CHAPTER IV

RESULTS AND DISCUSSION

4.1 Roles of ethanol in preparation of TiO_2 thin film

In this experiment, coating solutions were prepared by varying amount of ethanol (without any organic additives) to amount of titanium tetraisopropoxide (TTiP) in term of the mole ratio of TTiP:ethanol at 1:20, 1:30, 1:40, 1:50 and 1:60. The coated gels were calcined at 500°C in a furnace for 30 min. The results from the experiment not only showed the roles of the solvent but the optimum amount of ethanol were also obtained.

4.1.1 Results of weight by scale, adhesive and corrosive tests

Mass of TiO_2 thin film coated on stainless steel is shown in Table 4.1. The results were calculated by weighing substrate before and after coating with the film.

Table 4.1 Mass of TiO_2 thin film after coating for each mole ratio of ethanol

Mole ratio of TTiP:Ethanol	**Mass 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**
1:20	0.133	0.150	0.117	0.150	0.133	0.137	0.014
1:30	0.133	0.100	0.100	0.117	0.100	0.110	0.015
1:40	0.067	0.100	0.083	0.083	0.083	0.083	0.012
1:50	0.100	0.050	0.050	0.067	0.067	0.067	0.020
1:60	0.083	0.083	0.050	0.050	0.050	0.063	0.018

Remark: Increased of TiO_2 mass was calculated from the film with three-coating cycle. The area of stainless steel covered by TiO_2 layer was approximately 6 cm^2.

From Table 4.1, the TiO_2 weights of all samples were increased after coating. The thin film obtained from the mole ratio of TTiP:ethanol at 1:20 provided the highest amount of TiO_2. Moreover, the mass was decreased with increasing amount of ethanol. Since ethanol is used as a solvent to dissolve TiO_2 in sol solution; therefore, the more mole ratio of ethanol was applied, the less of TiO_2 mass was obtained. This result was in accordance with the results observed by Vicente et al. (2001). Furthermore, concentration of ethanol had an effect on the film thickness. They indicated that the layer thickness could be tailored by controlling the titanium and ethanol ratio in the solution. In addition, the ethanol is easily decomposed during the heat treatment; hence, the mass shown in Table 4.1 was presented only the mass of TiO_2.

The results of adhesive and corrosive tests are presented in Table 4.2. These tests were conducted to examine the film robustness by adhering with Scotch Tape™ for adhesive test, and dipping in acid and alkali solution for corrosive test.

Table 4.2 Results of adhesive and corrosive tests of TiO_2 thin film at different ratios of ethanol

Mole ratio of TTiP:Ethanol	Adhesive Test	Corrosive Test in acid solution	Corrosive Test in alkali solution
1:20	✗	✗	✗
1:30	✗	✓	✓
1:40	✓	✓	✓
1:50	✓	✓	✓
1:60	✓	✓	✓

Remark: ✓ means the film passed the test and ✗ means the film failed in this test

From Table 4.2, TiO_2 thin films prepared at low concentration of ethanol did not pass adhesive and corrosive tests. At TTiP:ethanol of 1:20 and 1:30, the films were easily detached from stainless steel surface by adhesive test. In addition, those films were peeled off from the stainless steel when dipped in acid and alkali solution. On the other hand, at the mole ratio of TTiP to ethanol equaled to 1:40, 1:50 and 1:60, the films were well attached on the substrate and their surface did not change when dipped in both acid and alkali solution. However, the results from this experimental set could not identify the optimum ratio of TTiP to ethanol for thin film preparation. All films were taken to examine for further characteristic information using scanning electron microscope (SEM) and x-ray diffractometer (XRD).

4.1.2 Thin film surface morphology analysis by SEM

The images of original stainless surface, illustrated in Figure 4.1 and Figure 4.2 show the surface morphology of TiO_2 thin film at different mole ratios of TTiP to ethanol.

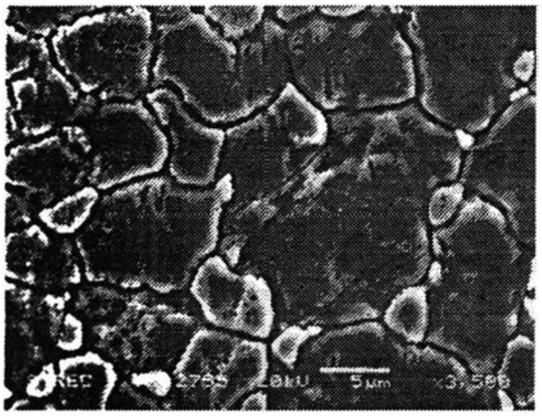
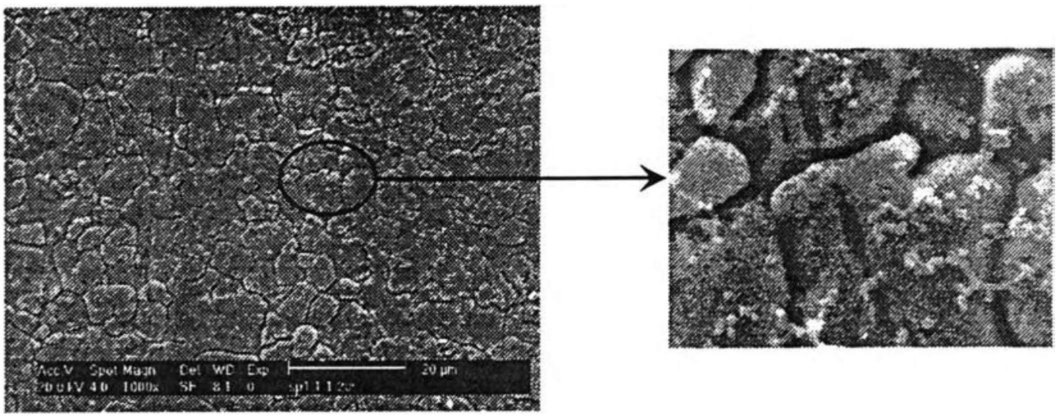
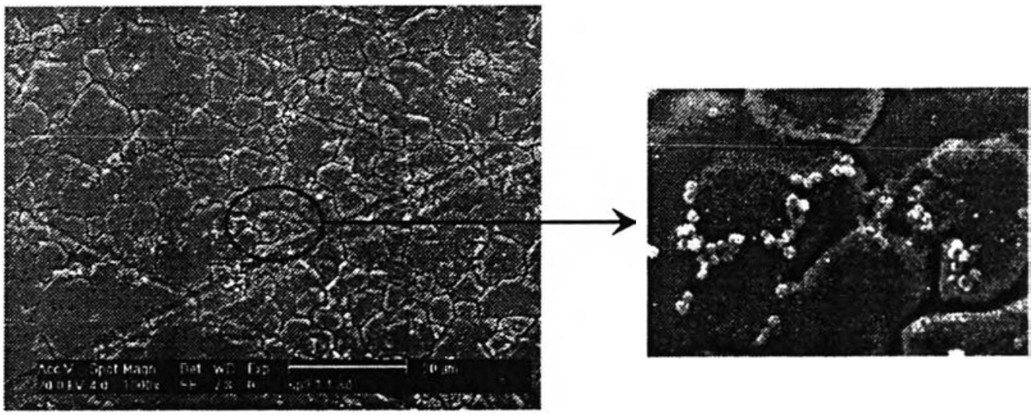


Figure 4.1 Stainless steel surface without TiO_2 thin film at 3500 × magnification



1000 × magnification 3500 × magnification

a) TTiP:ethanol = 1:20



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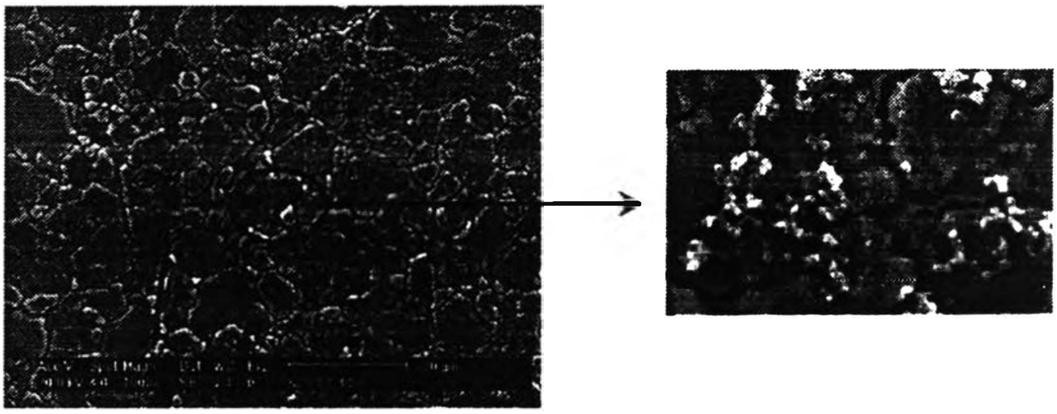
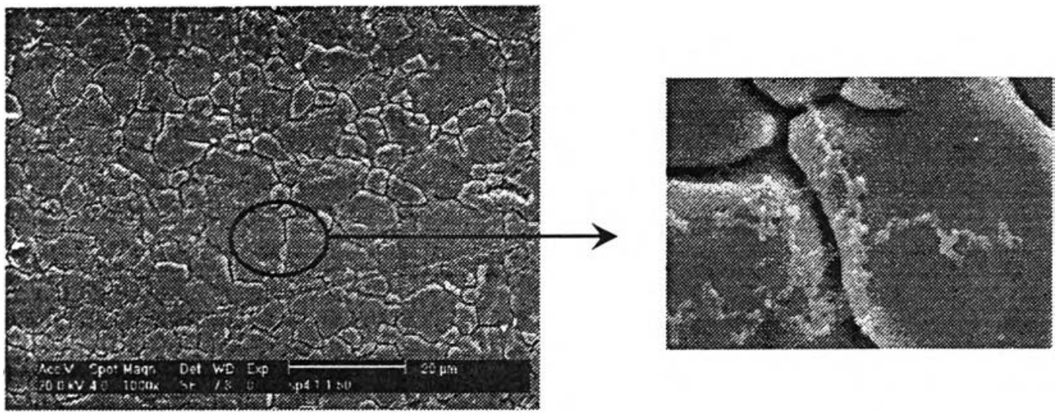
b) TTiP:ethanol = 1:30



1000 × magnification 3500 × magnification

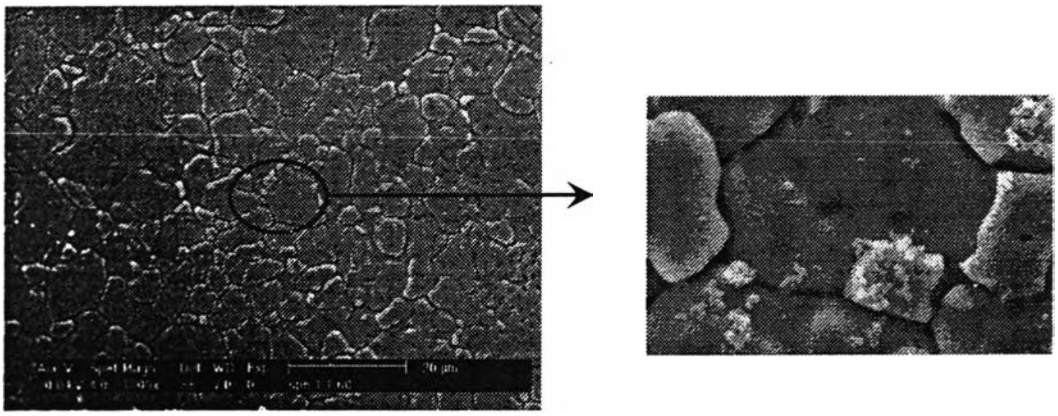
c) TTiP:ethanol = 1:40

Figure 4.2 Scanning electron micrographs of the TiO_2 thin film surface prepared with different ratios of TTiP to ethanol



1000 × magnification 3500 × magnification

d) TTiP:ethanol = 1:50



1000 × magnification 3500 × magnification

e) TTiP:ethanol = 1:60

Figure 4.2 (*cont.*) Scanning electron micrographs of the TiO_2 thin film surface prepared with different ratios of TTiP to ethanol

Figure 4.1 shows the original macroscopic morphology of stainless steel without any deposition of TiO_2 on the surface. The grain boundaries of stainless steel were clearly seen. After coated with TiO_2 thin film (Figure 4.2), the boundary was shallow as TiO_2 film covered on both stainless grain and its surface. With a higher magnification in Figure 4.2 (a) – (e), it is obvious that some particles left on the surface of the thin film. It is anticipated that the particles remaining on the surface of the thin film were the developed TiO_2 (Kajitvichyanukul and Amornchat, 2005) since the organic components of the unfired coatings were decomposed during the heat treatment.

The coating phenomena using ethanol as a solvent could be explained by Hu et al. (1992). When adding ethanol to coating solution, the rate of hydrolysis and condensation of metal alkoxide was considerably slow comparing to the use of isopropanol as a solvent. This low reaction rates gave rise to the formation of particles in the sol and provided a smooth surface of the film.

4.1.3 Crystallization of TiO_2 thin film

For crystallization analysis, it is worthy to note that all samples were prepared with 3-coating cycle as it provided the suitable thickness to detect the anatase and rutile peaks of TiO_2. The X-ray diffraction patterns of the TiO_2 thin film obtained from different mole ratios of TTiP to ethanol are shown in Figure 4.3. In general, the peaks of anatase crystalline can be detected at the 2Θ angles of 25.3°, 37.8°, 48.04°, 53.9° and 62.1° and peaks of rutile can be detected at 2Θ angles of 27.4°, 36.08°, 41.2° and 56.6°.

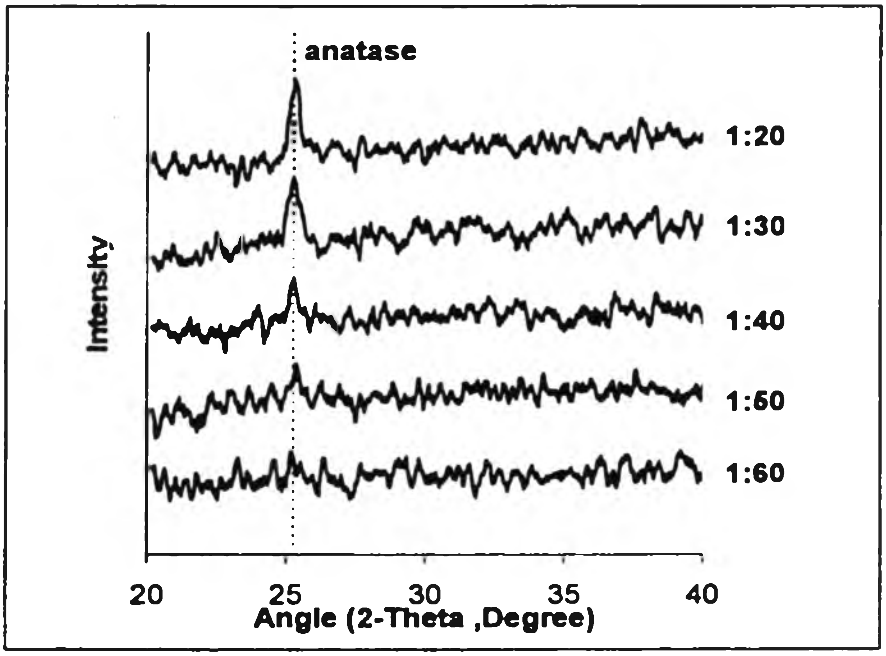


Figure 4.3 X-ray diffraction pattern of TiO_2 thin film obtained from different mole ratios of TTiP to ethanol

The films from this work exhibited the main peak of 2Θ at 25.3°, thus, their crystalline are mainly an anatase phase. At TTiP:ethanol = 1:20, the highest peak of anatase was obtained and at 1:60, no peak of anatase was observed. The intensity of XRD peak of anatase increased with the decreasing amount of solvent. Since the peak intensity was depended on mass of TiO_2 which was also correlated with the result from 4.1.1 in that the higher amount of solvent used resulted in less amount of TiO_2 deposited on the stainless steel plate. In addition, two strong peaks were observed at 43.58° and 50.8°, which resulted from the diffraction of stainless steel substrate from the heat treatment process (Figure 4.4).

