethanol : HCl : acetylacetone.

Titanium(IV) butoxide : ethanol : HCl : acetylacetone	Amount of TiO ₂ per unit of surface area (10 ⁻³ g/cm ²)						
	No.1	No.2	No.3	No.4	No.5	Average	SD
1:30:0.5:0	0.053	0.093	0.120	0.147	0.013	0.085	0.053
1:30:0.5:1	0.053	0.080	0.067	0.093	0.093	0.077	0.017
1:30:0.5:2	0.093	0.067	0.067	0.080	0.053	0.072	0.015
1:30:0.5:3	0.120	0.080	0.013	0.093	0.027	0.067	0.045

Remark: Amount of TiO₂ was calculated from the film with 3 coating cycles.

The area of glass plate coated with TiO₂ film is about 7.5 cm³.

4.3.2 Adhesive test and corrosive test

From this empirical method, with the increasing amount of acetylacetone, surfaces of all TiO₂ films were not peeled off by stubborn conditions. Therefore, the more mole ratio of acetylacetone was performed, the more robustness of TiO₂ film was obtained. These results were in agreement with the result observed by Verma *et al* and Liu *et al* (2003). They indicated that acetylacetone which was used as stabilizing agent offered the compact films with good adherence. It was important to note that the compactness, the uniformity and the interfacial stability of the film play a significant role in their corrosion resistance. The results were presented in Table 4.10.

Table 4.10 Results of adhesive and corrosive tests of TiO₂ thin film at different ratios of titanium(IV) butoxide : ethanol : HCl : acetylacetone.

Titanium(IV) butoxide : ethanol : HCl : acetylacetone	Adhesive Test	Corrosive Test	
		Acidic condition	Basic condition
1:30:0.5:0	✓	✓	✓
1:30:0.5:1	✓	✓	✓
1:30:0.5:2	✓	✓	✓
1:30:0.5:3	✓	✓	✓

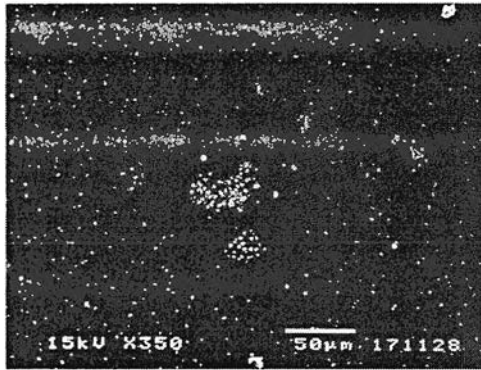
Remark: ✓ means the film was passed the test

✗ means the film was fail in this test

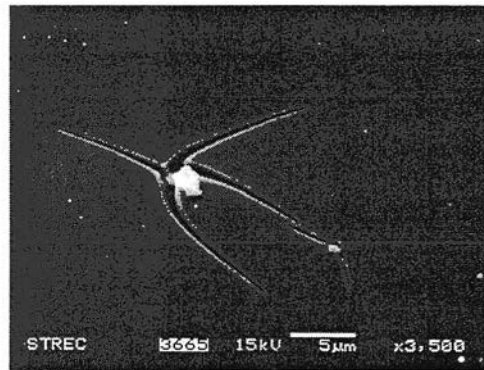
4.3.3 Surface morphology by SEM (Scanning Electron Microscopy)

Figure 4.7 (a), (b), (c) and (d) show the effects of acetylacetone on surface morphology of TiO₂ thin film. It can be seen that without acetylacetone, there were some TiO₂ particles left on the film surface. When small amount of acetylacetone was applied, these left particles were disappeared from TiO₂ thin films. Moreover, as the amount of acetylacetone increased, the smooth films like the TiO₂ sheets were obtained. With this experimental method, the sol in the presence of acetylacetone was

stable and homogeneous (Liu *et al.*, 2003). Therefore, the good quality of the resulting thin films can be observed with no crack and smooth surface (Legrand-Buscema *et al.*, 2002). It could be indicated that acetylaceton played an important role in the stability of sol. In addition, the qualities of the film surface strongly depend on acetylaceton presented in the solution.



