

Structure and Photocatalytic Characteristics of TiO₂ Thin Film Coated on Stainless Steel for Chromium (VI) Removal Application

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ABSTRACT

In this work, TiO₂ films with high photocatalytic activities were coated on stainless steel plate by the sol-gel method. Stainless steel plate is a good substrate due to its large surface area, being corrosion-resistant and commercially-available. It was found that TiO₂ films exhibited a uniform surface with high in anatase structure. With increasing of calcination temperature, the higher amount of anatase and the bigger size of nanoparticle in the films were obtained. With multiple coating cycles of the thin film, the increase of thickness can be expected. The photocatalytic activity in chromium(VI) removal of the TiO₂ film coated on stainless steel plate can be related to its crystallization and the thickness. Thicker and better crystallization of TiO₂ film resulted in its higher photocatalytic activity which was evaluated by the photocatalytic reduction of chromium (VI) in a cylindrical photoreactor. Results showed that chromium (VI) was successfully removed from aqueous solution in photocatalysis system using the obtained thin film in which percentage of anatase phase, nanoparticle size, and film thickness were major parameters controlling the photoactivity.

Key words: TiO₂ (Titanium dioxide), Thin film, Photocatalysis, Chromium(VI)

INTRODUCTION

Photocatalytic process has been of continuous interest in the treatment and purification of air and water since it can complete the reduction of metal ions. Furthermore, organic species can be completely mineralized to carbon dioxide or become nontoxic materials by photocatalytic pathway. Titanium dioxide (TiO₂) has been widely used as a photocatalyst due to its activity, photostability, non-toxicity and commercial availability (Oppenländer, 2003). As a result of the cost and difficulties in separating the TiO₂ particles from the suspension after completion of the reaction, the powder TiO₂ application is not found to be practical for commercial use (Matthews, 1987; Hilmi et al., 1999; Zhang et al., 2003). In order to overcome these disadvantages, preparations of TiO₂ thin film have been developed by different techniques, for example, chemical vapor deposition, chemical spray pyrolysis, electrodeposition and the sol-gel method. Many researches have focused on preparation by the sol-gel process since this method is very simple, easy to operate and can be applied to complex surfaces or large surface areas. Moreover, this technique is suitable for thin film deposition

on many substrates such as stainless steel, alumina, silica/glass, etc., (Pozzo et al., 1997; Sonawane et al., 2002). By controlling the photocatalytic property, the synthetic TiO_2 thin film can be used in industrial application.

The main objective of this work was to synthesize TiO_2 thin film which was coated on stainless steel, using the sol-gel method for photocatalytic reduction of chromium(VI). In this work, stainless steel was selected as a substrate as it was inexpensive, having large surface area, corrosion-resistant and commercially-available. Besides, it can be modified to any shape that is suitable for photoreactor. For application of the developed thin film TiO_2 on stainless steel, chromium was selected as the tested pollutant as it is frequently found in effluent streams discharging from chrome plating, electronic, metallurgical and leather-tanning industries (Richard, 1998; Schrank et al., 2002). The structure of the TiO_2 coated on stainless steel plate was related to its photocatalytic activity and tested in a photoreactor with chromium (VI) as the model pollutant. The results confirmed that the sol-gel method was a good way to prepare anatase TiO_2 film coated on stainless steel firmly and this film exhibited high photocatalytic activity for the photocatalytic reduction of chromium(VI).

MATERIALS AND METHODS

Materials

All chemicals in this research were of analytical grade and were used as received. Titanium tetraisopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$) or TTiP obtained from Aldrich and absolute ethanol supplied by Merck were used as a Ti-precursor and a solvent, respectively. Polyethylene glycol with molecular weight 600 (PEG 600) from Acros and diethylene glycol (DEG) from Unilab were used as organic additives.

Thin film preparation

The thin nanostructured film of TiO_2 was deposited on stainless steel plate with the surface cleaning prior to use. The synthesis of various sols of TiO_2 was prepared as follows. The TiO_2 precursor solutions were prepared first by stabilizing titanium tetraisopropoxide, dissolved in ethanol, with DEG and PEG 600 as appropriate amount, stirring for 30 min at room temperature. The molar ratios of TTiP to ethanol to PEG 600 and DEG in this study were 1:20:0.5:0.5. The substrates were dipped into the sol and withdrawn at a constant speed to make a gel-coating film. After drying, samples were put directly into a furnace which was maintained at a given temperature in a range of 300–700°C.