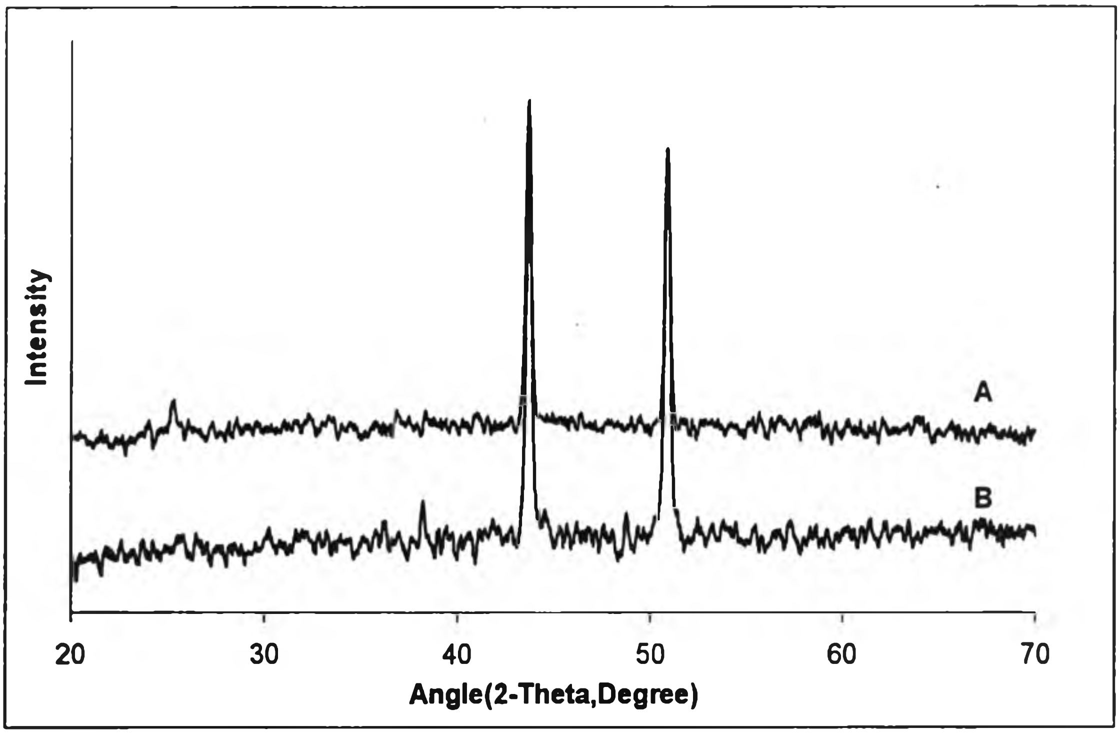


Figure 4.4 X-ray diffraction pattern of (A) TiO_2 thin film coated on stainless steel and (B) stainless steel

The crystallize sizes of the catalysts can be determined from the broadening of the anatase main peak using the Debye-Scherrer equation. The crystallize sizes of TiO_2 prepared with different mole ratios of ethanol are presented in Table 4.3. The result showed that amount of ethanol exerted an effect on crystallite size. Crystallize size of anatase increased with the decrease of ethanol concentration. This phenomenon was correlated with the previous work done by Legrand-Buscema et al.

(2002) who found that decreasing of ethanol concentration increased not only the film thickness but also TiO_2 grain size.

Table 4.3 Crystallite size of TiO_2 thin film with different mole ratios of ethanol

Mole ratio of TTiP:Ethanol	Crystallite Size (nm)
1:20	46.7
1:30	45.0
1:40	43.9
1:50	42.7

Although, the films prepared at 20 and 30 mole of ethanol showed high amount of anatase which have high activity for photocatalytic reaction, the adherence property and the corrosive resistance were relatively poor. The films obtained from 40 mole of ethanol were considered as the appropriate thin films, because of their good adherence property, corrosive resistance and high anatase crystalline, thus, they were used in subsequent experiments.

4.2 Roles of PEG600 in preparation of TiO_2 thin film

In this experiment, coating solutions were prepared by varying amounts of polyethylene glycol with molecular weight 600 g/mol (PEG600). The mole ratio of TTiP:ethanol:PEG600 used were 1:40:0, 1:40:0.5, 1:40:1 and 1:40:1.5. The coated gels were calcined at 500°C in a furnace for 30 min. In addition, the mole ratio of TTiP:ethanol at 1:20 was included in this set in order to illustrate roles of PEG600 on TiO_2 thin film prepared with the low solvent ratio.

4.2.1 Results of weight by scale, adhesive and corrosive tests

Amount of TiO_2 attached to substrate and the results of adhesive and corrosive tests are summarized in Tables 4.4 and 4.5.

Table 4.4 Mass of TiO_2 thin film after coating for each mole ratio of PEG600

Mole ratio of TTiP:Ethanol:PEG600	**Mass 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**
1:40:0	0.067	0.100	0.083	0.083	0.083	0.083	0.012
1:40:0.5	0.100	0.083	0.100	0.067	0.083	0.087	0.014
1:40:1	0.133	0.100	0.100	0.083	0.100	0.103	0.018
1:40:1.5	0.100	0.100	0.100	0.100	0.100	0.100	0
1:20:0	0.133	0.150	0.117	0.150	0.133	0.137	0.014
1:20:0.5	0.200	0.200	0.183	0.167	0.150	0.180	0.022
1:20:1	0.200	0.200	0.217	0.150	0.183	0.190	0.025

Remark: Increased of TiO_2 mass was calculated from the film with three-coating cycle. The area of stainless steel covered by TiO_2 layer was approximately 6 cm^2.

It can be seen that the mass of TiO_2 was slightly increased with the increased amount of PEG600 (Table 4.4). As PEG600 has higher viscosity comparing with ethanol, the sol solution in this case was relatively thick. The film thickness was increased with the increase in the viscosity of the precursor sol (Sonawane et al., 2002). Therefore, adding higher amount of PEG600, the amount of TiO_2 attached to the substrate was increased. However, the thickness of films was hardly influenced by the addition of PEG if the molecular weight was not too high (Zhang, Au et al., 2004). In addition, PEG600 is organic compound which is decomposed at high temperature; thus, the mass in Table 4.4 is presented only the mass of TiO_2.

When adding PEG600, TiO_2 thin films from all tested ratios of TTiP to ethanol and PEG600 were passed the adhesive and corrosive tests (Table 4.5). The film robustness was improved when applied PEG600 to the coating solution with low ethanol concentration (TTiP:ethanol = 1:20). At this ratio but without PEG600, the adhesion of the obtained film was very poor. When only small amount of PEG600 was applied, the film adherence was substantially improved. Moreover, the films were not removed from the substrate surface even when they were dipped in 10 M of NaOH and HNO_3.

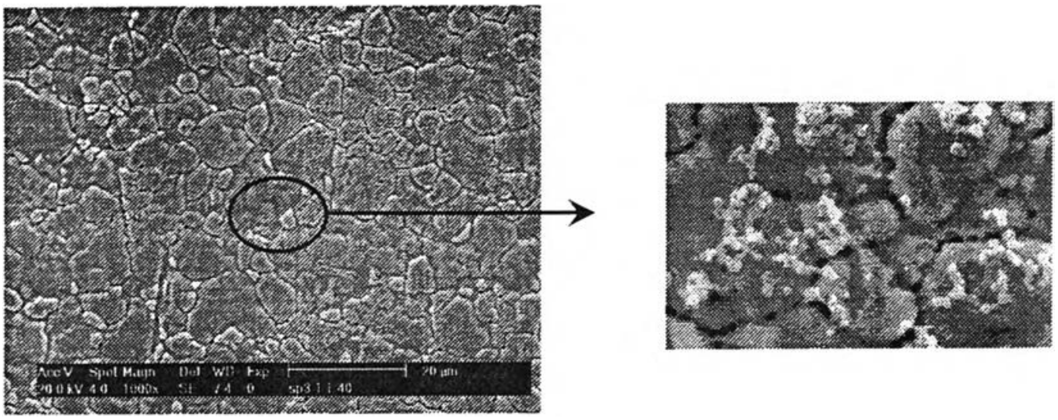
Table 4.5 Results of adhesive and corrosive tests of TiO_2 thin film at different ratios of PEG600

Mole ratio of TTiP:Ethanol:PEG600	Adhesive Test	Corrosive Test in acid solution	Corrosive Test in alkali solution
1:40:0	✓	✓	✓
1:40:0.5	✓	✓	✓
1:40:1	✓	✓	✓
1:40:1.5	✓	✓	✓
1:20:0	✗	✗	✗
1:20:0.5	✓	✓	✓
1:20:1	✓	✓	✓

Remark: ✓ means the film passed the test and ✗ means the film failed in this test

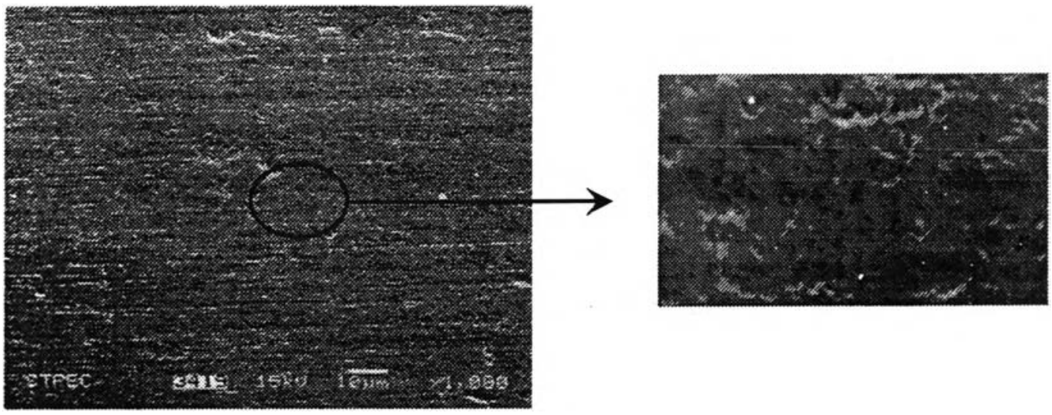
4.2.2 Thin film surface morphology analysis by SEM

Figure 4.5 and 4.6 show the surface morphology of TiO_2 thin film at different amounts of PEG600 with TTiP:ethanol = 1:20 and 1:40. Without PEG600, there were some particles on the film surface. These particles were disappeared when applied only small amount of PEG600 to the sol solution. The flat and smoothness of TiO_2 thin film was also obtained. Moreover, the film appeared thicker by adding PEG600. The film surfaces did not exhibit significantly difference when higher PEG600 content was applied.



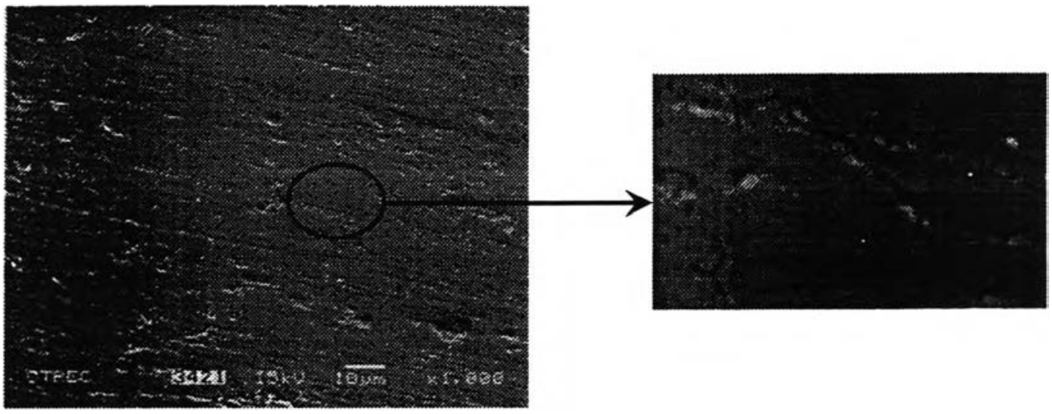
1000 × magnification 3500 × magnification

a) TTiP:ethanol:PEG600 = 1:40:0



1000 × magnification 3500 × magnification

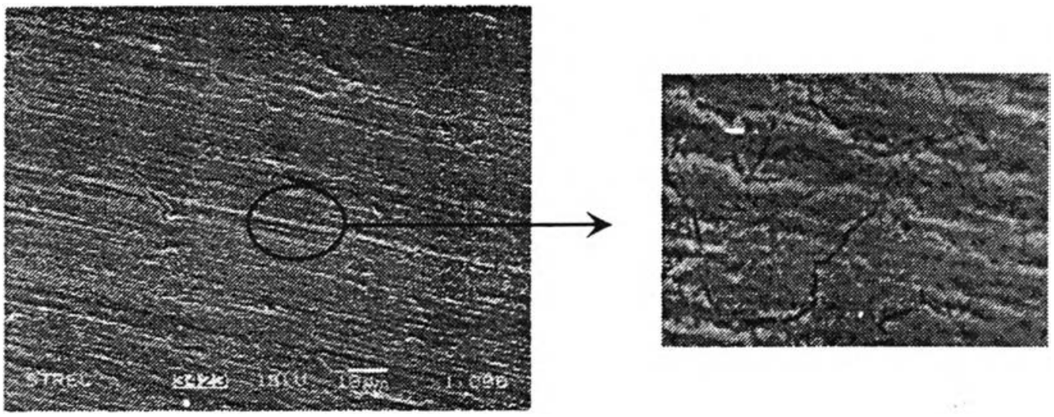
b) TTiP:ethanol:PEG600 = 1:40:0.5



1000 × magnification 3500 × magnification

c) TTiP:ethanol:PEG600 = 1:40:1

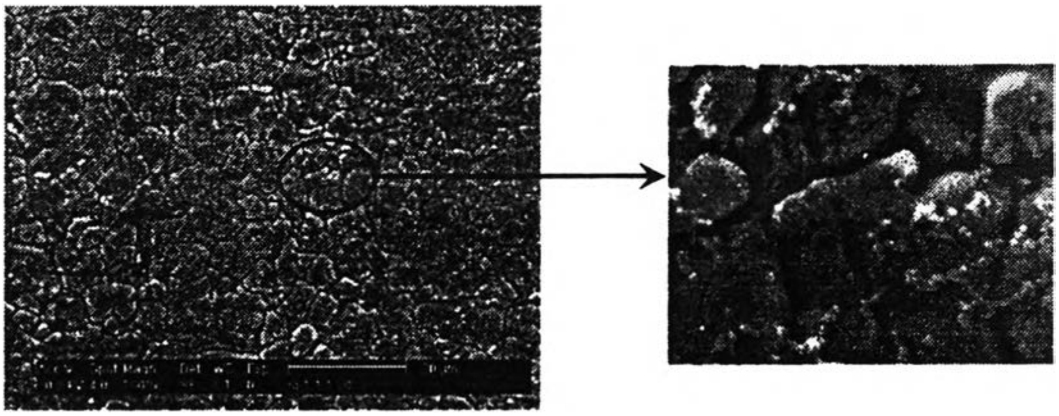
Figure 4.5 Scanning electron micrographs of the TiO_2 thin film surface prepared with the mole ratio of TTiP:ethanol:PEG600 at (a)1:40:0, (b)1:40:0.5, (c)1:40:1 and (d)1:40:1.5



