Effect of Acetyl Acetone on Property of TiO_2 Thin Film for Photocatalytic Reduction of Chromium(VI) from Aqueous Solution

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ABSTRACT

In this research, a sol-gel technique with dip coating method was used to prepare photocatalytic TiO_2 thin films immobilized on glass plates. Titanium(IV) butoxide was used as initial substrate. The solvent was ethanol and the additive substrate was acetyl acetone. Molar ratios of TiO_2 to acetyl acetone were varied as studied parameters. This study was aimed to investigate the effect of acetyl acetone on TiO_2 thin film properties that are adherence and corrosive property, surface morphology of thin film, TiO_2 molecular structure and photoactivity. It was found that acetyl acetone played an important role on TiO_2 thin film properties. It significantly enhanced the adherence property and provided the smooth surface of TiO_2 thin film. On the contrary, acetyl acetone exerted less effect on the crystal structure of TiO_2 film and increased nanoparticle size of TiO_2, which results in the decreasing of photocatalytic activity of the film. Findings from this research can be beneficial for the developments of thin film TiO_2 preparation for environmental application.

Key words: Thin films, TiO_2, Acetyl acetone, Photocatalytic activity

INTRODUCTION

In recent years, the emission of hazardous pollutants has become a very serious problem and caused different degrees of hazard to human health and environment. In order to eliminate their presence in the environment, much attention has been paid to find practical ways to introduce efficient remedial technologies.

Photocatalysis process using titanium dioxide, TiO_2, as a catalyst is emerging as one of the more promising candidates for the elimination of hazardous substances in polluted air and wastewater (Linsebigler et al., 1995; Ollis, 2000). Under favorable conditions, a wide range of organic and inorganic compounds can be mineralized to mineral acids, carbon dioxide and water or transformed into harmless species (Huang et al., 1993; Litter, 1999). TiO_2 as used in the photocatalysis process always exists in two forms, one is the suspended form of fine particles dispersed in a liquid medium, and the other is the immobilized form as thin films. Although the suspended TiO_2 can be used without any preparation techniques, it is associated with the difficult problem of powder separation and the catalyst recycle after use. For this reason, several techniques have been developed to immobilize TiO_2 on different substrates with suitable properties to offer a highly-active surface area, photoactivity and

effective separation properties (Ding et al., 2001; Srikanth et al., 2001).

This research is one among several works focusing on the study of the preparation of TiO_2 thin film, using the sol-gel technique which is the most widely used and appropriate technique to immobilize TiO_2 on substrates (Pozzo et al., 1997). In addition, the application of the developed TiO_2 thin film to the wastewater treatment is one of the aims of this work. In this research, TiO_2 thin films were prepared using titanium(IV) butoxide as a precursor, ethanol as a solvent, HCl as a acidic catalyst and acetyl acetone as studied additive substance. Acetyl acetone was expected to play a major role as a stabilizer in thin film preparation and it can improve the quality of the film (Liu et al., 2003). The soda-lime glass was used as the substrate for the thin films due to the advantages of its properties that are corrosion-resistant, commercially-available, inexpensive and stable for the reaction. Furthermore, it can be applied to many shapes such as plate, bead and rod.

To study this, variations of molar ratio between titanium(IV) butoxide to acetyl acetone and photocatalytic reduction of Cr(VI) were investigated in order to find the role of acetyl acetone and its effects on TiO_2 thin film preparation using sol-gel technique. The results, obtained from this research would provide useful information to further photocatalytic works for contaminant removal from water/wastewater.

MATERIALS AND METHOD

Materials

The reagents used in this research were of analytical grade. Nanocrystalline titanium dioxide was prepared via sol-gel hydrolysis and condensation of ethanol solutions (Merck Chemicals) of titanium(IV) butoxide ($Ti(OC_4H_9)_4$, Aldrich chemicals). Acetyl acetone was purchased from Carlo erba chemical. Analytical grade K_2CrO_4 (Merck Chemicals) together with 18 M deionization water were used to prepare the Cr(VI) solutions for photoactivity test. The pH of the solution was adjusted to the desired value by adding NaOH or H_2SO_4. Both chemicals were prepared by Merck Company, and used as received.