Characterization of TiO_2 thin film

The coating mass of TiO_2 per surface area was determined by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM). The crystal phase of thin film was analyzed by thin film XRD analysis which was recorded on a Philip diffractometer using Cu K α radiation and a step size of 0.02° in the range $10-80^\circ$. The step time was 1 second, adequate to obtain a good signal-to-noise ratio in the mean reflections of the two studied TiO_2 crystalline phases, (101) anatase ($2\theta \sim 25.17^\circ$) and (110) rutile ($2\theta \sim 27.35^\circ$). Scanning Electron Microscope (Philip) was used to examine the smoothness of thin film surface.

Photocatalytic reaction

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

range of 25–31°C, preventing excessive heating of the reaction. A lamp was placed inside the cooling water jacket. The volume of aqueous in all experiments conducted was 500 ml. A total of six stainless steel plates of thin film TiO₂ were placed in the reactor to perform photoactivity experiments. The reaction solution was stirred with a magnetic stirrer at a constant speed to keep it well-mixed during the experiments.

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

RESULTS AND DISCUSSION

Texture of TiO₂ films coated on stainless steel plate

Figure 1 (a) shows the original macroscopic morphology of stainless steel without any deposition of TiO₂ on the surface. The grain boundary of stainless steel is clearly seen. The macroscopic morphology of TiO₂ thin film deposited on stainless steel plate in the absence of any additive is shown in Figure 1 (b) with 1000x magnifications. It is noteworthy that the morphology is similar to the original stainless steel plate. With a higher magnification, inset picture in Figure 1(b), there are some particles left on the surface of the thin film. Due to the organic components of the unfired, coatings were decomposed during the heat treatment (Negishi et al., 1995). It is anticipated that the nanoparticles remaining on the surface of the thin film were the developed TiO₂. These particles disappeared in the presence of either PEG 600 or DEG in the sol solution. The flatness and smoothness of TiO₂ thin films on stainless steel as shown in Figure 1 (c) for PEG 600 addition and Figure 1 (d) for DEG were obtained.

Results from SEM clearly represented that addition of PEG600 yielded the high surface areas with many pores produced during the heat treatment. Zhang et al., (2003) elucidated the effect of PEG as the structure-directing agent. Ti-precursor was first hydrolyzed by water to form sol particles. The particles can be covered by the PEG chain to form “particles-PEG” complexes. The resulting complexes then self-assemble through cross-linking and polymerization to form mesoscopically-ordered inorganic/polymer composites. Schematic presentation to illustrate the tentative structure-directing process of PEG in the precursor sol in this experiment is shown in Figure 2. During heating, PEG was oxidized and decomposed to carbon dioxide. Pores were generated by the elimination of the gas phase from the coating (Kato et al., 1996). When adding only DEG to the sol solution, the film was flat and smooth but some cracks were observed. Effect of DEG on the thin film TiO₂ was possibly similar to that of PEG600. With the small chain of DEG, the short cross-linkages of inorganic/polymer composites were formed and the small cracks along the stainless steel plate could be expected. The coating solution which contained both PEG600 and DEG also gave the film smoothness without any cracks. The coating solution containing both PEG600 and DEG provided the film smoothness without any cracks as seen in Figure 3.