1000 × magnification 3500 × magnification

d) TTiP:ethanol:PEG600 = 1:40:1.5

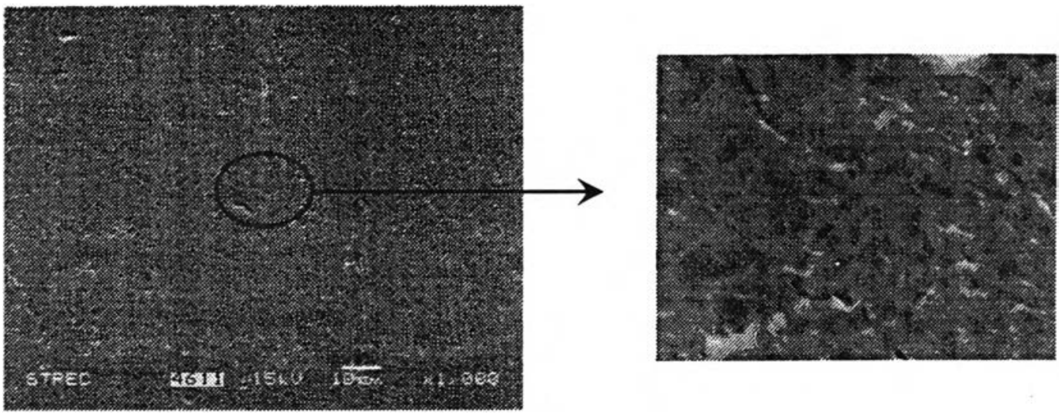
Figure 4.5 (*cont.*)Scanning electron micrographs of the TiO_2 thin film surface prepared with the mole ratio of TTiP:ethanol:PEG600 at (a)1:40:0, (b)1:40:0.5, (c)1:40:1 and (d)1:40:1.5



1000 × magnification 3500 × magnification

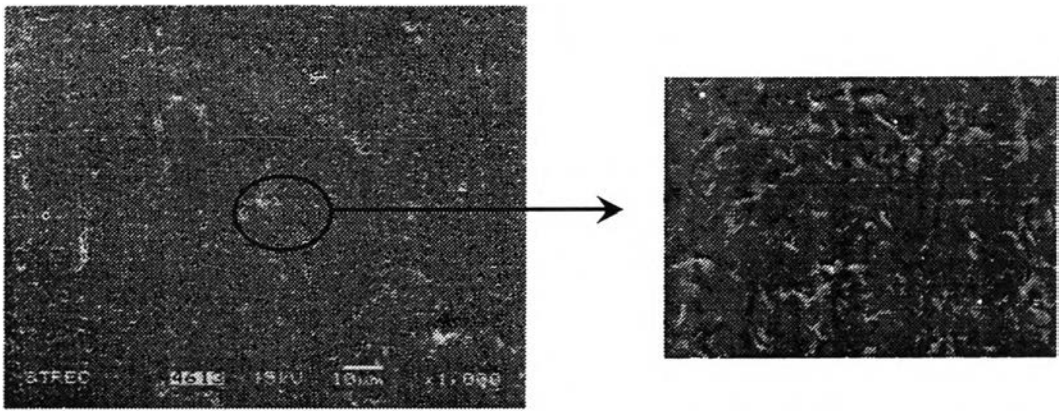
a) TTiP:ethanol:PEG600 = 1:20:0

Figure 4.6 Scanning electron micrographs of the TiO_2 thin film surface prepared with the mole ratio of TTiP:ethanol:PEG600 at (a)1:20:0, (b)1:20:0.5 and



1000 × magnification 3500 × magnification

b) TTiP:ethanol:PEG600 = 1:20:0.5



1000 × magnification 3500 × magnification

c) TTiP:ethanol:PEG600 = 1:20:1

Figure 4.6 (*cont.*) Scanning electron micrographs of the TiO_2 thin film surface prepared with the mole ratio of TTiP:ethanol:PEG600 at (a)1:20:0, (b)1:20:0.5 and (c)1:20:1

With a higher magnification in Figure 4.5 (b)-(d) and Figure 4.6 (b)-(c), it is obvious that the film surface was rough. Many pores were produced in the films which resulted in a high surface area. Zhang, Zhu 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. This process can be illustrated in Figure 4.7. During heating, PEG was oxidized and decomposed to carbon dioxide. Pores were generated by the elimination of the gas phase from the coating (Kato, Tsuge and Niihara, 1996).

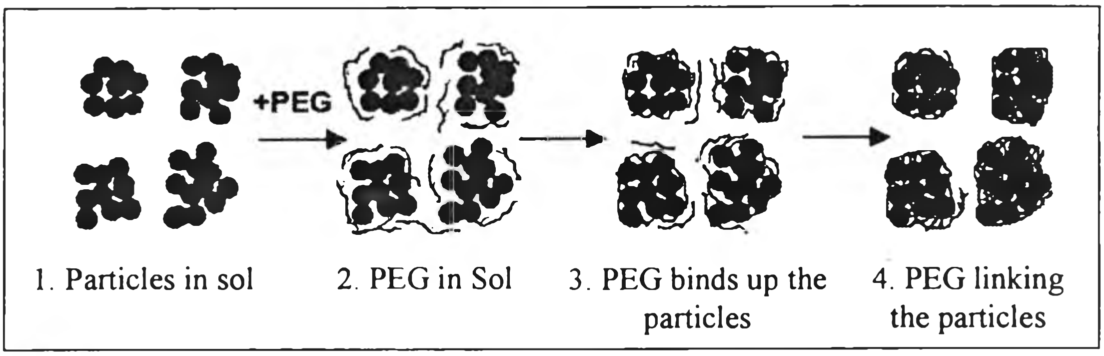


Figure 4.7 Structure-directing process of PEG in the precursor sol (Zhang, Zhu et al., 2003)

4.2.3 Crystallization of TiO_2 thin film

Figure 4.8 shows the XRD pattern of the TiO_2 thin film coated on stainless steel plate using the mole ratio of TTiP to ethanol at 1:20 with different amounts of PEG600. The films obtained from ratio of TTiP to ethanol at 1:20 were selected for crystallization analysis as their XRD patterns were easy to observe.

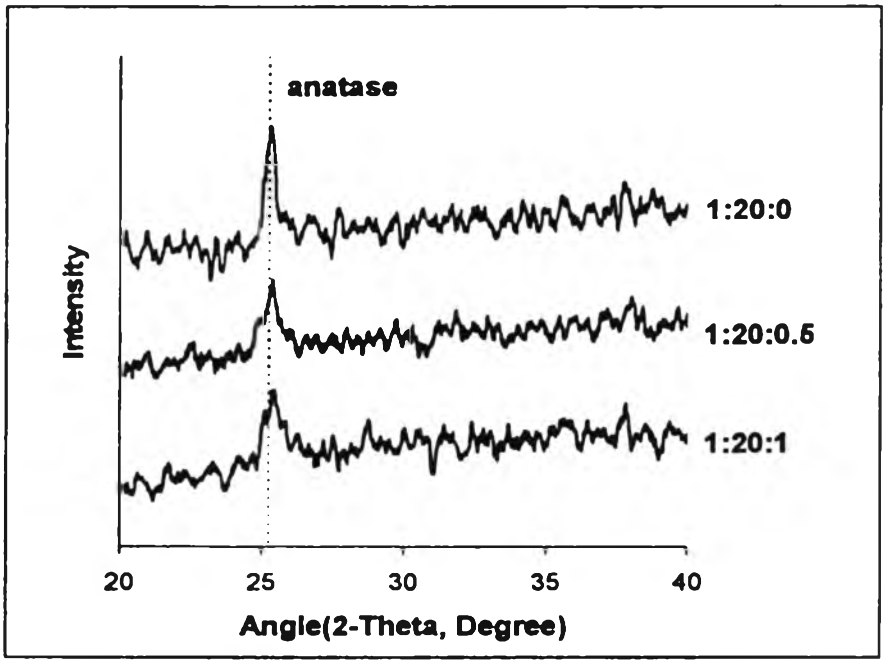


Figure 4.8 X-ray diffraction pattern of TiO_2 thin film prepared with different mole ratios of PEG600

The crystalline was still mainly composed of anatase phase while PEG600 was added. The anatase of the film prepared with PEG600 0.5 mole was slightly higher in intensity comparing to PEG600 1 mole. The addition of PEG600 did not remarkably increase the anatase intensity although the mass of TiO_2 increased with high PEG600 concentration. It was indicated that adding PEG600 to the sol solution resulted in relatively lower peak of anatase. This result was in agreement with Zhang, Au et al. (2004) who found that the XRD pattern of indium tin oxide (TIO) thin film was decreased when PEG with molecular weight 400 was applied to the sol.

The crystallite sizes of each PEG600 concentration are not much different as presented in Table 4.6. Therefore, it can be concluded that amount of PEG600 did not have any effect on the particle size.

Table 4.6 Crystallite size of TiO_2 thin film with different mole ratios of PEG600

Mole ratio of TTiP:Ethanol:PEG600	Crystallite Size (nm)
1:20:0	46.7
1:20:0.5	46.7
1:20:1	50.0

4.2.4 Photocatalytic reduction of chromium(VI)

Since the results of film characterization (XRD and SEM) could not identify the optimum amount of PEG600 used, the films obtained from TTiP to ethanol at 1:20 with different mole ratios of PEG600 were taken to measure photocatalytic efficiency by chromium(VI) removal.

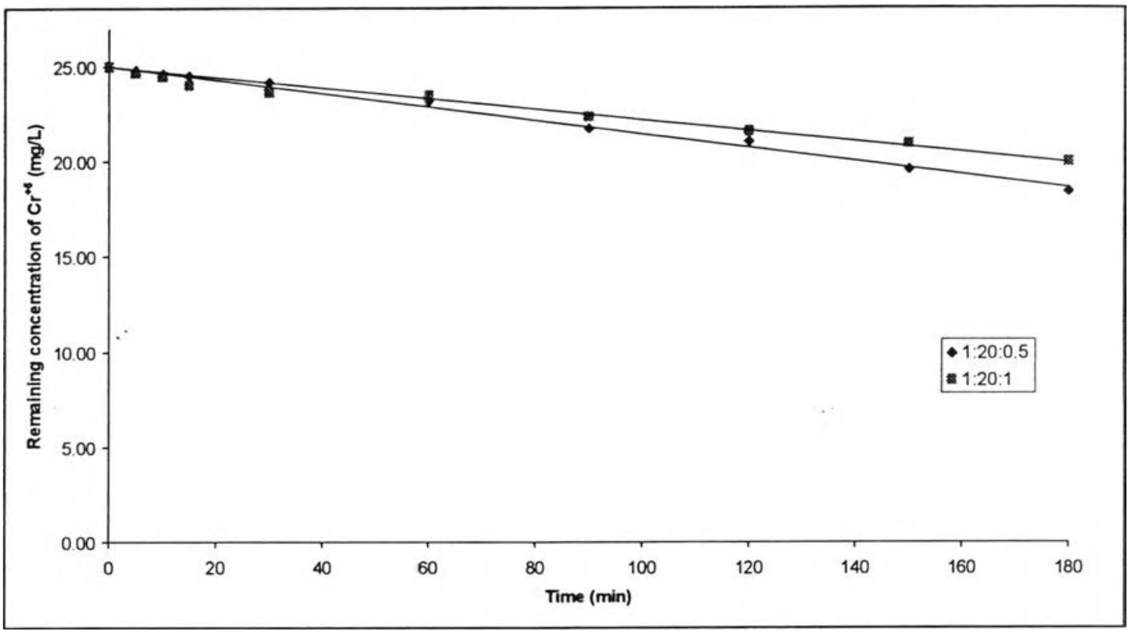


Figure 4.9 Photocatalytic reduction of chromium(VI) on TiO_2 thin film prepared with different mole ratios of PEG600

Figure 4.9 shows the photocatalytic reduction of chromium(VI) on the TiO_2 thin films obtained from different amounts of PEG600. The chromium(VI) concentration was decreased with increasing irradiation time. The reaction rates were found to follow the zero order kinetic model, of which the reaction rate constants were determined by fitting statistically with the experimental data. The calculated reaction rate constants were 0.0353 and 0.0280 mg/(L.min) for the thin film obtained from the ratio of TTiP to ethanol to PEG600 at 1:20:0.5 and 1:20:1, respectively, as shown in Table 4.7. The results indicated that the efficiency for chromium(VI) removal of the film prepared with 0.5 mole of PEG600 was higher than 1 mole of PEG600. It can be explained from the amount of anatase presented in the film as described earlier via the XRD pattern. With addition PEG 0.5 mole to the sol, it is possible that the higher photoactivity of chromium(VI) removal can be achived with the higher amount of anatase. In addition, smaller crystallite size of TiO_2 prepared by PEG 0.5 mole addition might cause the increasing of surface which resulted in higher photocatalytic efficiency.

Table 4.7 Reaction rate constants for chromium(VI) removal of TiO_2 films prepared with different amounts of PEG600

TTiP:ethanol:PEG600	**Rate constant (k, mg/(L.min))**	r^2
1:20:0.5	0.0353	0.9941
1:20:1	0.0280	0.9710

From the results of this experimental set, PEG600 not only played an important role in increasing of film smoothness and film surface but also improved the film adherence and corrosive resistance as seen from the film prepared with low solvent ratio. The TiO_2 film obtained at TTiP to ethanol to PEG600 of 1:20:0.5 was considered as the suitable condition for the further experiment. At this ratio, the quantity of PEG600 was minimum that gave the film smoothness with high surface areas and good adherence on stainless surface. Besides, it exhibited the higher photocatalytic of chromium(VI) removal. The mole ratio of TTiP:ethanol at 1:20 was used instead of 1:40 since the former provided the higher amount of anatase.

4.3 Roles of DEG in preparation of TiO_2 thin film

In this experimental set, the sol solutions were prepared by varying amounts of diethylene glycol (DEG) to amount of titanium tetraisopropoxide (TTiP) and ethanol. The mole ratio of TTiP:ethanol:DEG used were 1:40:0, 1:40:0.5, 1:40:1 and 1:40:1.5. The coated gels were calcined at 500°C in a furnace for 30 min. The mole ratio of TTiP:ethanol at 1:20 was also included in this set in order to observe the effect of DEG on TiO_2 thin film prepared with the low ethanol ratio.