350 magnification

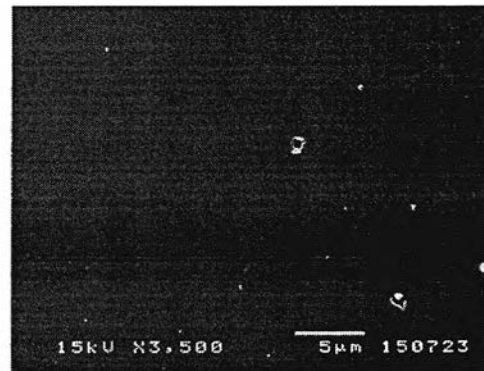


3,500 magnification

(a) titanium(IV) butoxide : ethanol : HCl : acetylaceton = **1:30:0.5:0**

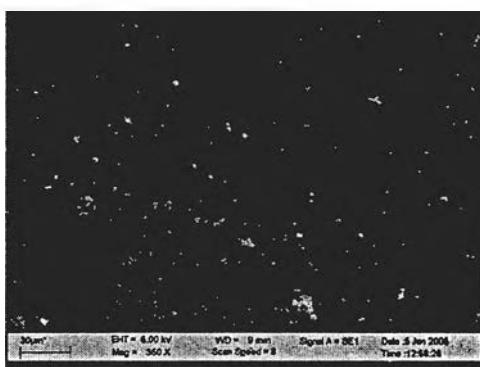


350 magnification

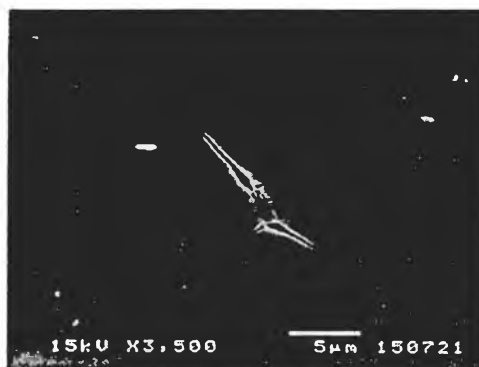


3,500 magnification

(b) titanium(IV) butoxide : ethanol : HCl : acetylaceton = **1:30:0.5:1**

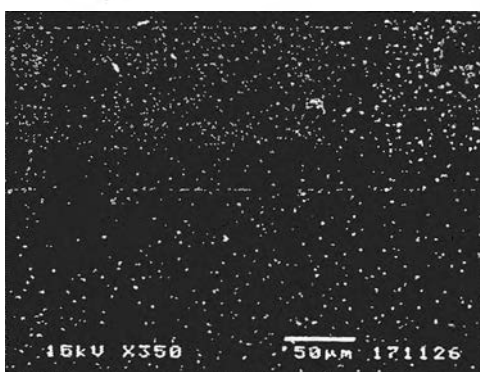


350 magnification



3,500 magnification

(c) titanium(IV) butoxide : ethanol : HCl : acetylacetonone = 1:30:0.5:2



350 magnification



3,500 magnification

(d) titanium(IV) butoxide : ethanol : HCl : acetylacetonone = 1:30:0.5:3

Figure 4.7 (a)-(d) SEM photographs of the TiO_2 coating films derived from different mole ratios of titanium(IV) butoxide : ethanol : HCl : acetylacetonone.

4.3.4 Crystal structures of TiO_2 thin films by XRD (X-ray diffraction)

The X-ray diffraction pattern of the TiO_2 thin film prepared with different mole ratios of acetylacetonone is shown in Figure 4.8. At all preparation conditions, the TiO_2 films with anatase phase were the predominant structure. Moreover, the intensity of anatase peaks is not significantly different as the mole ratio of acetylacetonone increased. With heat-treating of TiO_2 films at 500°C , the rutile phase was not observed because acetylacetonone stabilizes the anatase phase even at temperatures as high as 900°C . Therefore, during the heat-treatment, acetylacetonone strongly affects on the anatase to rutile phase transition of TiO_2 thin films (Djaoued *et al.*, 2002).

Although the intensity of main anatase peaks was not different, the crystallite size of TiO_2 films were slightly increased as the amount of acetylaceton increased. The results were summarized in Table 4.11.

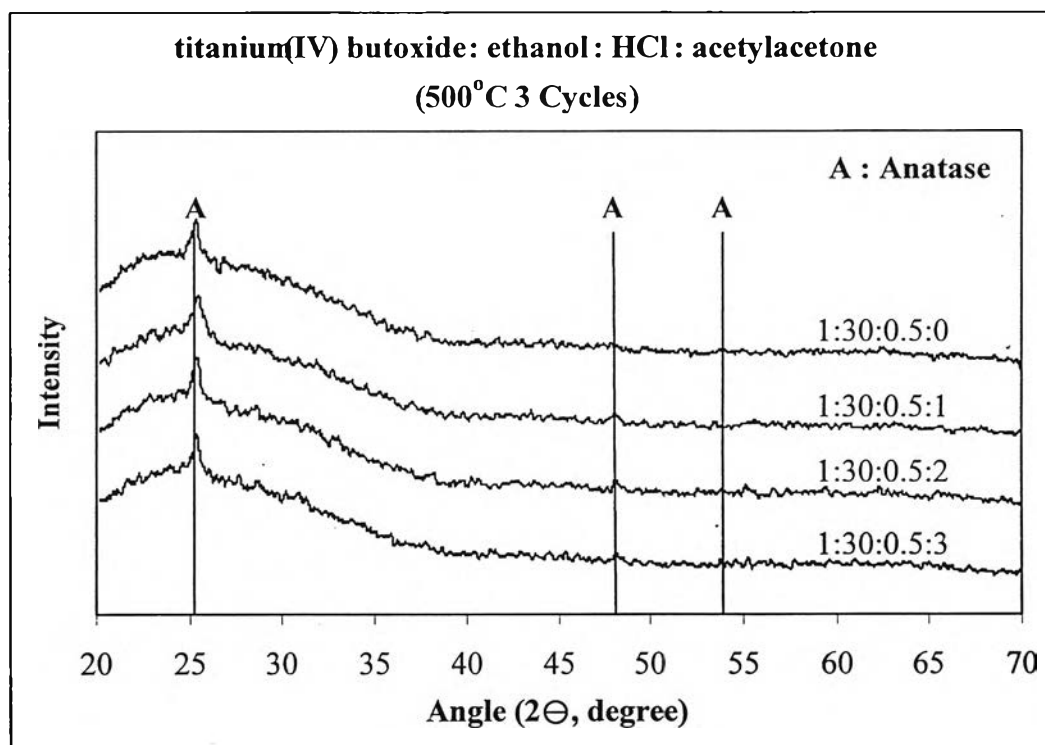


Figure 4.8 XRD patterns of TiO_2 thin films derived from different mole ratios of titanium(IV) butoxide : ethanol : HCl : acetylaceton.

Table 4.11 Crystallite size of TiO_2 films prepared from different mole ratios of titanium(IV) butoxide : ethanol : HCl : acetylaceton.