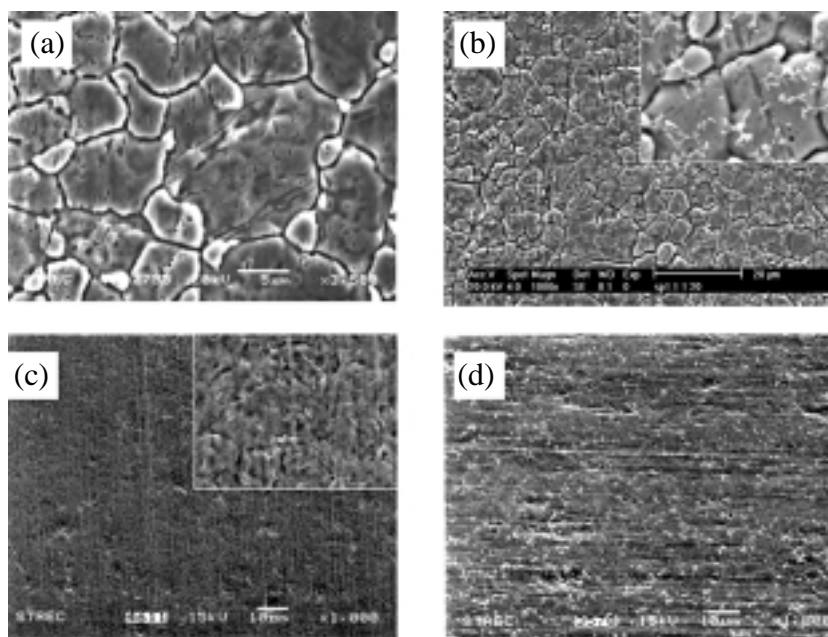


Figure 1. SEM images of (A) stainless steel plate without TiO₂; (B) thin film TiO₂ on stainless steel plate; (C) thin film TiO₂ with PEG 600 deposited on stainless steel plate and (D) thin film TiO₂ with DEG deposited on stainless steel plate.

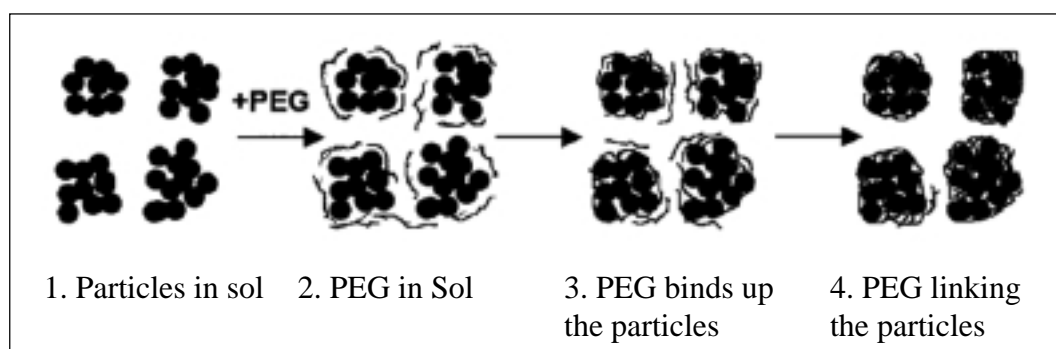


Figure 2. Tentative structure-directing process of PEG in the precursor sol.

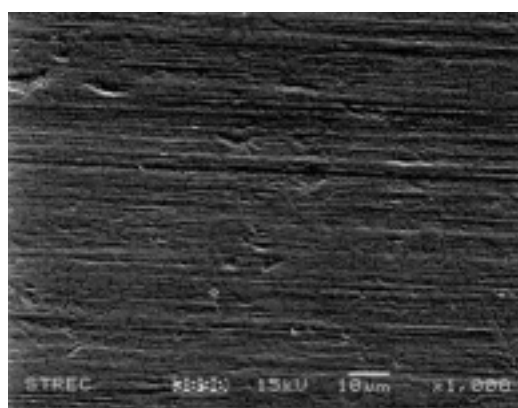


Figure 3. Smooth surface of thin film TiO₂ with addition of PEG 600 and DEG.

Crystallization of TiO₂ films

X-ray diffraction was used to investigate the crystallization of the TiO₂ films on the stainless steel plate. Figure 4 illustrates the XRD diffraction patterns with the peaks in the range of $2\theta = 20$ – 40 degree of the TiO₂ thin film coated on the stainless steel, which were prepared by calcining at different temperatures in the range of 300 – 600°C . A good signal-to-noise ratio in the mean reflections of the studied TiO₂ crystalline anatase phase (101) at $2\theta = 25.17$ degree was clearly shown in each XRD pattern.