4.3.1 Results of weight by scale, adhesive and corrosive tests

Table 4.8 demonstrates that the mass of TiO_2 in all samples was increased after coating. The amount of TiO_2 was slightly increased when adding DEG. TiO_2 weight did not show much change even the high amounts of DEG were applied.

Table 4.8 Mass of TiO_2 thin film after coating using different mole ratios of DEG

Mole ratio of TTiP:Ethanol:DEG	**Mass 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**
1:40:0	0.067	0.100	0.083	0.083	0.083	0.083	0.012
1:40:0.5	0.100	0.100	0.133	0.117	0.117	0.113	0.014
1:40:1	0.117	0.117	0.100	0.133	0.100	0.113	0.014
1:40:1.5	0.117	0.117	0.117	0.117	0.100	0.114	0.008
1:20:0	0.133	0.150	0.117	0.150	0.133	0.137	0.014
1:20:0.5	0.167	0.150	0.200	0.217	0.167	0.180	0.027
1:20:1	0.183	0.167	0.200	0.167	0.150	0.173	0.019
1:20:1.5	0.150	0.150	0.200	0.233	0.183	0.183	0.035

Remark: Increased of TiO_2 mass was calculated from the film with three-coating cycle. The area of stainless steel covered by TiO_2 layer was approximately 6 cm^2.

The thin film obtained from DEG addition showed good adherence property and corrosive resistance. As represented in Table 4.9, with the low concentration of ethanol and in the absence of DEG, the thin film is peeled off and failed in the adhesive test. The adherence of thin film on stainless steel was substantially improved even small amounts of DEG was applied to the sol. Moreover, the TiO_2 thin films were not removed from the stainless steel substrate even with 10 M NaOH and concentrated HNO_3. In the step of coating solution preparation, the solution was unstable in the absence of DEG. TiO_2 particles were clearly seen after mixing the solution for several minutes.

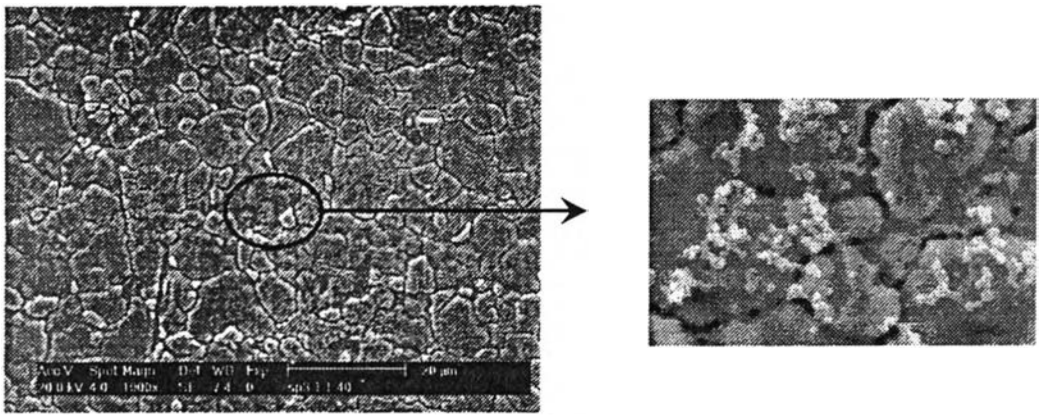
Table 4.9 Results of adhesive and corrosive tests of TiO_2 thin film at different ratios of DEG

Mole ratio of TTiP:Ethanol:DEG	**Adhesive Test**	**Corrosive Test in acid solution**	**Corrosive Test in alkali solution**
1:40:0	✓	✓	✓
1:40:0.5	✓	✓	✓
1:40:1	✓	✓	✓
1:40:1.5	✓	✓	✓
1:20:0	✗	✗	✗
1:20:0.5	✓	✓	✓
1:20:1	✓	✓	✓
1:20:1.5	✓	✓	✓

Remark: ✓ means the film passed the test and ✗ means the film failed in this test

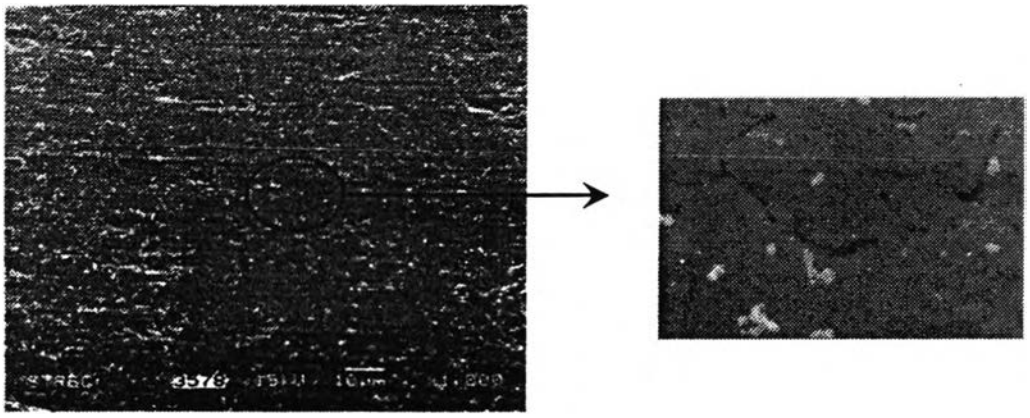
4.3.2 Thin film surface morphology analysis by SEM

Figure 4.10 and Figure 4.11 show the surface morphology of TiO_2 thin film at different amounts of DEG. The flat and smoothness of TiO_2 thin film was obtained when only small amount of DEG was applied to the coating solution. However, the film surfaces were not much different when higher mole ratio of DEG was applied.



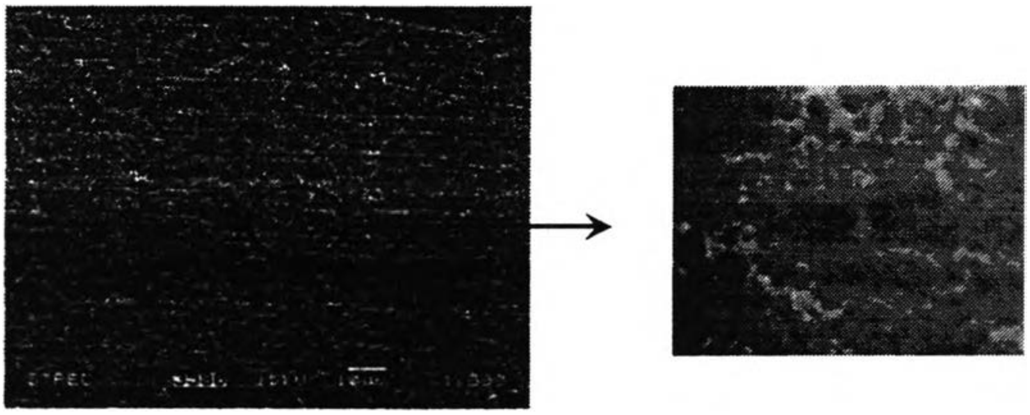
1000 × magnification 3500 × magnification

a) TTiP:ethanol:DEG = 1:40:0



1000 × magnification 3500 × magnification

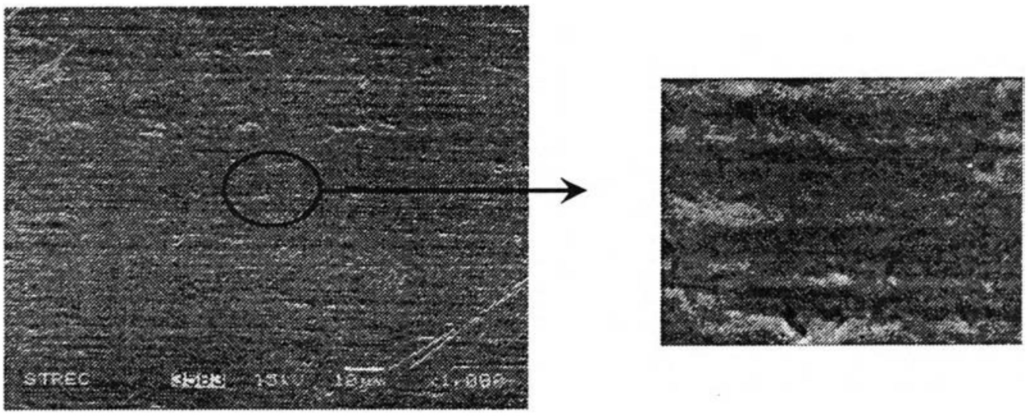
b) TTiP:ethanol:DEG = 1:40:0.5



1000 × magnification 3500 × magnification

c) TTiP:ethanol:DEG = 1:40:1

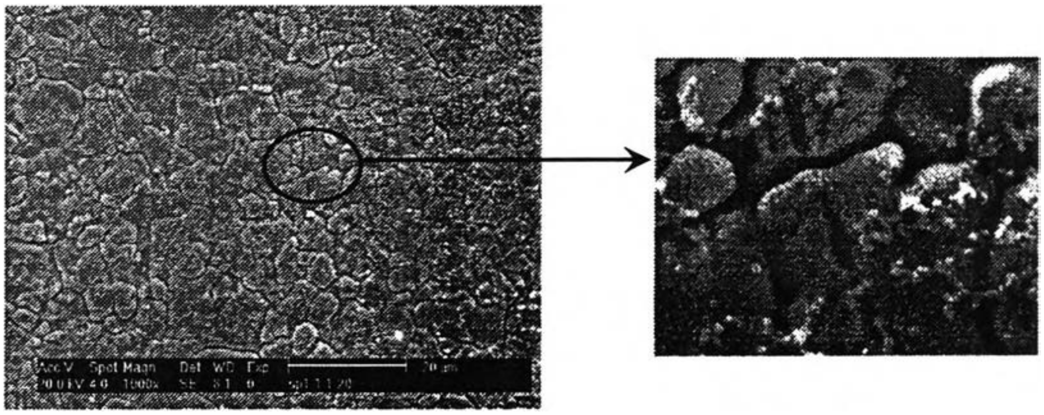
Figure 4.10 Scanning electron micrographs of the TiO_2 thin film surface prepared with the mole ratio of TTiP:ethanol:DEG at (a)1:40:0, (b)1:40:0.5, (c)1:40:1 and (d)1:40:1.5



1000 × magnification   3500 × magnification

d) TTiP:ethanol:DEG = 1:40:1.5

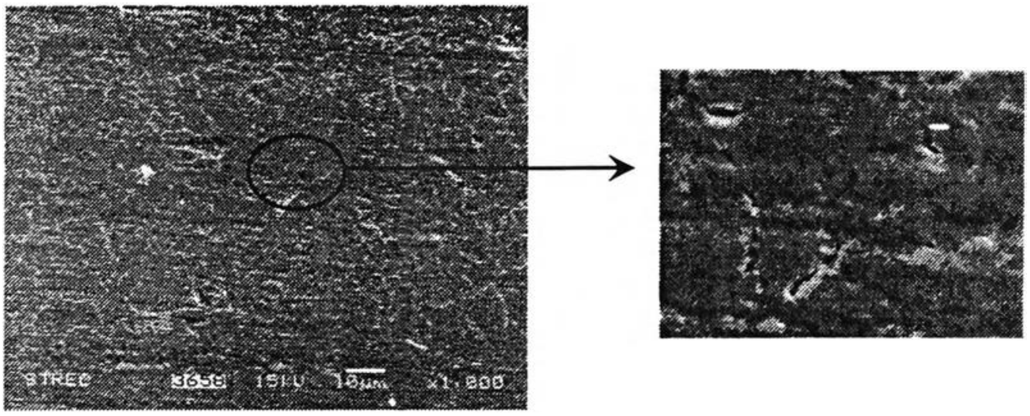
Figure 4.10 (*cont.*) Scanning electron micrographs of the TiO_2 thin film surface prepared with the mole ratio of TTiP:ethanol:DEG at (a)1:40:0, (b)1:40:0.5, (c)1:40:1 and (d)1:40:1.5



1000 × magnification   3500 × magnification

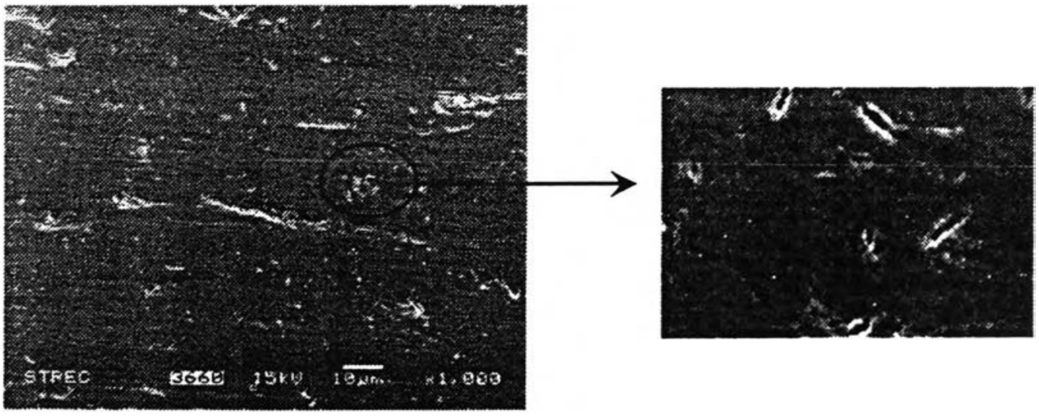
a) TTiP:ethanol:DEG = 1:20:0

Figure 4.11 Scanning electron micrographs of the TiO_2 thin film surface prepared with the mole ratio of **TTiP:ethanol:DEG at (a)**1:20:0, (b)1:20:0.5, (c)1:20:1 and (d)1:20:1.5



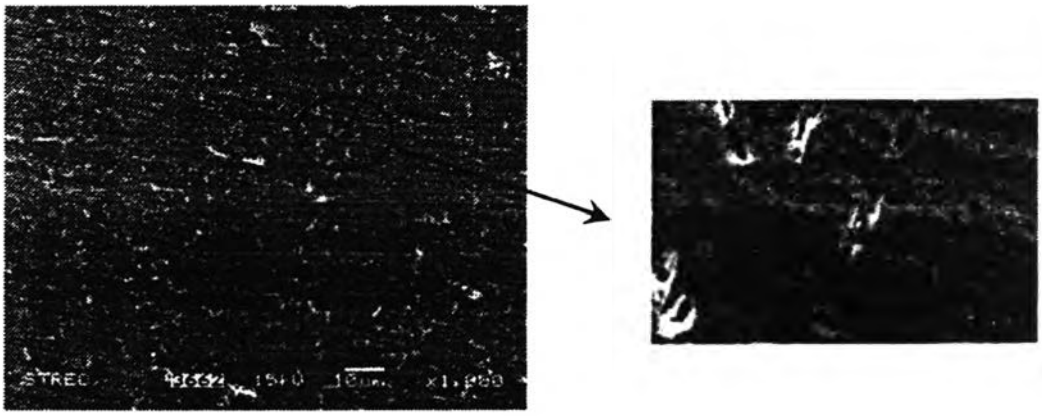
1000 × magnification 3500 × magnification

b) TTiP:ethanol:DEG = 1:20:0.5



1000 × magnification 3500 × magnification

c) TTiP:ethanol:DEG = 1:20:1



1000 × magnification 3500 × magnification

d) TTiP:ethanol:DEG = 1:20:1.5

Figure 4.11 (*cont.*) Scanning electron micrographs of the TiO_2 thin film surface prepared with the mole ratio of TTiP:ethanol:DEG at (a)1:20:0, (b)1:20:0.5, (c)1:20:1 and (d)1:20:1.5

4.3.3 Crystallization of TiO$_2$ thin film

Figure 4.12 shows the XRD pattern of the TiO$_2$ thin film coated on stainless steel plate using the mole ratio of TTiP to ethanol at 1:20 with different amounts of DEG. The crystalline patterns with similarity in intensity were obtained even high DEG concentration was applied. This sol additive exerted less effect on the crystallization of the film.