Titanium(IV) butoxide : ethanol : HCl : acetylaceton	Crystallite Size (nm)
1:30:0.5:0	12.59
1:30:0.5:1	16.12
1:30:0.5:2	20.15
1:30:0.5:3	21.78

4.3.5 Photocatalytic activity

Photocatalytic activity of the prepared TiO_2 films using different mole ratios of acetylacetone was shown in Figure 4.9 and Table 4.12. The results indicated that the reaction rate constants of all conditions were quite similar. The rate constants were slightly decreased as acetylacetone increased. These phenomena were in concordance with the increasing of particle grain size of TiO_2 films. As the size of TiO_2 becomes larger, the number of grain boundaries that serve as active sites decreases.

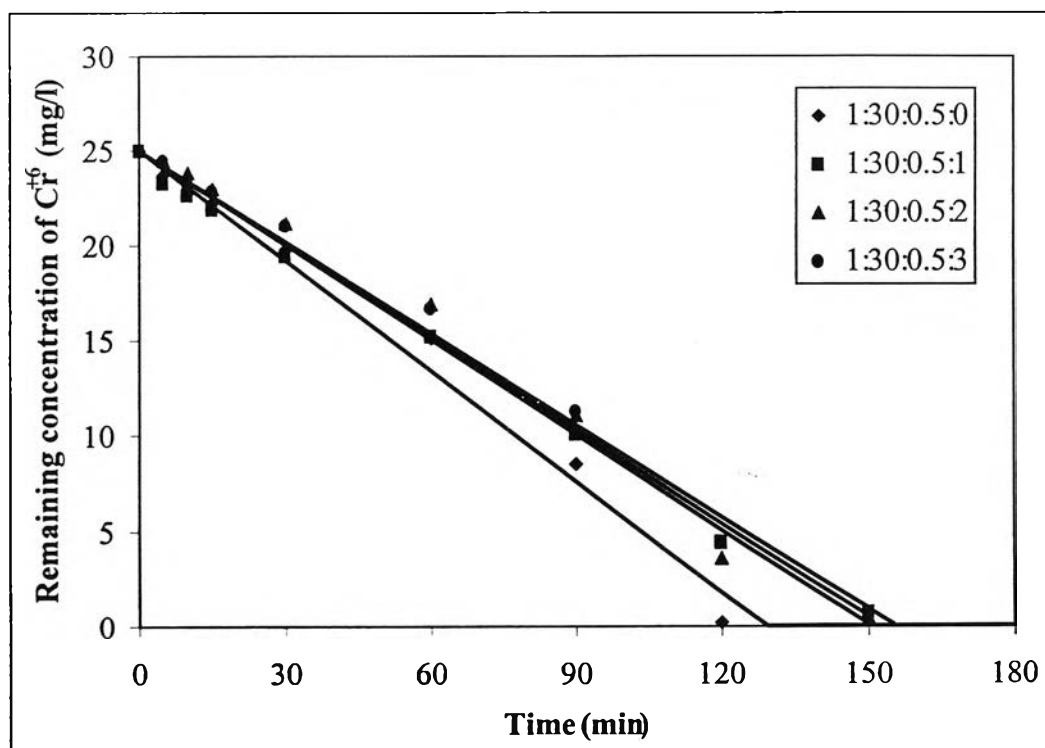


Figure 4.9 Photocatalytic reduction of Cr(VI) on TiO_2 thin film derived from different mole ratios of titanium(IV) butoxide : ethanol : HCl : acetylacetone.

Table 4.12 Reaction rate constants for chromium(VI) photocatalytic removal using thin film TiO₂ derived from different mole ratios of titanium(IV) butoxide : ethanol : HCl : acetylacetone.

Titanium(IV) butoxide : ethanol : HCl : acetylacetone	Rate constant (k, mg/l-min)	r²
1:30:0.5:0	0.1930	0.9877
1:30:0.5:1	0.1659	0.9957
1:30:0.5:2	0.1634	0.9884
1:30:0.5:3	0.1605	0.9927

Therefore, the TiO₂ thin films obtained from titanium(IV) butoxide : ethanol : HCl : acetylacetone with the value of 1:30:0.5:1 were taken to investigate the effect of calcination temperature.

4.4 Effect of calcination temperature on preparations of TiO₂ thin film

The optimum ratio in TiO₂ thin films preparation obtaining from the earlier experiments was used to investigate the effect of calcination temperature. In this study, titanium(IV) butoxide : ethanol : HCl : acetylacetone ratio was fixed as 1:30:0.5:1. The TiO₂ gel films were heated to temperatures ranging from 300°C to 600°C in air for 30 min with 3 coating cycles.

4.4.1 Weighing by scale

The results in Table 4.13 show that the TiO₂ film calcined at 300°C exhibit the highest amount of TiO₂. With the increasing of calcination temperature, a amount of TiO₂ attached onto substrate was decreased. Regarding to the heat-treating at low temperature, organic components were not completely decomposed. The over weight of TiO₂ film may be result in the amount of remained organic components. On the other hand, as the calcination temperature increased, the amount of thin film was decreased because more components were decomposed.

Table 4.13 Amount of TiO₂ thin film derived from different calcination temperatures.

Calcination temperature	Amount of TiO ₂ per unit of surface area (10 ⁻³ g/cm ²)						
	No.1	No.2	No.3	No.4	No.5	Average	SD
300°C	0.160	0.147	0.173	0.253	0.200	0.187	0.042
400°C	0.040	0.160	0.160	0.107	0.067	0.107	0.054
500°C	0.053	0.080	0.067	0.093	0.093	0.077	0.017
600°C	0.053	0.053	0.067	0.080	0.067	0.064	0.011

Remark: Amount of TiO₂ was calculated from the film with 3 coating cycles.