Thin film preparation

Thin films of titanium dioxide for dip coating were prepared using ethanol as the solvent in addition to small amount of hydrochloric acid. The molar ratio of titanium(IV) butoxide to acetyl acetone were varied as 1:0, 1:1 and 1:2, respectively. The transparent microscopy glass plates were used as substrates. The substrates were dipped into the sol and withdrawn at a constant speed to make a gel-coating film. The TiO_2 gel films were heated at temperature of 500¡C for 30 min in air using an electric furnace. The samples were put directly into a furnace which was maintained at a given temperature.

Characterization of TiO_2 thin film

The coating mass of TiO_2 per surface area was determined by Scanning Electron Microscope (SEM) and X-ray diffraction (XRD). Scanning Electron Microscope was used to examine the smoothness of thin film surface. X-ray diffraction patterns of the samples were recorded on a Philip diffractometer, using Cu Kα radiation and a step size of 0.02¡ in the range of 10Ð80¡. 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 ($2\theta \sim 25.3$¡) and (110) rutile ($2\theta \sim 27.35$¡).

Photocatalysis Experiment

The photoreduction of Cr(VI) was performed in a 1.2 liter double-jacked quartz reactor, the volume of reaction mixture was 1.1 liter. The photoreactor includes two compartments, consisting of outer and inner compartments. The outer compartment contained the treated wastewater and the chemical reagents with 2 sampling ports. The inner part was an angular vessel (30 mm. ID) for 10-watt low-pressure mercury lamp with a major emission at 254 nm. This inner well was jacked to permit a water flow for cooling purpose. The cooling water was provided for the inner part to prevent excessive heating of the reaction. Six glass plates of thin film TiO_2 were placed in the reactor to perform photoactivity experiments. The reaction solution was stirred with a magnetic stirrer at a constant speed to maintain a well-mixed solution during the experiments.

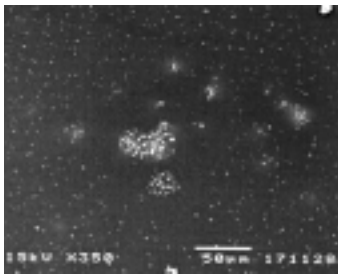
Before turning on the UV lamp, the pH of the solution was adjusted to pH 3. The solution was placed in the dark, shielded with aluminum foil and kept stirring for a certain time until the pH was stable, indicative of adsorption equilibrium. After the dark adsorption, the UV light was turn on to illuminate the TiO_2 thin films for 180 min. Residual chromium solutions were syringed out from the photoreactor for analysis during a period of time.

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

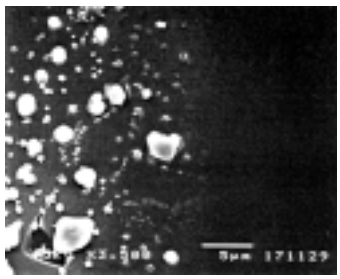
RESULTS AND DISCUSSION

Surface morphology by SEM (Scanning Electron Microscopy)

Figure 1 (a), (b) and (c) shows the effects of acetyl acetone on surface morphology of TiO_2 thin film. It can been seen that without acetyl acetone, there were some TiO_2 particles left on the film surface. When small amount of acetyl acetone was applied, these remaining particles disappeared from TiO_2 thin films. Moreover, as the amount of acetyl acetone increased, the smooth films like the TiO_2 sheets were obtained. With this experimental method, the sol in the presence of acetyl acetone was stable and homogeneous (Liu et al., 2003). Therefore, the good quality of the resulting thin films can be observed with no crack and with smooth surface (Legrand-Buscema et al., 2002).



x350 magnification



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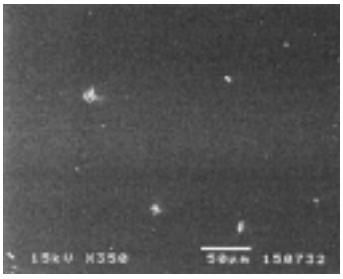
(a) titanium(IV) butoxide : acetyl acetone = 1:0



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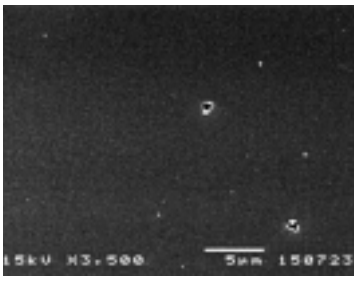