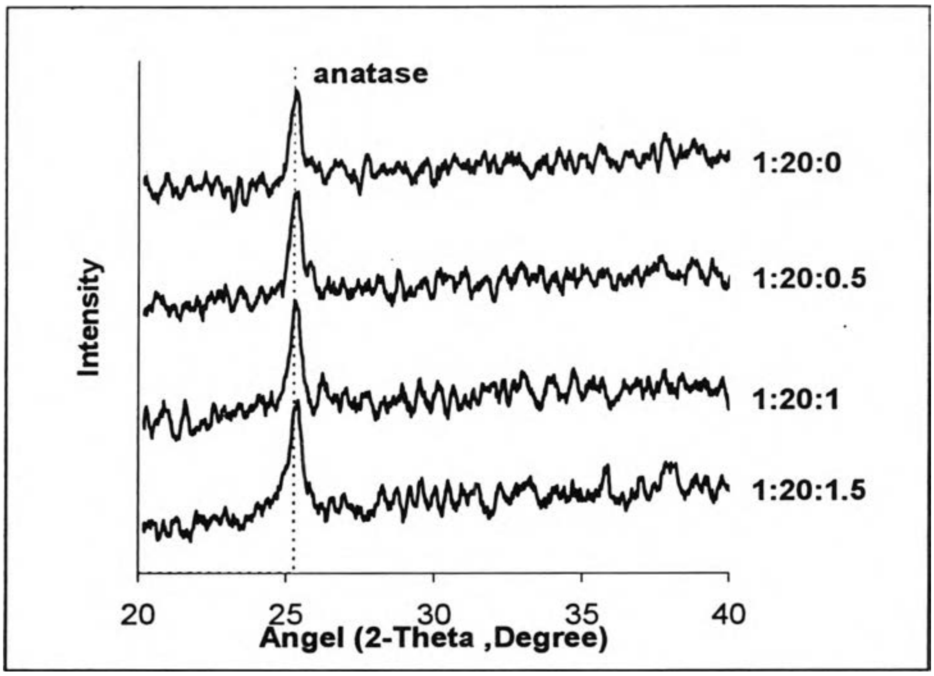


Figure 4.12 X-ray diffraction pattern of TiO$_2$ thin film prepared using different mole ratios of DEG

The crystallite sizes from each DEG concentration are slightly increased when high amount of DEG to the solution was applied, as presented in Table 4.10.

Table 4.10 Crystallite size of TiO_2 thin film with different mole ratios of DEG

Mole ratio of TTiP:Ethanol:DEG	Crystallite Size (nm)
1:20:0	46.7
1:20:0.5	45.2
1:20:1	48.3
1.20:1.5	51.8

4.3.4 Photocatalytic reduction of chromium(VI)

The result obtained in this test confirmed the XRD pattern in that the anatase intensity was not changed even high amount of DEG was applied to the coating solution (Figure 4.13). The calculated reaction rate constants were 0.0349, 0.0329 and 0.0324 mg/(L.min) for the thin film obtained from the ratio of TTiP to ethanol to DEG at 1:20:0.5, 1:20:1 and 1:20:1.5, respectively, as shown in Table 4.11. The reaction rate did not significantly change when high amount of DEG was applied to the sol.

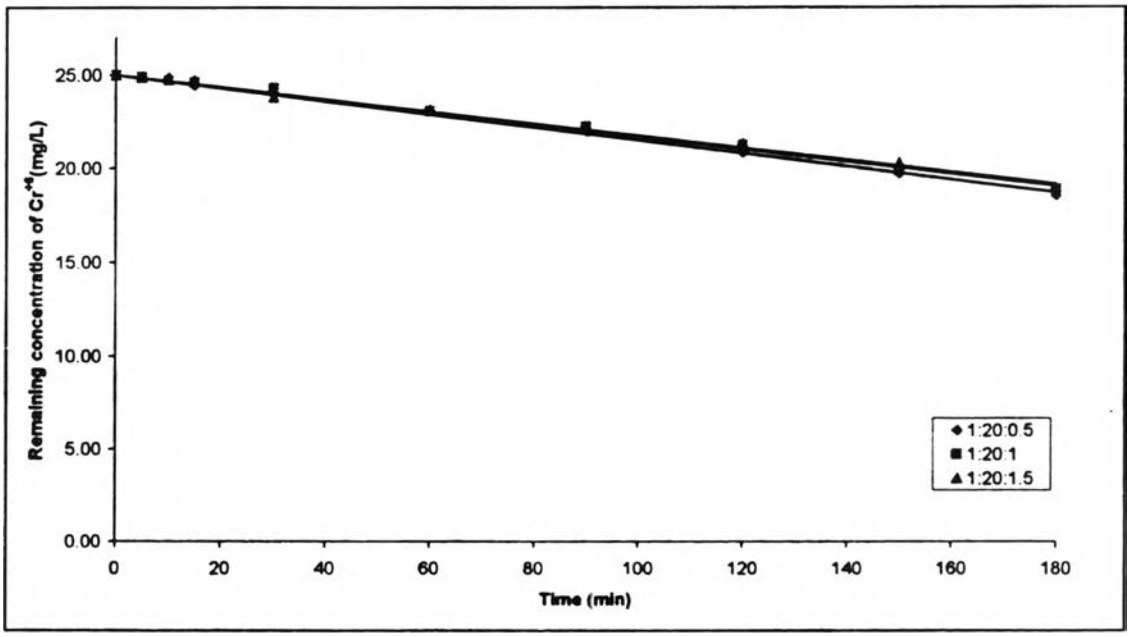


Figure 4.13 Photocatalytic reduction of chromium(VI) on TiO_2 thin film prepared with different mole ratios of DEG.

Table 4.11 Reaction rate constants for chromium(VI) removal of TiO_2 films prepared with different amounts of DEG

TTiP:ethanol:DEG	Rate constant (k, mg/(L.min))	r^2
1:20:0.5	0.0349	0.9968
1:20:1	0.0329	0.9940
1:20:1.5	0.0324	0.9913

It can be concluded the roles of DEG that it enhanced the adherence of the film on the stainless steel substrate, film robustness and surface smoothness. Moreover, adding DEG has minimum effect on anatase intensity and photoreduction of chromium(VI). In the next experiment, the mole ratio of TTiP:ethanol at 1:20 was used instead of 1:40 resulting from higher anatase obtained. The TiO_2 film obtained at TTiP to ethanol to DEG at 1:20:0.5 was considered as the optimum condition for the further experimental set because these ratios provided the film smoothness and film adherence, and showed the higher photocatalytic activity.

4.4 Comparing between PEG600, DEG, and PEG600+DEG

In this experiment, the sol solutions were prepared using the mole ratio of TTiP to ethanol to PEG600 to DEG at 1:20:0.5:0, 1:20:0:0.5 and 1:20:0.5:0.5. The coated gels were calcined at 500°C in a furnace for 30 min. The film property and photoactivity of each condition were compared in order to find the optimum ratio for further experiment.

4.4.1 Results of weight by scale, adhesive and corrosive tests

The mass of TiO_2 prepared from the sol solution that contained only PEG600, DEG, and both PEG600 and DEG are not different as presented in Table 4.12.

Table 4.12 Mass of TiO_2 thin film prepared from different chemical additives

Mole ratio of TTiP:Ethanol:PEG600:DEG	Mass 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
1:20:0:0	0.133	0.150	0.117	0.150	0.133	0.137	0.014
1:20:0.5:0	0.200	0.200	0.183	0.167	0.150	0.180	0.022
1:20:0:0.5	0.167	0.150	0.200	0.217	0.167	0.180	0.027
1:20:0.5:0.5	0.150	0.183	0.167	0.200	0.167	0.173	0.019

Remark: Increased of TiO_2 mass was calculated from the film with three-coating cycle. The area of stainless steel covered by TiO_2 layer was approximately 6 cm^2.

TiO_2 thin films obtained from the sol with chemical additives show the resistance to peeling with adhesive test and to corrosion with strong acid and base, as showed in Table 4.13. It can be stated that PEG600 and DEG played an important roles to improve the film adherence and film robustness.

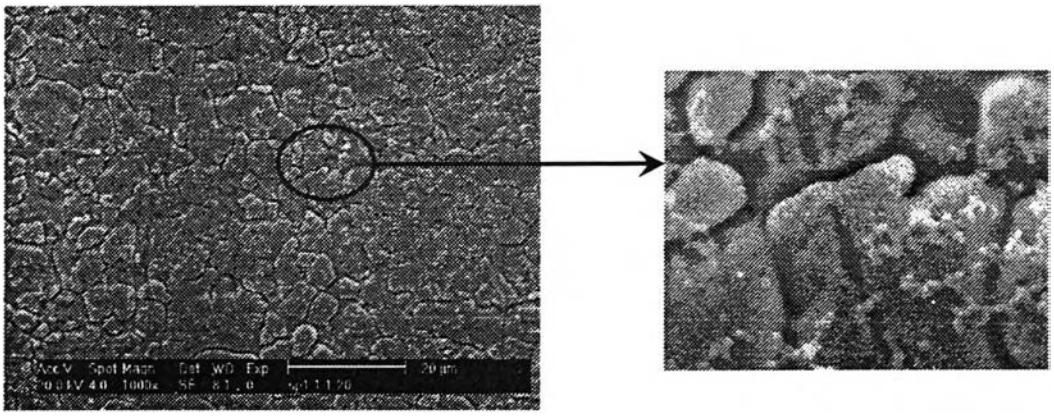
Table 4.13 Results of adhesive and corrosive tests of TiO_2 thin film prepared from different chemical additives

Mole ratio of TTiP:Ethanol:DEG	Adhesive Test	Corrosive Test in acid solution	Corrosive Test in alkali solution
1:20:0:0	✗	✗	✗
1:20:0.5:0	✓	✓	✓
1:20:0:0.5	✓	✓	✓
1:20:0.5:0.5	✓	✓	✓

Remark: ✓ means the film passed the test and ✗ means the film failed in this test

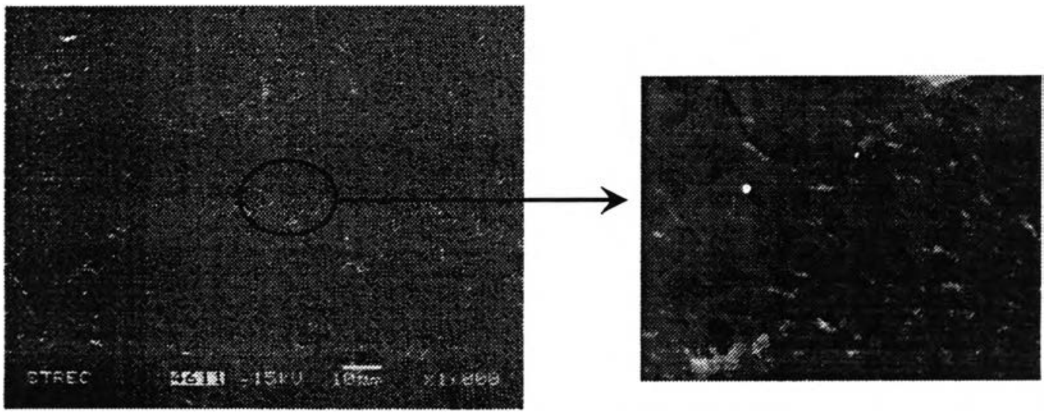
4.4.2 Thin film surface morphology analysis by SEM

Figure 4.14 (a), (b), (c) and (d) show the surface morphology of TiO_2 thin film prepared with different chemical additives. Without the additives, the film was not smooth and there were TiO_2 particles left on the film surface. After adding PEG600, the film had high surface areas with many pores produced during the heat treatment. When adding only DEG to the sol solution, the film was flat and smooth but some cracks were observed. The coating solution contained both PEG600 and DEG also gave the film smooth without any cracks.



1000 × magnification 3500 × magnification

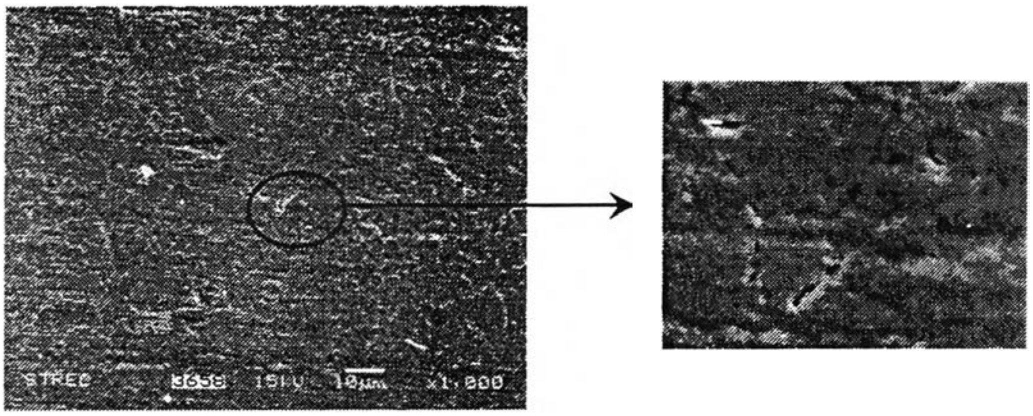
a) TTiP:ethanol:PEG600:DEG = 1:20:0:0



1000 × magnification 3500 × magnification

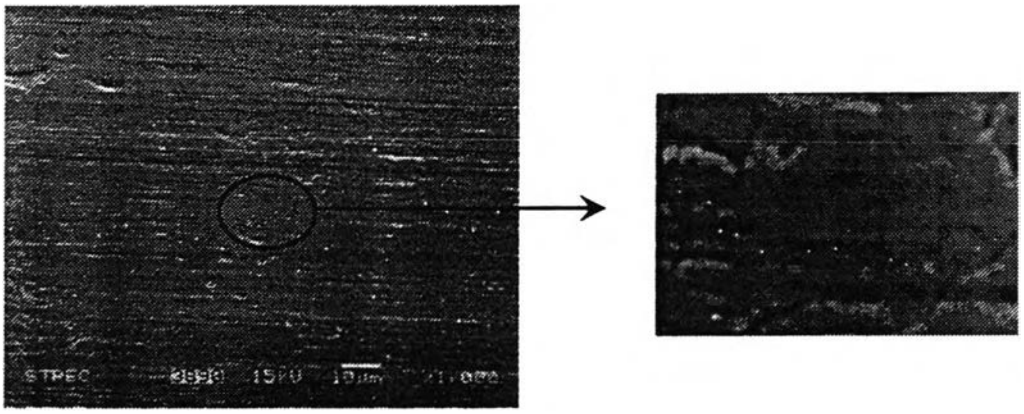
b) TTiP:ethanol:PEG600:DEG = 1:20:0.5:0

Figure 4.14 Scanning electron micrographs of the TiO_2 thin film surface prepared with different chemical additives



1000 × magnification 3500 × magnification

c) TTiP:ethanol:PEG600:DEG = 1:20:0:0.5



1000 × magnification 3500 × magnification

d) TTiP:ethanol:PEG600:DEG = 1:20:0.5:0.5

Figure 4.14 (*cont.*) Scanning electron micrographs of the TiO_2 thin film surface prepared with different chemical additives

4.4.3 Crystallization of TiO_2 thin film

The XRD patterns of the TiO_2 thin film coated on stainless steel plate with different chemical additives are illustrated in Figure 4.15.