The area of glass plate coated with TiO₂ film is about 7.5 cm³.

4.4.2 Adhesive test and corrosive test

Normally, the heat-treatment can improve the adhesion of the TiO₂ film onto the substrate (Liqiang *et al.*, 2003). Due to the wet gel films can be converted into the dense and rigid oxide films by calcination temperature. Thus, TiO₂ films calcined at all experimental temperatures performed good properties in adhesive and corrosive resistance. The above results were shown in Table 4.14.

Table 4.14 Results of adhesive and corrosive tests of TiO₂ thin film derived from different calcination temperatures.

Calcination temperature	Adhesive Test	Corrosive Test	
		Acidic condition	Basic condition
300°C	✓	✓	✓
400°C	✓	✓	✓
500°C	✓	✓	✓
600°C	✓	✓	✓

Remark: ✓ means the film was passed the test

✗ means the film was fail in this test

4.4.3 Surface morphology by SEM (Scanning Electron Microscopy)

The surface morphology of TiO₂ films was carried out through Figure 4.10. Figure 4.10 (a), (b), (c) and (d) present the surface morphology of TiO₂ film calcined at 300°C, 400°C, 500°C and 600°C, respectively. The SEM photographs showed that TiO₂ film derived from different temperatures exhibited different fractures. Calcining the TiO₂ film at low temperature such as 300°C, there were few cracks and they tend to be increased at higher temperatures. As the TiO₂ films calcined at high temperature, more shrinkage and more cracks were obtained. This was in good accordance with the investigation of Liqiang *et al.* (2003). They demonstrated that TiO₂ film with less surface area and porosity might be result from condensation in the high calcination temperature. Moreover, the retardation of calcination times also lead to the more shrinkage of TiO₂ films.

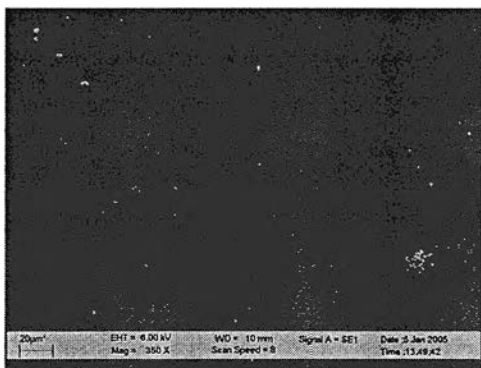


350 magnification

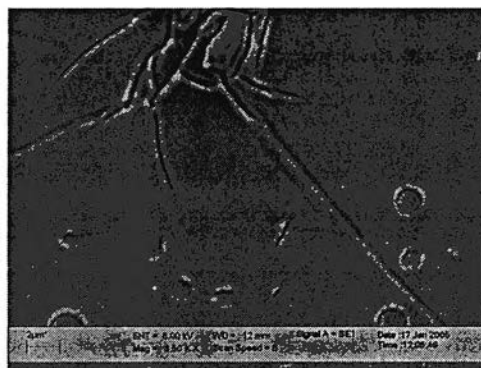


3,500 magnification

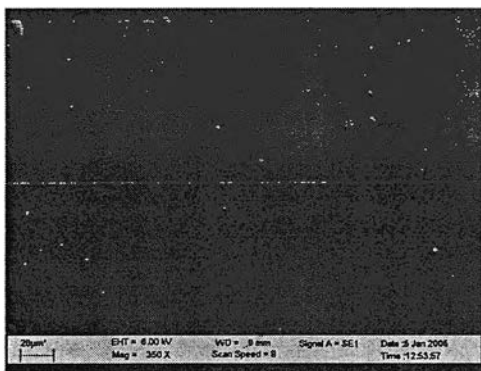
(a) TiO₂ thin film calcined at 300°C



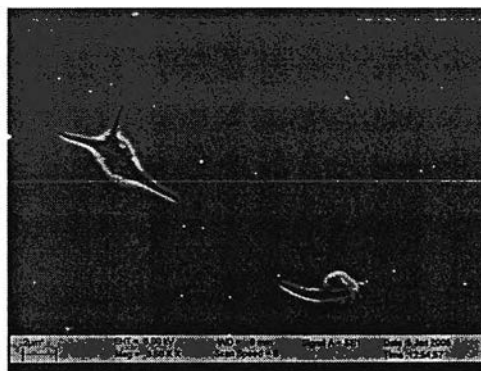
350 magnification



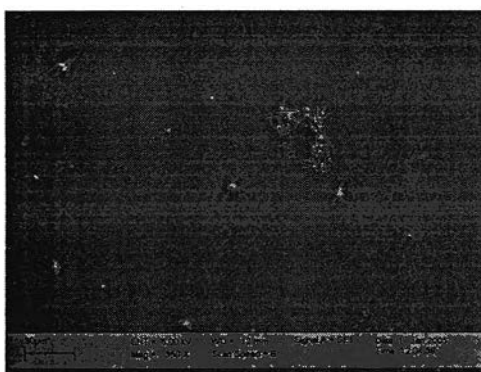
3,500 magnification

(b) TiO₂ thin film calcined at 400°C

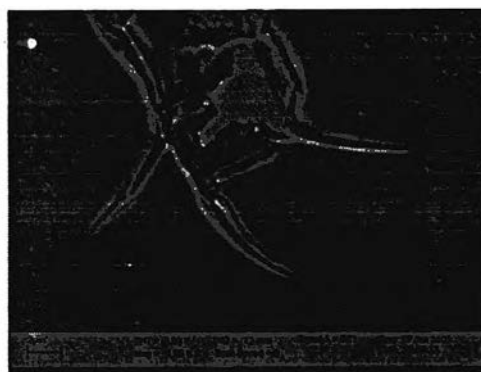
350 magnification



3,500 magnification

(c) TiO₂ thin film calcined at 500°C

350 magnification



3,500 magnification

(d) TiO₂ thin film calcined at 600°C

Figure 4.10 (a)-(d) SEM photographs of the TiO₂ coating films derived from different calcination temperatures.