Calcination is a common treatment that can be used to improve the crystallinity of TiO₂ particles. The XRD results from this work indicated that TiO₂ 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 (Liu et al., 2003), the retardation of the phase transition temperature might come from types of supporting material. For example, the rutile phase of TiO₂ films coated on NiTi alloy existed simultaneously at temperature of 600 – 750°C , while the phase transition from anatase to rutile began to appear at 600°C when coated TiO₂ on titanium plate (Liqiang et al., 2003) and at 1000°C when coated TiO₂ on quartz glass (Kim et al., 2001). Findings from this work suggested that at the studied calcination temperature at 600°C , the transformation of anatase to rutile phase on stainless steel plate did not occur. In addition, it is worth to note that the oxidation transformation of Fe to Fe₂O₃ was detected at the studied calcination temperature at 600°C , as shown in $2\theta = 33.21$ degree in Figure 4.

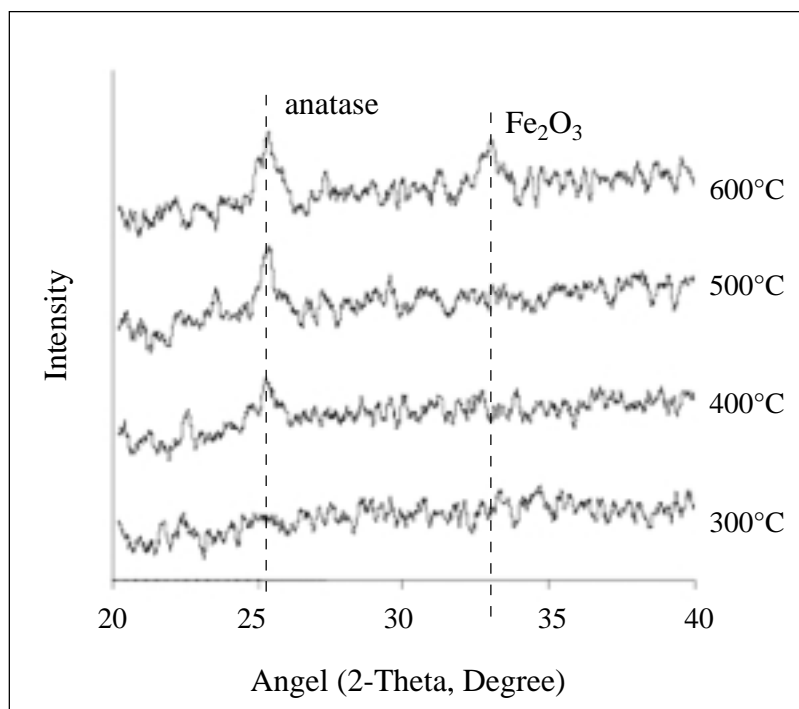


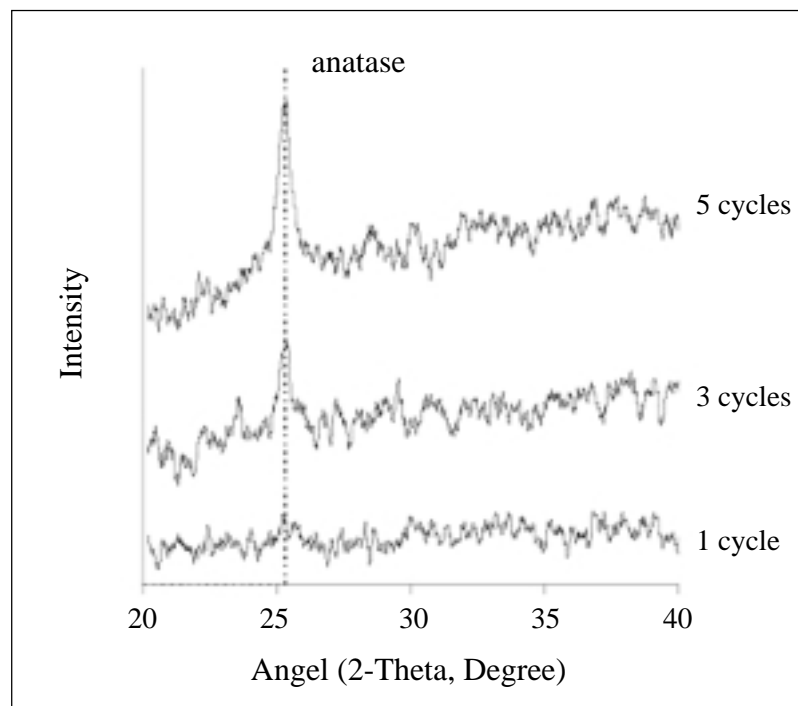
Figure 4. X-ray diffraction pattern of TiO₂ thin film calcined at 300°C to 600°C .