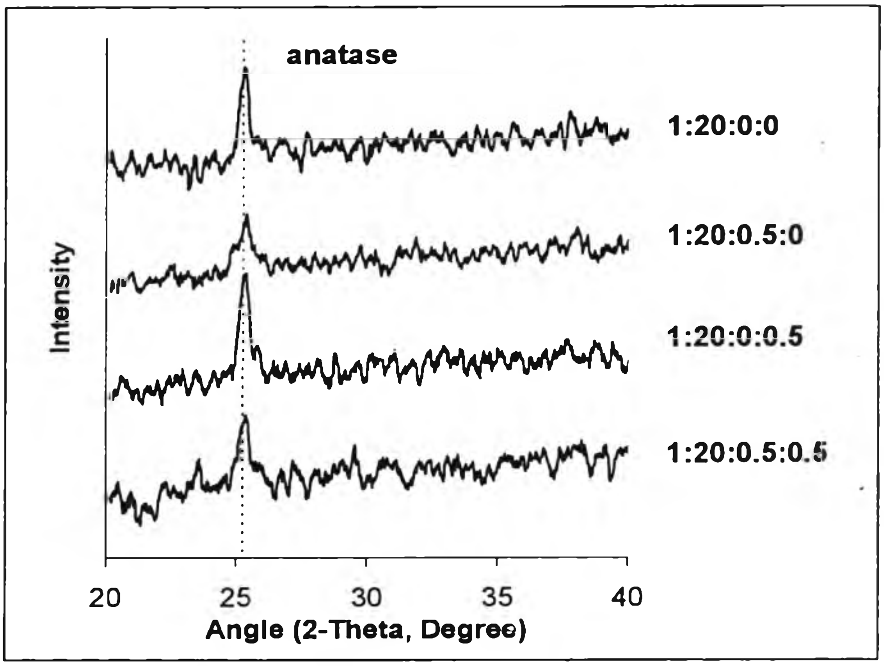


Figure 4.15 X-ray diffraction pattern of TiO_2 thin film prepared with TTiP: ethanol:PEG600:DEG at 1:20:0:0, 1:20:0.5:0, 1:20:0:0.5 and 1:20:0.5:0.5

The film crystalline was mainly composed of anatase phase as shown by the main peak of 2Θ at 25.3°. Addition of the organic additive to the coating solution did not show any effect on the crystallization of the films. When added only PEG600, the film had high porosity and contained less anatase. While added only DEG, the film was smooth and had high amount of anatase. In the solution contained both PEG600 and DEG, the anatase did not exhibit a sharp peak as DEG. The film porosity was less compared to PEG600. Moreover, the additives showed less effect on the crystallite size as presented in Table 4.14.

Table 4.14 Crystallite size of TiO_2 thin film prepared from different chemical additives

Mole ratio of TTiP:Ethanol:PEG600:DEG	Crystallite Size (nm)
1:20:0	46.7
1:20:0.5:0	46.7
1:20:0:0.5	45.2
1:20:0.5:0.5	45.0

4.4.4 Photocatalytic reduction of chromium(VI)

The photocatalytic reduction of chromium(VI) on the TiO_2 thin films obtained from different chemical additives is presented in Figure 4.16. The calculated reaction rate constants are 0.0353, 0.349 and 0.0377 mg/(L.min) for the thin film obtained from the ratio of TTiP to ethanol to PEG600 and DEG at 1:20:0.5:0, 1:20:0:0.5 and 1:20:0.5:0.5, respectively, as shown in Table 4.15.

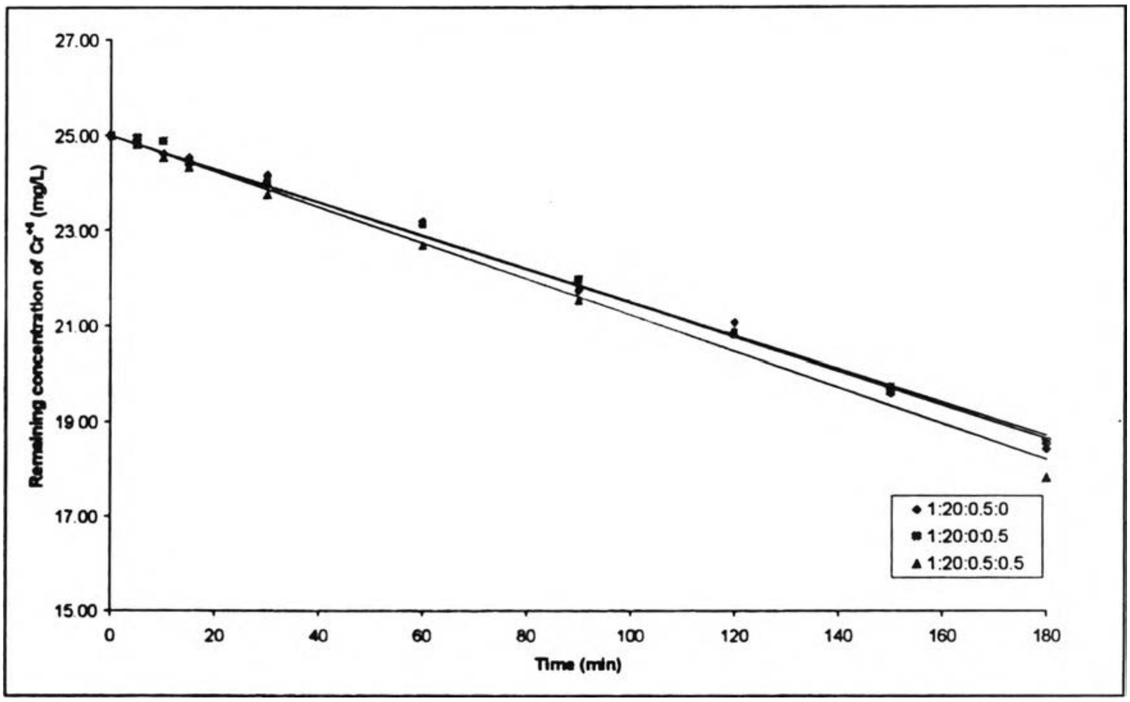


Figure 4.16 Photocatalytic reduction of chromium(VI) on TiO_2 thin film prepared with TTiP:ethanol:PEG600:DEG at 1:20:0.5:0, 1:20:0:0.5 and 1:20:0.5:0.5

The photocatalytic activity of PEG600 was governed by high surface area for reaction of the thin film. The film with high surface area enhanced light absorption and pollutant adsorption conducted to higher photoactivity (Xagas et al., 1999). The photocatalytic activity of DEG was controlled by anatase proportion in thin film. Comparison of both reaction rates (Table 4.15) with same amount of PEG600 and DEG, the high surface of film and the anatase proportion exerted no significance role for chromium(VI) removal. In addition, the film, prepared from the solution consisted of PEG600 and DEG, had high amount of anatase than the film prepared with only PEG600 and the film surface was more porosity than the film prepared with only DEG. The co-effect of both substances provided the film with high efficiency in photocatalytic activity.

Table 4.15 Reaction rate constants for chromium(VI) removal of TiO_2 films prepared with different chemical additives

TTiP:ethanol:PEG600:DEG	**Rate constant (k, mg/(L.min))**	r^2
1:20:0.5:0	0.0353	0.9941
1:20:0:0.5	0.0349	0.9968
1:20:0.5:0.5	0.0377	0.9898

From the above experimental set, the film prepared with PEG600 and DEG provided high amount of anatase and high porosity. The coating solution containing the mole ratio of TTiP to ethanol to PEG600 to DEG at 1:20:0.5:0.5 was considered as the optimum ratio for TiO_2 thin film preparation. The obtained film was strengthen with smooth surface and less cracks, resisted to both acid and alkali corrosion, and showed the highest photoreduction of chromium(VI). Furthermore, the coating precursor solution showed long term stability since DEG was included in the solution. The obtained solution was used to prepare the film for further experiment.

4.5 Effects of calcination temperature on TiO_2 thin film properties

In this experiment set, coating solution was prepared using mole ratio of TTiP to ethanol to PEG600 to DEG at 1:20:0.5:0.5. Coated substrates were calcined at 300, 400, 500, 600, 700 and 800°C in a furnace for 30 min.

4.5.1 Results of weight by scale, adhesive and corrosive tests

The changes of TiO_2 weight after coating are presented in Table 4.16.

Table 4.16 Mass of TiO_2 thin film prepared with various calcined temperatures

Calcination temperature (°C)	**Mass 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	0.200	0.217	0.217	0.200	0.217	0.210	0.009
400	0.200	0.183	0.217	0.200	0.200	0.200	0.012
500	0.150	0.183	0.167	0.200	0.167	0.173	0.019
600	0.233	0.200	0.217	0.250	0.250	0.230	0.021
700	0.567	0.650	0.567	0.667	0.567	0.604	0.050
800	1.700	1.800	1.800	1.867	2.100	1.853	0.150

Remark: Increased of TiO_2 mass was calculated from the film with three-coating cycle. The area of stainless steel covered by TiO_2 layer was approximately 6 cm^2.

The mass of TiO_2 thin film did not significantly change with calcination temperature at 300-600°C. Besides, TiO_2 mass sharply increased with calcination temperature at 700-800°C. The films calcined in all temperatures pass adhesive and corrosive tests, as shown in Table 4.17.

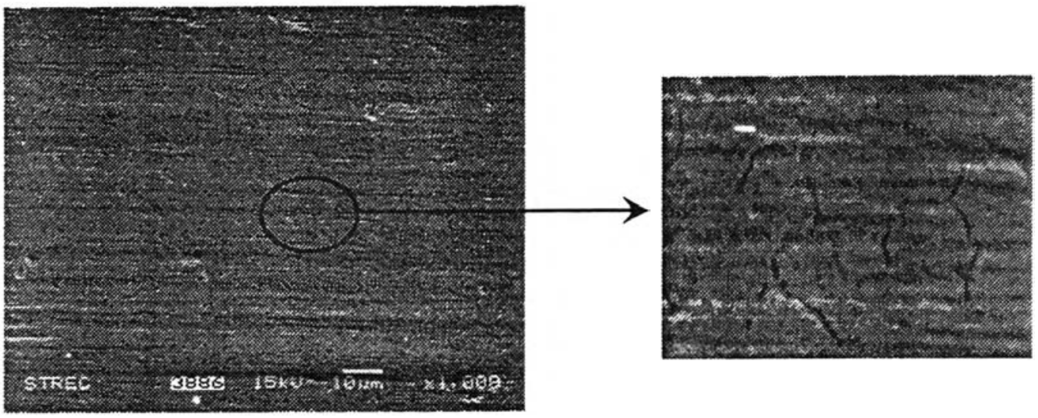
Table 4.17 Results of adhesive and corrosive tests of TiO_2 thin film prepared with various calcined temperatures

Calcination temperature (°C)	**Adhesive Test**	**Corrosive Test in acid solution**	**Corrosive Test in alkali solution**
300	✓	✓	✓
400	✓	✓	✓
500	✓	✓	✓
600	✓	✓	✓
700	✓	✓	✓
800	✓	✓	✓

Remark: ✓ means the film passed the test and ✗ means the film failed in this test

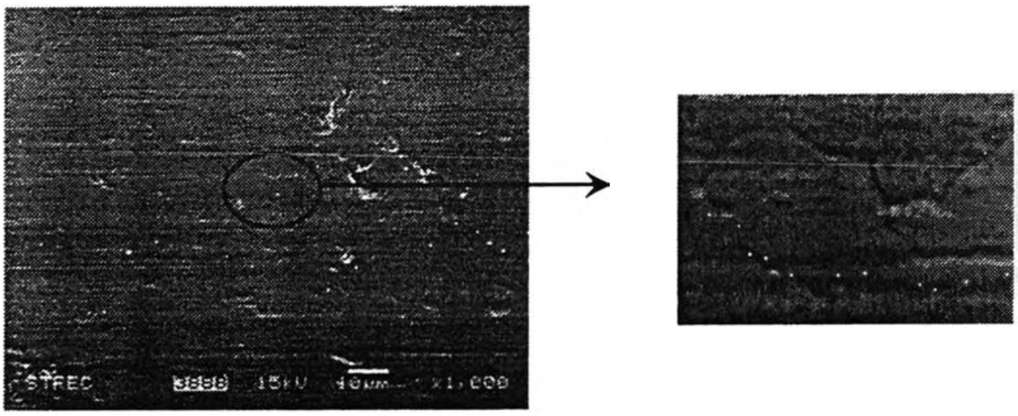
4.5.2 Thin film surface morphology analysis by SEM

The SEM images of TiO_2 thin film prepared with calcination temperatures at 300, 400, 500, 600, 700 and 800°C are illustrated in Figure 4.17. The films obtained from 300 to 500°C were not much different. Their surfaces were uniform, smooth, less crack and slightly rough. At calcined temperature over 600°C, the film surfaces were obviously changed with increasing of the roughness and porosity. It is obvious that the obtained stainless steels from calcination at high temperature of 600°C changed in their structure.