4.4.4 Crystal structures of TiO₂ thin films by XRD (X-ray diffraction)

Figure 4.11 showed the XRD patterns of the TiO₂ films prepared using sol-gel process by calcining at different temperatures. It can be found that calcination at 500°C yields TiO₂ in the anatase crystal structure that did not get transformed into the rutile form even at 600°C. As the temperature increased from 300°C to 600°C, the intensities of the anatase peaks were increased implying and improvement in crystallinity. It was reported that the films annealed at temperature less than 400°C were amorphous (Hu *et al.*, 1992). In corresponding to the previous study (Hu *et al.*, 1992), with the isopropanol as solvent, anatase phase precipitated at 350-400°C. As the heat treatment proceeds, the TiO₂ gel films tend to shrink resulting in pore disappearance and densification. According to Kim *et al.* (2002), the anatase-to-rutile phase transformation occurred at 1000°C. While Zheng *et al.* (2001) reported that the anatase-to-rutile phase transformation took place at temperatures of 500-850°C. The discrepancy of this transformation may be due to the difference in crystallite structure and size of TiO₂ films as shown in Table 4.15.

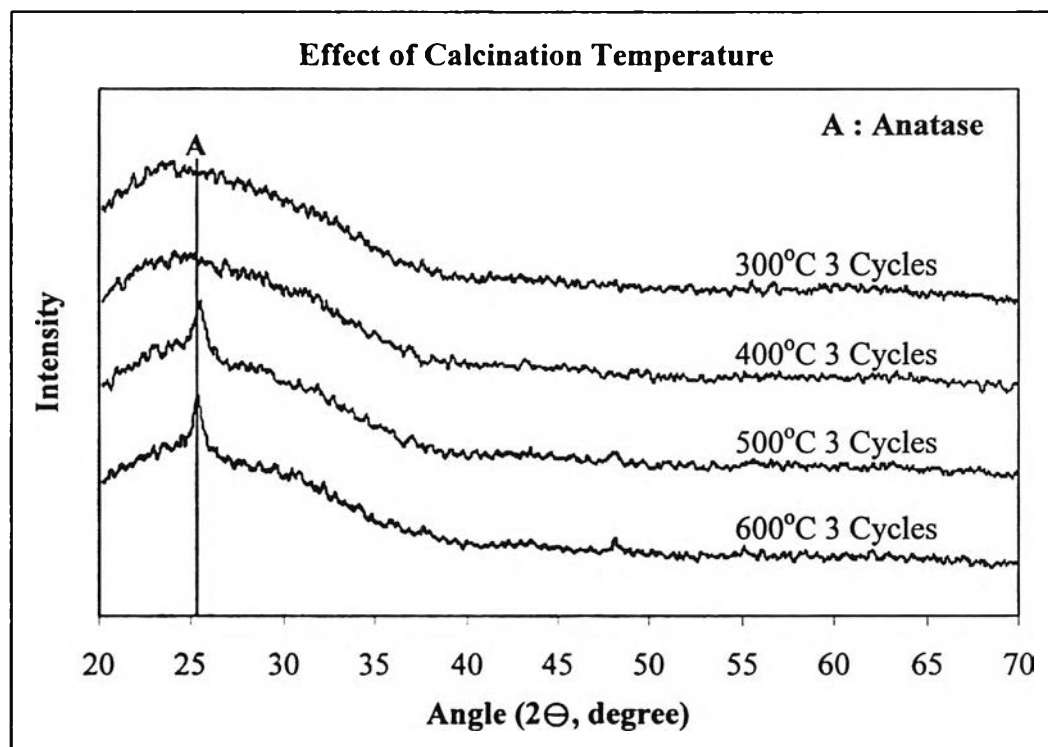


Figure 4.11 XRD patterns of TiO₂ thin films derived from different calcination temperatures.

Table 4.15 Crystallite size of TiO₂ films prepared from different calcination temperatures.

Calcinations temperature	Crystallite Size (nm)
500°C	16.12
600°C	5.97

4.4.5 Photocatalytic activity

The amount of Cr(VI) reduced over experimental time during photocatalytic reactions using films calcined at various temperatures was shown in Figure 4.12. The reaction rate constant increases between 400°C and 500°C as calcination temperature increase and then begin to decrease at 600°C. From these results, the highest efficiency for the photocatalytic reduction was obtained with a film calcined at 500°C. This phenomenon of decreased efficiency at 600°C is probably due to the decrease in porosity of TiO₂ with an increased densification.