The average crystallite sizes of TiO₂ thin film were calculated as shown in Table 1. The crystallite size of the anatase phase was increased from 39.9 to 46.1 nm as the calcination temperature increased from 400 to 600°C . This is in good agreement with the early results reported by Kim et al., (2001) and Liqiang et al., (2003) that the particle growth was enhanced by increasing of calcination temperature.

Table 1. Crystallite size of TiO₂ thin film prepared with various calcined temperatures.

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

Structures of a TiO₂ thin film calcinated at 500°C with multiple coating numbers of 1-, 3- and 5- times were analyzed by XRD as shown in Figure 5. For one-coating film, the XRD pattern shows the lowest intensity of anatase due to an insufficient content of TiO₂. With the increase of coating cycles, higher amount of anatase was obtained. The five-coating cycle film shows the highest intensity of anatase with no rutile phase.

**Figure 5.** X-ray diffraction pattern of TiO₂ thin film with multiple coating cycles.

Crystallite sizes of TiO₂ thin film prepared with different coating cycles are shown in Table 2. It was found that crystallite size of anatase decreased at higher coating cycle from 60.9 to 40.2 nm with 1- to 5-coating time.

Table 2. Crystallite size of TiO₂ thin film prepared with different coating cycles.

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

Photocatalytic activity

The photocatalytic reduction of chromium(VI) using 1-, 3- and 5-coating cycles and calculated reaction rates are shown in Table 3. The total chromium in the aqueous solution was removed from the water within 180 minutes with different reaction rates of each thin film condition. It was found that TiO₂ thin film with 5-coating cycles performed the highest photoactivity in chromium(VI) removal with the reaction rate constant at 0.0505 mg/(L.min). As the coating cycle increased, the amount of deposited titanium dioxide and its anatase was increased, resulting in high activity of photocatalytic process. This behavior can be seen clearly from the reaction rates when the coating cycle was increased from 1 cycle to 5 cycles. Moreover, with the smaller nanoparticle sizes obtained from multiple coating, for example, 40.2 nm with 5 coating cycles and 60.9 nm with 1 coating cycle, the high surface area of active size for photocatalytic process could be expected.

Other factor that might play a role here is the thickness of the film. The thin film obtained from 5 coating cycles was relatively thicker than that obtained from 1 coating cycle. Yu et al., (2001) found that the rate constant increased with increasing film thickness and approached a limiting value at thick film. The latter mainly resulted from the two factors: (a) aggregation of TiO₂ 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 TiO₂ thick films, leading to decrease in the passage of irradiation through the film. Findings from this work suggested that percentage of anatase crystallite, nanoparticle size and thickness of thin film TiO₂ deposited on stainless steel plate are the major factors which play an important role in photocatalytic reduction of chromium (VI).

Table 3. Reaction rate constants for chromium(VI) removal of TiO₂ films prepared with different coating cycles.

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

CONCLUSION

A good morphology and crystalline phase of TiO₂ film (40–60 nm) with a high photocatalytic activity can be obtained by sol-gel method coated on stainless steel plate. The addition of polyethylene glycol (PEG600) and diethylene glycol (DEG) drastically improved the quality of the thin film TiO₂ deposited on stainless steel plate. Calcination temperatures and multiple coating were important operating factors in controlling the nanoparticle size and the percentage of anatase of thin film TiO₂. The obtained thin film TiO₂ coated on stainless steel exhibited high photoactivity in chromium (VI) removal. Major factors controlling the photoactivity of the films included percentage of anatase crystallite, nanoparticle size and thickness of thin film TiO₂ deposited on stainless steel.

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