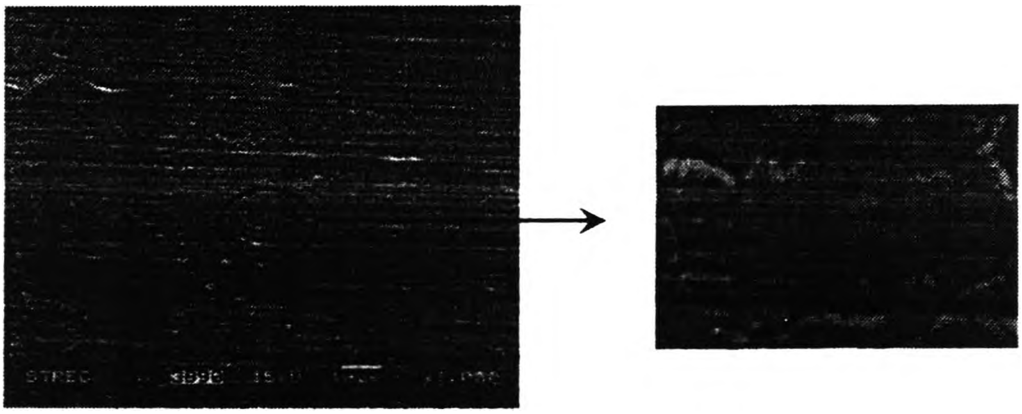
1000 × magnification 3500 × magnification

a) TTiP:ethanol:PEG600:DEG = 1:20:0.5:0.5, calcined at 300°C



1000 × magnification 3500 × magnification

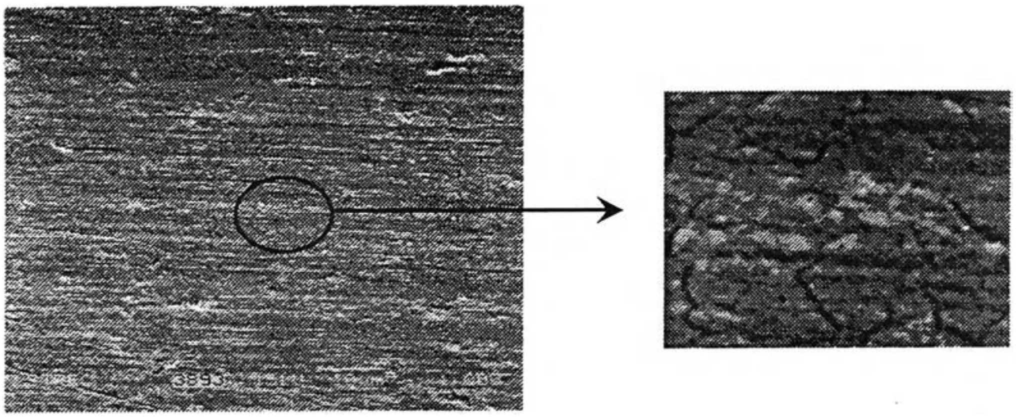
b) TTiP:ethanol:PEG600:DEG = 1:20:0.5:0.5, calcined at 400°C



1000 × magnification 3500 × magnification

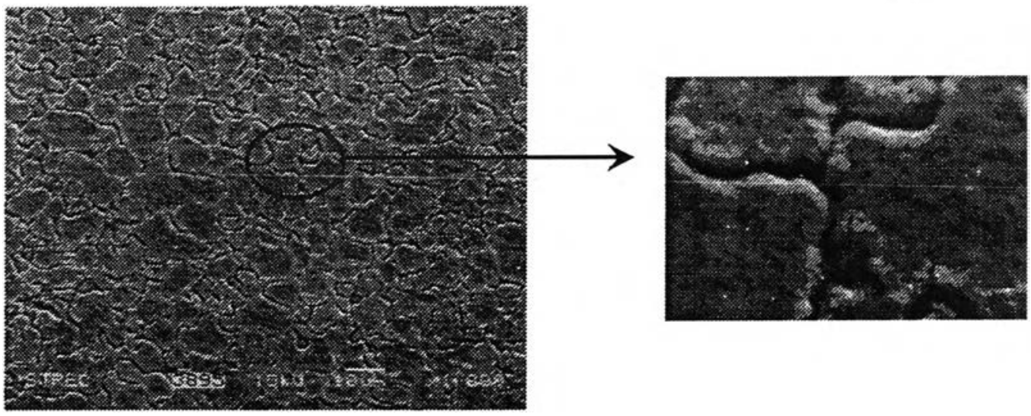
c) TTiP:ethanol:PEG600:DEG = 1:20:0.5:0.5, calcined at 500°C

Figure 4.17 Scanning electron micrographs of the TiO_2 thin film surface prepared with various calcined temperatures



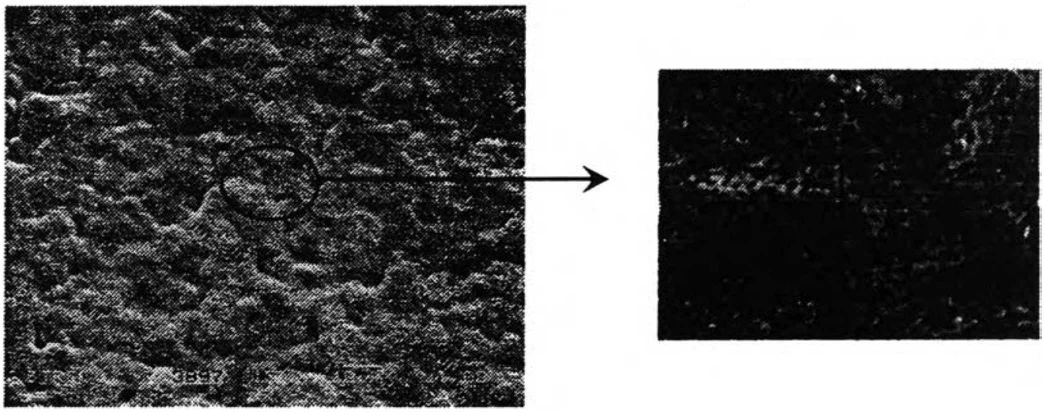
1000 × magnification 3500 × magnification

d) TTiP:ethanol:PEG600:DEG = 1:20:0.5:0.5, calcined at 600°C



1000 × magnification 3500 × magnification

e) TTiP:ethanol:PEG600:DEG = 1:20:0.5:0.5, calcined at 700°C



1000 × magnification 3500 × magnification

f) TTiP:ethanol:PEG600:DEG = 1:20:0.5:0.5, calcined at 800°C

Figure 4.17 (*cont.*) Scanning electron micrographs of the TiO_2 thin film surface prepared with various calcined temperatures

4.5.3 Crystallization of TiO_2 thin film

Figure 4.18 illustrates the XRD diffraction patterns of the TiO_2 thin film coated on the stainless steel, which were prepared by calcined at different temperatures

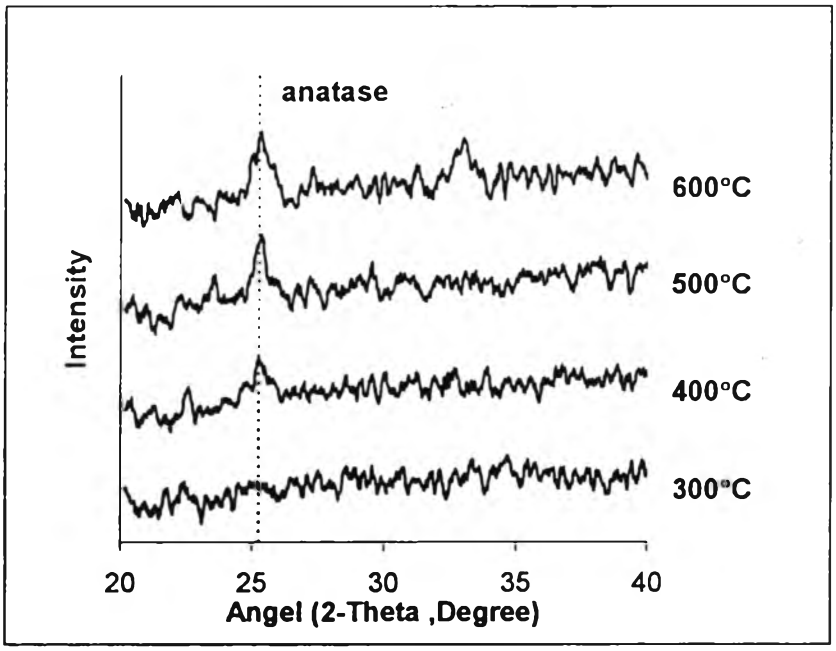


Figure 4.18 X-ray diffraction pattern of TiO_2 thin film calcined at 300°C to 600°C

Calcination is a common treatment that can be used to improve the crystallinity of TiO_2 particles The XRD results indicated that the TiO_2 thin film calcined at 300°C was amorphous. The anatase peak appeared at 400°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°C. From the previous work, the retardation of the phase transition temperature was caused by the types of supporting material. For example, the rutile phase of TiO_2 films coated on NiTi alloy existed simultaneously at temperature of 600 – 750°C (Liu et al., 2003), While the phase transition from anatase to rutile began to appear at 600°C when coated TiO_2 on titanium plate (Liqiang et al., 2003) and at 1000°C when coated TiO_2 on quartz glass (Kim, Hahn et al., 2002).

At 600°C, it can be observed peak at 2θ equal to 32.9° and at temperature higher than 600°C strong peaks were found at 24°, 32.9°, 35.5°, 40.6°, 49.2°, 53.6°, 62° and 63.7° (Figure 4.19). They were the diffraction pattern of stainless steel structure which was changed when temperature increased (Figure 4.20). Zhu et al. (2001) stated that Fe in a stainless steel substrate diffused into a TiO_2 film and reacted with oxygen from the air, then formed an interlayer of iron oxide during heat treatment. Consequently, it can be concluded that new phase of stainless structure began at temperature over 600°C.

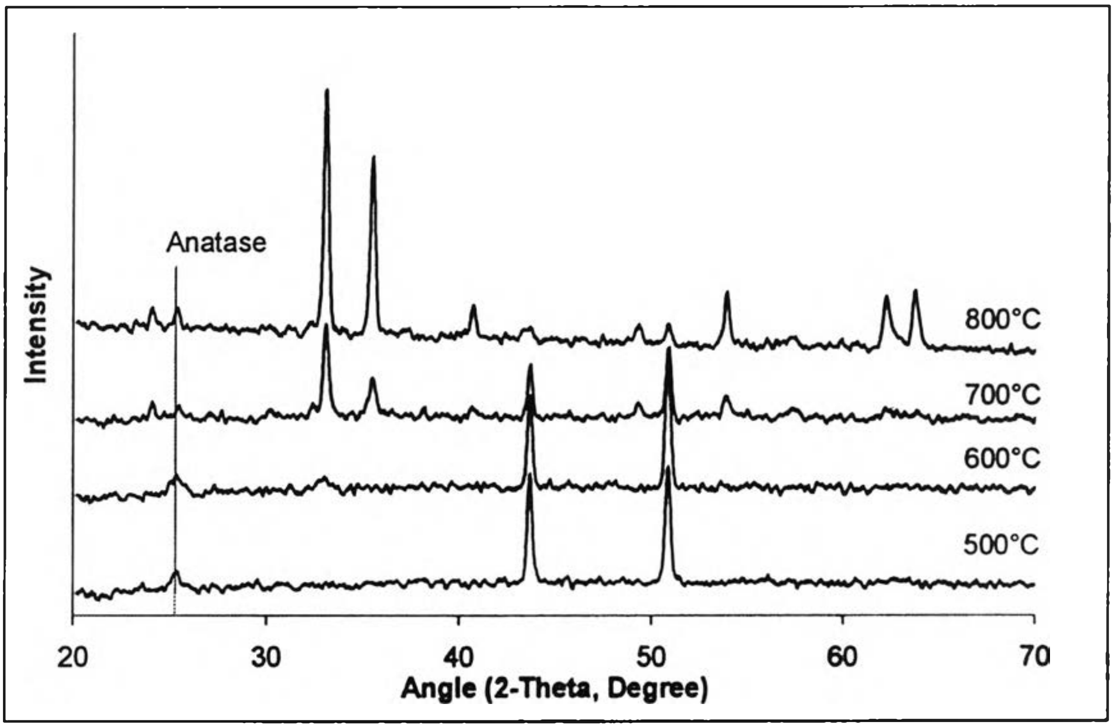


Figure 4.19 X-ray diffraction pattern of TiO_2 thin film calcined at temperature over 500°C

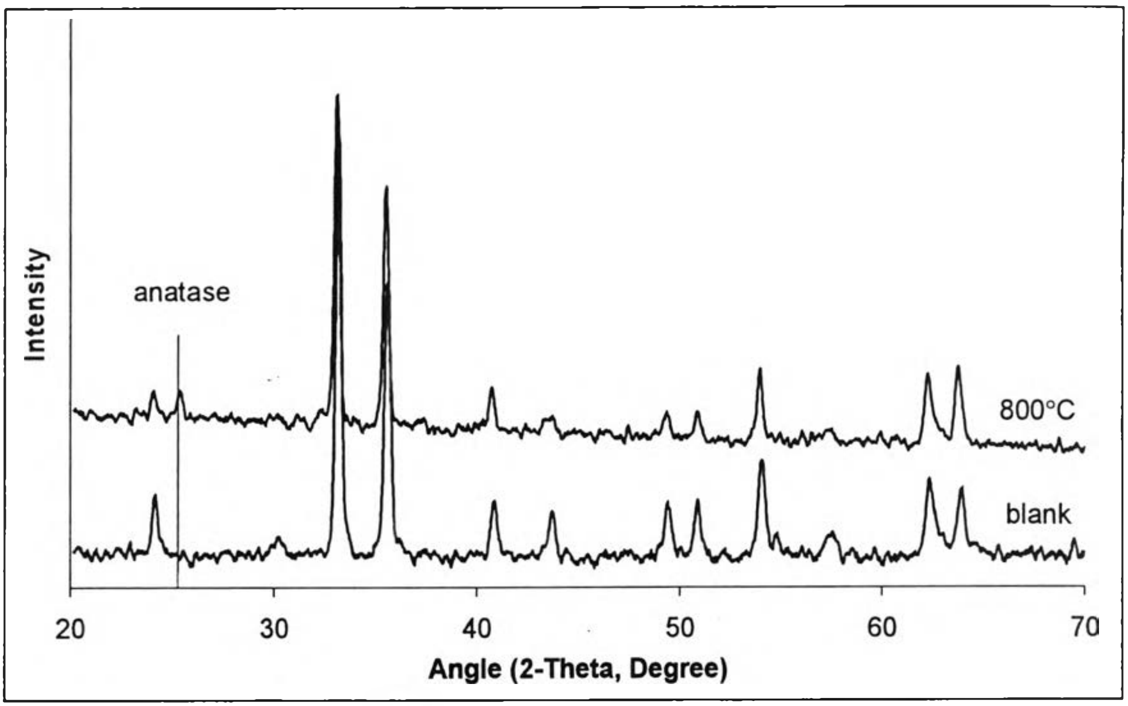


Figure 4.20 X-ray diffraction pattern of TiO_2 thin film calcined at 800°C comparing to stainless steel plate calcined at the same temperature

The average crystallite sizes of TiO_2 thin film were calculated in Table 4.18. The crystallite size of the anatase phase was increased from 39.9 to 63.4 nm as the calcination temperature increased from 400 to 800°C. The particle growth was enhanced by increasing of calcination temperature (Kim, Hahn et al., 2002; Liqiang et al., 2003).

Table 4.18 Crystallite size of TiO_2 thin film prepared with various calcined temperatures

Calcination temperature (°C)	Crystallite Size (nm)
400	39.9
500	45.0
600	46.1
700	61.8
800	63.4

4.5.4 Photocatalytic reduction of chromium(VI)

The photocatalytic reduction of chromium(VI) on the TiO_2 thin films prepared with different calcined temperatures is presented in Figure 4.21. The rate constant of the film calcined at 400 and 500°C are 0.0290 and 0.0377 mg/(L.min), respectively, as shown in Table 4.19. According to XRD patterns of TiO_2 thin film, at temperature over 600°C, stainless steel was changed to complex structures which can interfere in photoactivity of the film. More insight information was needed to investigate for thin film annealing at the temperature higher than 600°C which was beyond the scope of this work.