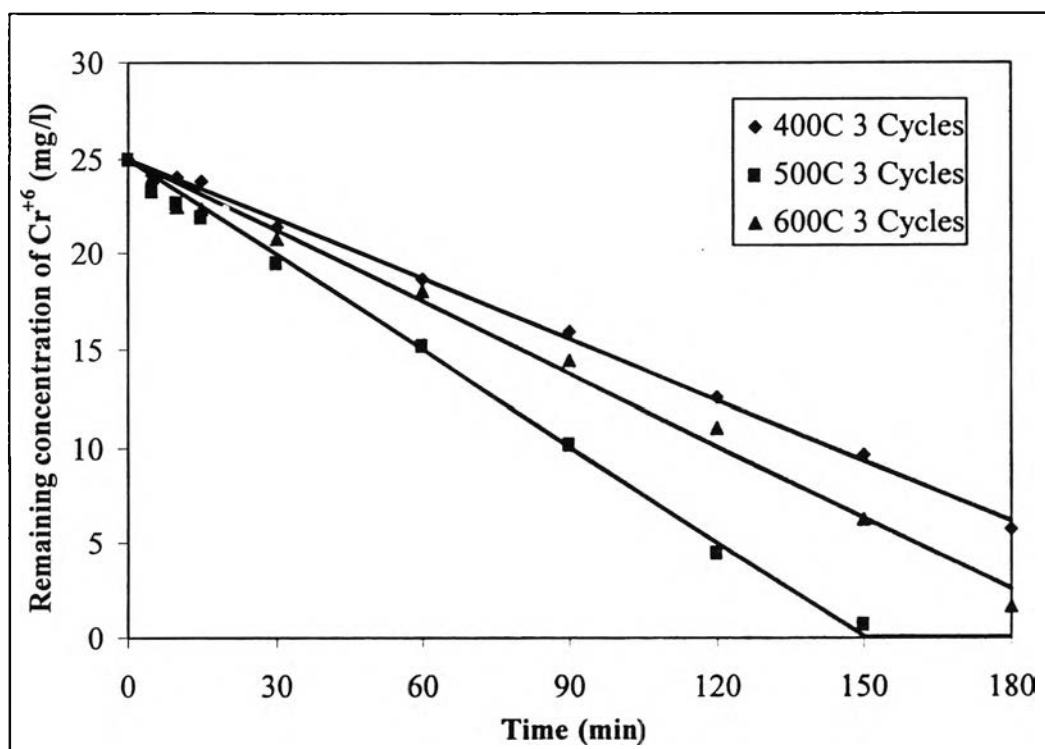


Figure 4.12 Photocatalytic reduction of Cr(VI) on TiO₂ thin film derived from different calcination temperatures.

Table 4.16 Reaction rate constants for chromium(VI) photocatalytic removal using thin film TiO₂ derived from different calcination temperatures.

Calcination temperature	Rate constant (k, mg/l-min)	r ²
400°C	0.1043	0.9979
500°C	0.1659	0.9957
600°C	0.1243	0.9910

4.5 Effect of coating cycles on preparations of TiO₂ thin film

This multistep coating can be performed by preparing coating solution with ratio of titanium(IV) butoxide : ethanol : HCl : acetylacetone as value of 1:30:0.5:1. Then, the substrates were dipped into sol for 1, 3 and 5 times, respectively and heated at 500 °C for 30 min after each coating. The use of multistep coating process was expected to lead the higher quality of thin films as compared to the one step coating.

4.5.1 Weighing by scale

Amount of TiO₂ attached on glass substrate was varied from 0.048 to 0.125 10⁻³g/cm² by increasing the coating cycles as shown in Table 4.17. From previous studies (Fretwell *et al.*, 2001; Takahashi *et al.*, 2001), amount of TiO₂ on the substrate increased as the film thickness increased, probably result in the number of coating cycles increased. Furthermore, the color of TiO₂ film strongly depends on the film thickness. As the thickness of TiO₂ films increases, the coloration becomes indistinct (Yu *et al.*, 2001).

Table 4.17 Amount of TiO₂ thin film derived from several coating cycles.

Coating cycles	Amount of TiO ₂ per unit of surface area (10 ⁻³ g/cm ²)						
	No.1	No.2	No.3	No.4	No.5	Average	SD
1 coating cycle	0.040	0.067	0.040	0.053	0.040	0.048	0.012
3 coating cycles	0.053	0.080	0.027	0.093	0.013	0.053	0.034
5 coating cycles	0.080	0.120	0.080	0.120	0.227	0.125	0.060

Remark: Amount of TiO₂ was calculated from the film with 3 coating cycles.

The area of glass plate coated with TiO₂ film is about 7.5 cm³.

4.5.2 Adhesive test and corrosive test

From the results shown in Table 4.18, as the coating cycles increased, all TiO₂ films were resistant to peeling with adhesive tape. Moreover, they also were not removed from the glass substrate even with 10M HNO₃ and NaOH.

Table 4.18 Results of adhesive and corrosive tests of TiO₂ thin film derived from several coating cycles.

Coating cycles	Adhesive Test	Corrosive Test	
		Acidic condition	Basic condition
1 coating cycle	✓	✓	✓
3 coating cycles	✓	✓	✓
5 coating cycles	✓	✓	✓

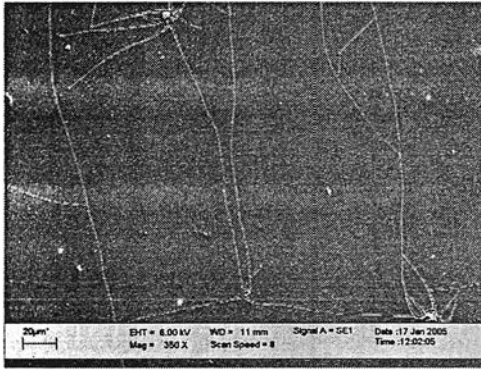
Remark: ✓ means the film was passed the test

✗ means the film was fail in this test

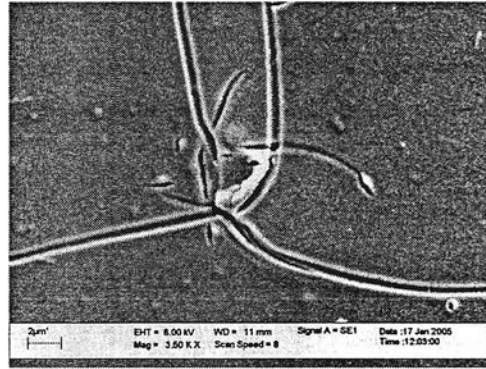
4.5.3 Surface morphology by SEM (Scanning Electron Microscopy)

TiO₂ film immobilized with the coating cycle of 1, 3 and 5 respectively, these SEM photographs were shown in Figure 4.13. The surface of TiO₂ film obtained from each coating cycle was very uniform. When TiO₂ films were observed along fissure at

higher magnification, the thickness of thin films was increased as coating cycle increased. In addition, the multistep TiO_2 thin films exhibit high homogeneity and increasing of adherence on glass substrates as well as influent the thickness of TiO_2 thin films.



350 magnification



3,500 magnification

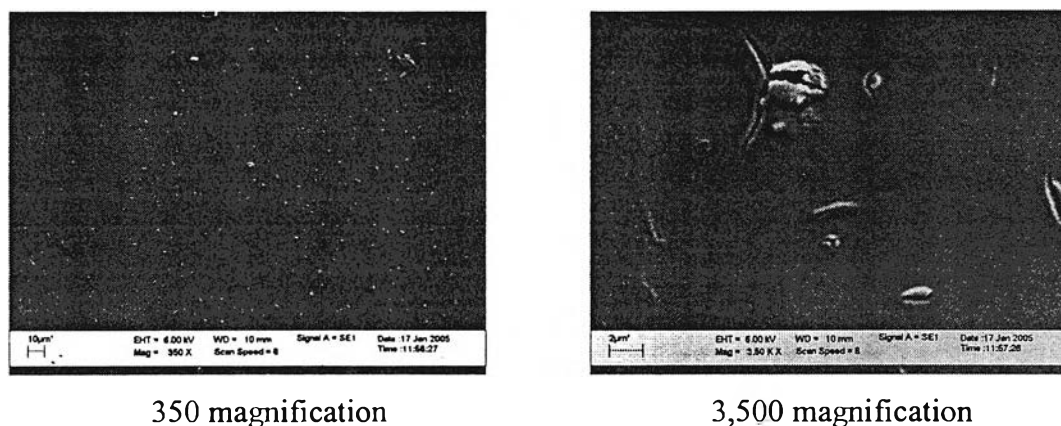
(a) TiO_2 thin film with 1 coating cycle

350 magnification



3,500 magnification

(b) TiO_2 thin film with 3 coating cycles



350 magnification

3,500 magnification

(c) TiO₂ thin film with 5 coating cycles

Figure 4.13 SEM photographs of TiO₂ thin film with multistep coating cycles (a) 1 cycle and (b) 3 cycles (c) 5 cycles.

4.5.4 Crystal structures of TiO₂ thin films by XRD (X-ray diffraction)

Figure 4.14 shows correlation between crystal structure and TiO₂ film immobilized with several coating cycles. The film with 1 coating cycle showed a lowest intensity of anatase peak. Especially, it should be note that the thickness was quite too thin resulting in less amount of TiO₂. As the number of coating cycles increased from 3 to 5 cycles, high amounts of anatase crystalline where the peaks show at 25.28°, 37.8° and 48.05° of 2θ were also obtained (Campbell *et al.*, 1986). This may be attributed to the high content of titanium dioxide with several coating cycles resulting the obvious peaks of anatase (Yu *et al.*, 2000). Kajitvichyanukul *et al.* (2005) investigated the effect of coating cycles on phase transformation of TiO₂ film. It was indicated that with the increasing of coating cycles up to 5, the rutile was shown. This information suggests that the transformation from anatase to rutile was more pronounced with high amount of coating cycle. Moreover, the rutile increment tends to increase with the coating cycle of TiO₂. In this study, although TiO₂ thin film was dip coated until 5 cycles, the crystals in rutile phase not appeared. It was possible from the effects of acetylacetone, which retards the phase transition from anatase to rutile exactly the same as its effect on calcination temperature. In addition, the crystallite size of TiO₂ films was improved with the increasing coating. The average crystallite size was calculated shown in Table 4.19.