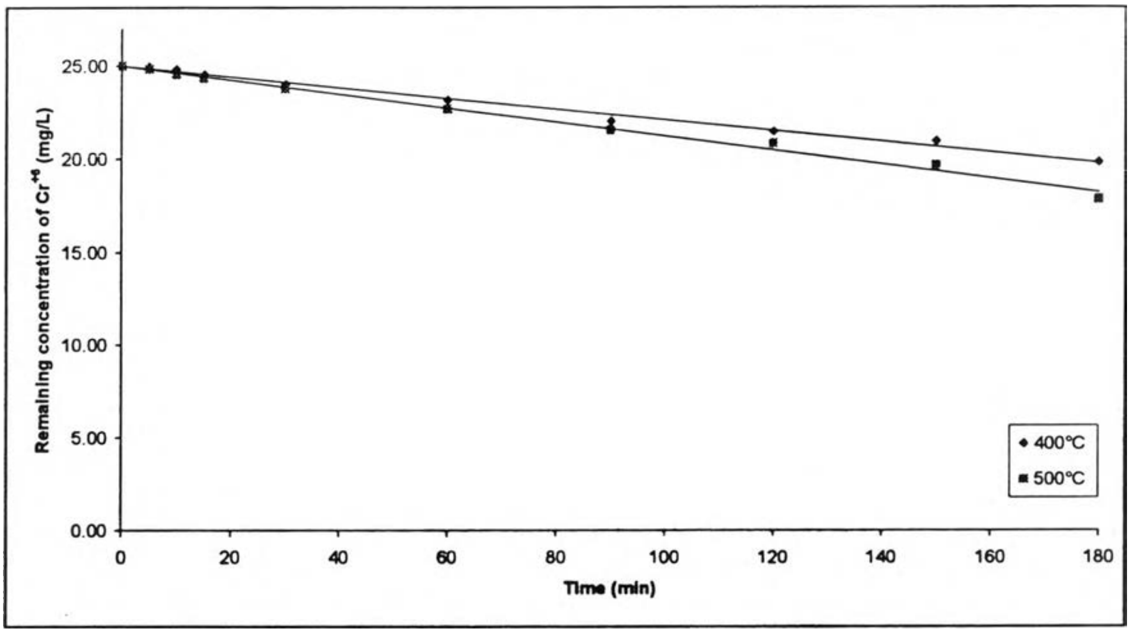


Figure 4.21 Photocatalytic reduction of chromium(VI) on TiO_2 thin film prepared with different calcined temperatures

Table 4.19 Reaction rate constants for chromium(VI) removal of TiO_2 films prepared with different calcined temperatures

Calcination temperature (°C)	**Rate constant (k, mg/(L.min))**	r^2
400	0.0290	0.9891
500	0.0377	0.9898

From overall result, the calcination temperature at 500°C was considered as optimum temperature that provides the film smooth, good adherence and corrosive resistance. Moreover, it was the temperature that showed the best efficiency for the photocatalytic reduction before the substrates change their structure.

4.6 Effects of coating cycle on TiO_2 thin film properties

In this experiment, the mole ratios of TTiP:ethanol:PEG600:DEG equaled to 1:20:0.5:0.5, were used for coating solution with calcined at 500°C in a furnace for 30 min. The substrates were coated at 1, 3 and 5 cycles.

4.6.1 Results of weight by scale, adhesive and corrosive tests

From Table 4.20, the coating cycle strongly effects on TiO_2 weight. Mass of TiO_2 was increased with multi-coating. This result was accordance with Yu, Zhao and Zhao, 2001, Fretwell and Douglas, 2001, and Lee et al., 2004. By increasing of cycle times, the more thickness of film would be obtained. When the film thickness increased, TiO_2 attached on substrate increased as well.

Table 4.20 Mass of TiO_2 thin film prepared with different coating cycles

Coating cycle	**Mass 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	0.083	0.067	0.050	0.050	0.050	0.060	0.015
3	0.150	0.183	0.167	0.200	0.167	0.173	0.019
5	0.283	0.283	0.333	0.333	0.317	0.310	0.025

Remark: The area of stainless steel covered by TiO_2 layer was approximately 6 cm^2.

The films in each coating cycle pass both adhesive and corrosive tests as presented in Table 4.21. The thickest film prepared with five-coating cycle was not removed by Scotch Tape™. Moreover, the film surface did not change even when the film was dipped in 10M of HNO_3 and NaOH.

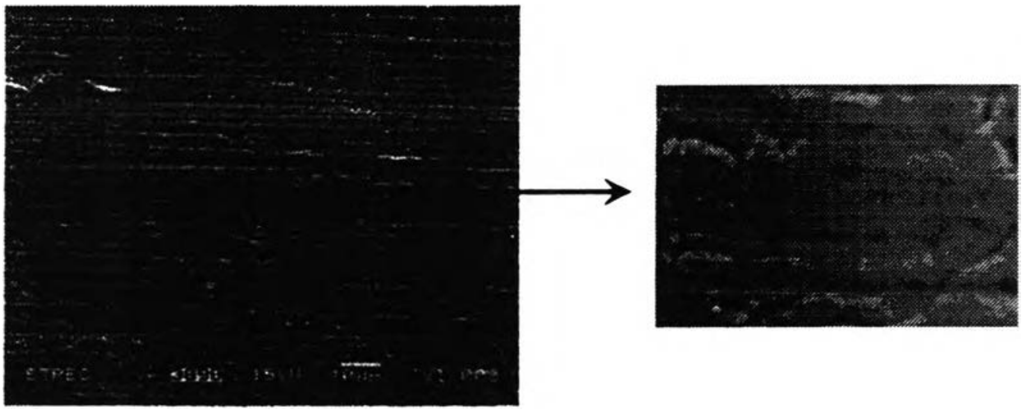
Table 4.21 Results of adhesive and corrosive tests of TiO_2 thin film prepared with different coating cycles

Coating cycle	Adhesive Test	Corrosive Test in acid solution	Corrosive Test in alkali solution
1	✓	✓	✓
3	✓	✓	✓
5	✓	✓	✓

Remark: ✓ means the film passed the test and ✗ means the film failed in this test

4.6.2 Thin film surface morphology analysis by SEM

The multi-coating of TiO_2 thin films is illustrated in Figure 4.22. The film surface was very smooth and uniform as increasing coating cycle. In addition, the thickness of the film can be observed at crack area with higher magnification.

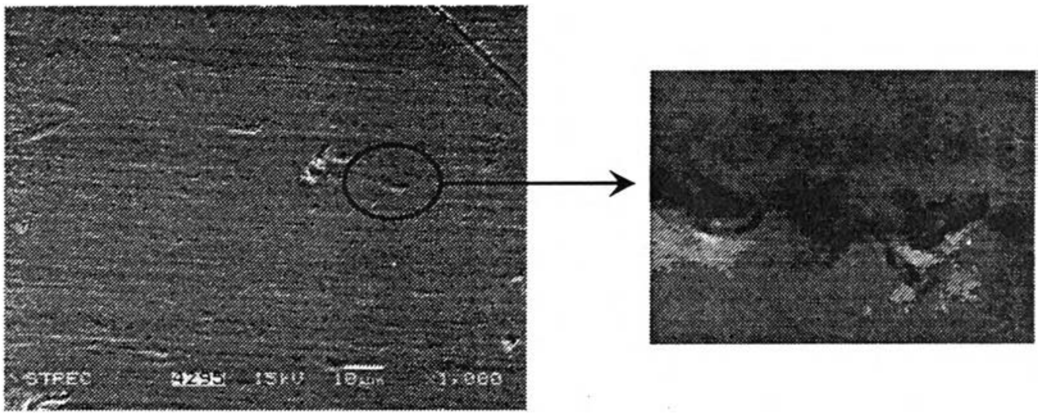


1000 × magnification

3500 × magnification

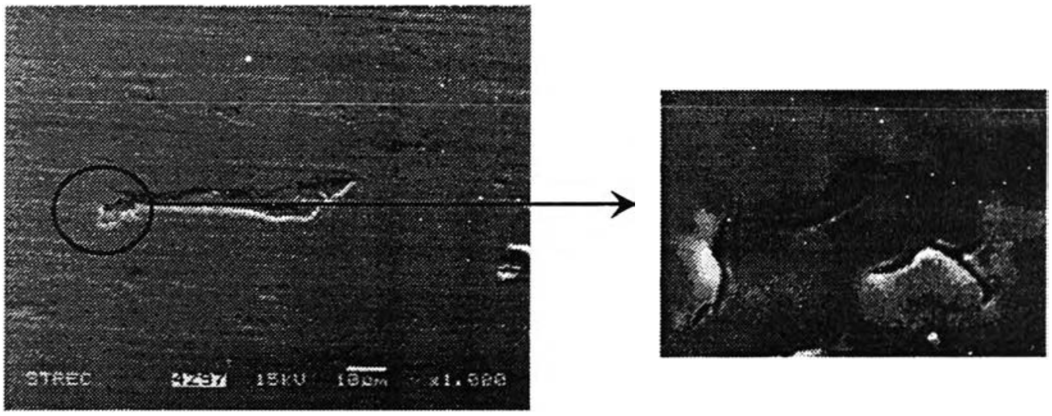
a) The film prepared with one-coating cycle

Figure 4.22 Scanning electron micrographs of the TiO_2 thin film surface prepared with different coating cycles



1000 × magnification 3500 × magnification

b) The film prepared with three-coating cycle



1000 × magnification 3500 × magnification

c) The film prepared with five-coating cycle

Figure 4.22 (*cont.*) Scanning electron micrographs of the TiO_2 thin film surface prepared with different coating cycles

4.6.3 Crystallization of TiO_2 thin film

Structure of a TiO_2 thin film with the coating number of 1-, 3- and 5- times was analyzed by XRD as shown in Figure 4.23. For one-coating film, the XRD pattern show the lowest intensity of anatase due to an insufficient content of TiO_2. With the increasing of coating cycles, high amount of anatase was obtained. The five-coating cycle film showed the highest intensity of anatase. From previous study (Lee et al., 2004) showed that amount of anatase and rutile increased with multi-coating on the film.

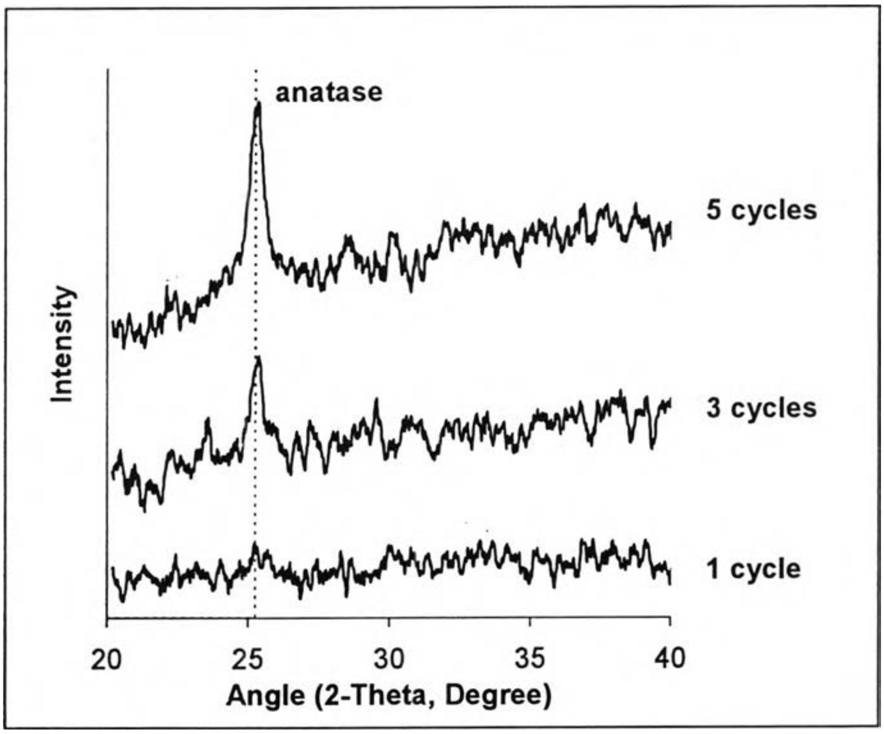


Figure 4.23 X-ray diffraction pattern of TiO_2 thin film prepared with different coating cycles

Table 4.22 shows that crystallite size of anatase decreased at higher coating cycle. The crystallite size of anatase phase decreased from 60.9 to 40.2 nm with 1- to 5-coating time.

Table 4.22 Crystallite size of TiO_2 thin film prepared with different coating cycles

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

4.6.4 Photocatalytic reduction of chromium(VI)

The photocatalytic reduction of chromium(VI) using 1-, 3- and 5-coating cycle is shown in Figure 4.24 and calculated reaction rate is shown in Table 4.23. It was found that TiO_2 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 TiO_2 and its anatase was increased resulting in high activity of photocatalytic process.

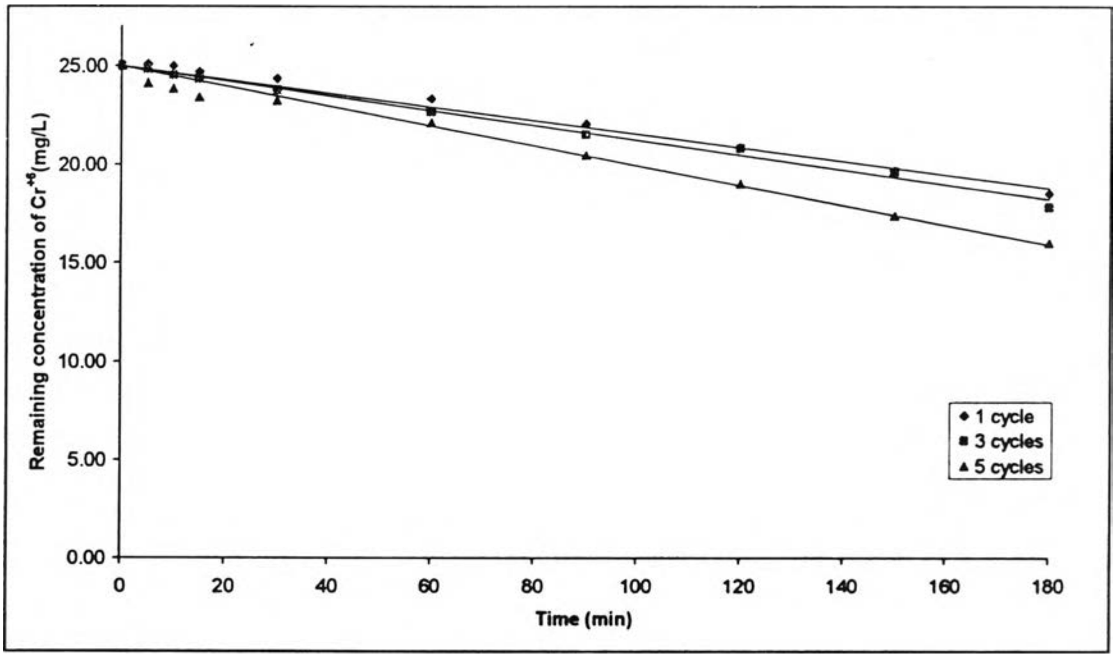


Figure 4.24 Photocatalytic reduction of chromium(VI) on TiO_2 thin film prepared with different coating cycles.

Table 4.23 Reaction rate constants for chromium(VI) removal of TiO_2 films prepared with different coating cycles.

Coating cycle	**Rate constant (k, mg/(L.min))**	r^2
1	0.0347	0.9876
3	0.0377	0.9924
5	0.0505	0.9898

Yu, Zhao and Zhao (2001) found that the rate constant increased with increasing the film thickness and approached a limiting value at thick film. The latter mainly resulted from the two factors: (a) aggregation of TiO_2 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_2 thick films, leading to decrease in the passage of irradiation through the film.