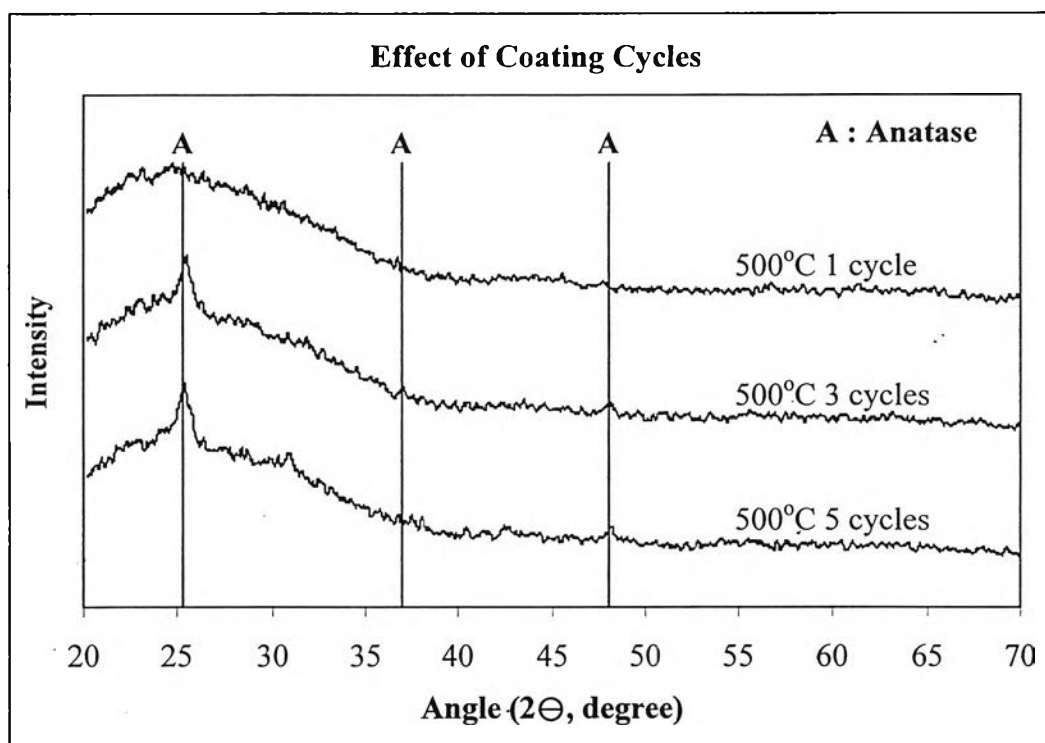


Figure 4.14 XRD patterns of TiO₂ thin films derived from several coating cycles.

Table 4.19 Crystallite size of TiO₂ films prepared from several coating cycles.

Coating cycles	Crystallite Size (nm)
3 coating cycles	16.12
5 coating cycles	18.31

4.5.5 Photocatalytic activity

Removal profiles under reducing conditions using TiO₂ films with different coating cycles were shown in Figure 4.15. The Cr(VI) concentrations increased when multilayer of TiO₂ were deposited on glass substrate. The removal efficiency of thin film with 3 coating cycles was higher than any other. The difference in photocatalytic efficiency may be due to the increased amount of TiO₂. Subsequent depositional cycles displayed essentially no increase in performance up to 5 coating cycles, even through the thickness of the film increased as the coating cycles increased.

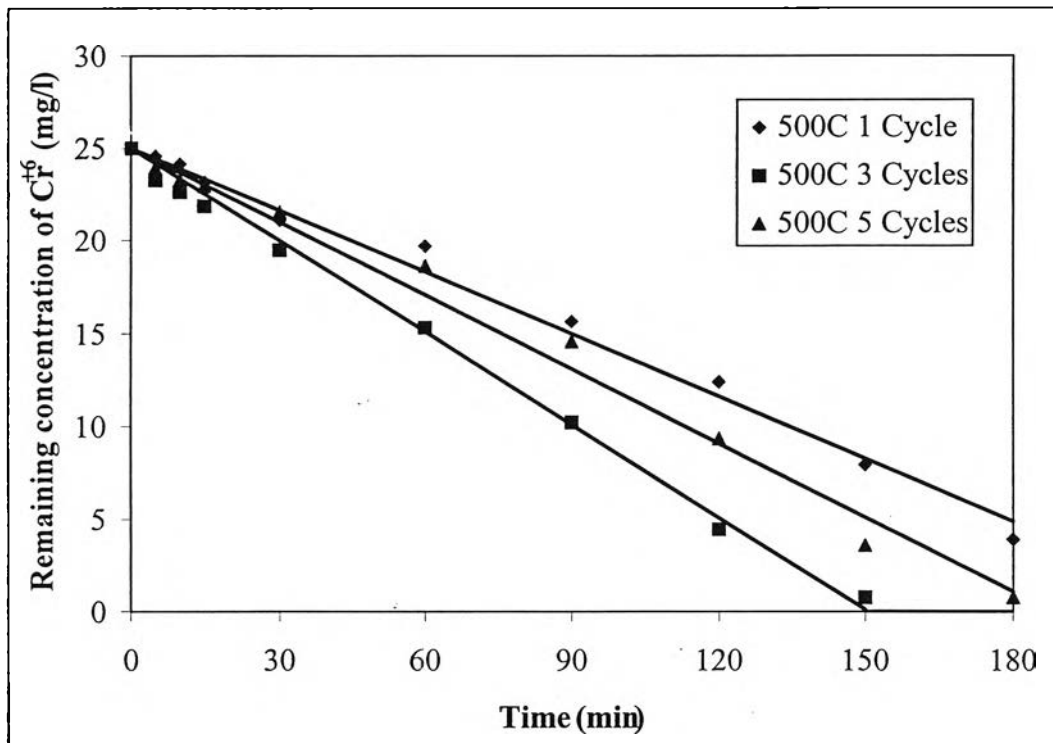


Figure 4.15 Photocatalytic reduction of Cr(VI) on TiO₂ thin film derived from several coating cycles.

It was clearly seen from Table 4.20 that rate constant with number of 1, 3 and 5 coating cycles were 0.1118, 0.1659 and 0.1331 mg/l-min. The rate constant (k) increased from 1 to 3 coating cycles and then decreased with 5 coating cycles. There are two major characteristics play role as a factor controlling photocatalytic activity. First, anatase proportion of TiO₂ films and, second, the particle sizes. As the coating cycles increased, the amount of deposited titanium dioxide and its anatase was increased resulting in high activity of photocatalytic process, but in this study, there is no significant different in intensity of anatase peak. On the other hand, as the particle size increased with the increasing of coating cycles, the photocatalytic reduction of Cr(VI) was decreased. In comparable, particle size plays as a major factor controlling photoactivity of the film here. Thus, the photocatalytic activity of TiO₂ thin films prepared with 5 coating cycles is less than the 3 coating cycles.

Table 4.20 Reaction rate constants for chromium(VI) photocatalytic removal using thin film TiO₂ derived from several coating cycles.

Coating cycles	Rate constant (k, mg/l-min)	r²
1 coating cycle	0.1118	0.9918
3 coating cycles	0.1659	0.9957
5 coating cycles	0.1331	0.9895