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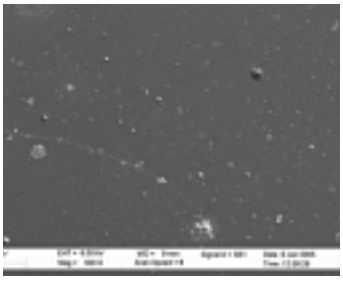
(b) titanium(IV) butoxide : acetyl acetone = 1:1



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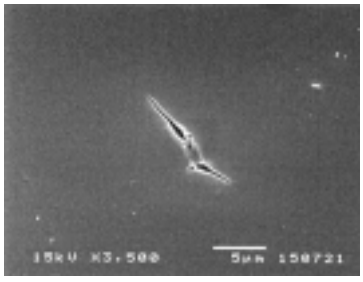

x3,500 magnification

(c) titanium(IV) butoxide : acetyl acetone = 1:2

Figure 1. (a)-(c) SEM photographs of the TiO_2 coating films derived from different molar ratios of acetyl acetone (continue).

Furthermore, surfaces of all TiO_2 films were resistant to peeling with adhesive tape and they could not be removed from the glass substrate even with 10M HNO_3 and NaOH. It is worth to note that acetyl acetone which was used as stabilizing agent of the sol offered the compact films with good adherence (Liu et al., 2003; Verma, in press). In addition, the compactness, the uniformity and the interfacial stability of the film play a significant role in their corrosion resistance. Findings from this part suggested that acetyl acetone provides significant effect on the improvement of film quality.

Crystallization behavior

The X-ray diffraction patterns of the films are shown in Figure 2. At all preparation conditions, the TiO_2 films with anatase phase were the predominant structure. A major peak corresponding to (1 0 1) reflections of the anatase phase of TiO_2 is shown at the angle of 25.3¡ while the minor peaks appeared at 48.05¡ and 53.90¡. Moreover, the intensity of anatase peaks is not significantly different as the molar ratio of acetyl acetone increased. The previous study also reported the effect of acetyl acetone that it stabilizes the anatase phase even at temperature as high as 900¡C (Djaoued et al., 2002). This statement supports that there is no transformation of anatase to rutile phase in this studied temperature.

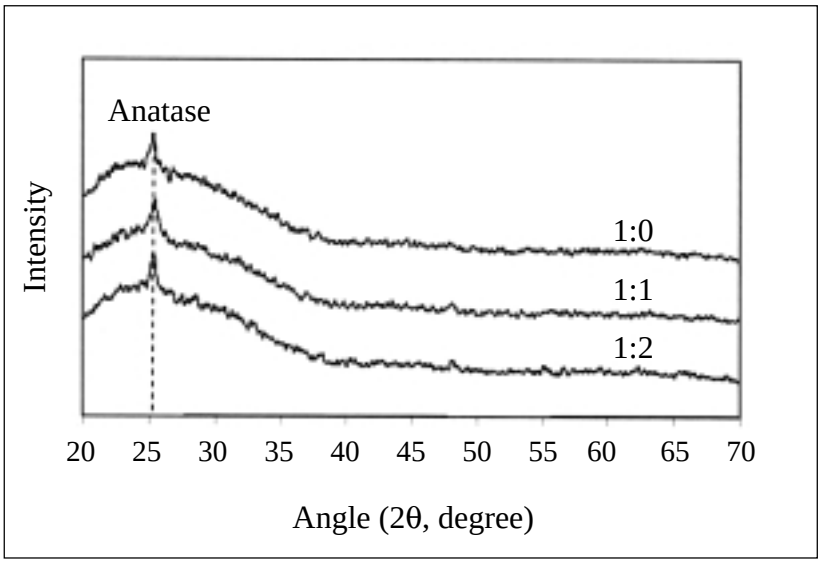

Figure 2. XRD patterns of TiO_2 thin films derived from different molar ratios of acetyl acetone.

To exhibit the effect of acetyle acetone on crystalline of TiO_2 deposited on glass plate clearly, crystallite sizes of TiO_2 can also be estimated from the broadening of corresponding X-ray spectral peaks by Debye-Scherrer equation (Liqiang et al., 2003):

$$L = \frac{K\lambda}{\beta cos\theta} \quad (1)$$

Where L is the crystallite size, K usually taken as 0.89, λ is the wavelength of the X-ray radiation (0.15418 nm), β is the line width at half-maximum height and θ is the half-diffraction angle of the centroid of the peak in degree. The results are listed in Table 1.

In this work, we found that as the amount of acetyl acetone increases, the TiO_2 crystallites continue to grow. The crystallite size of anatase phase was increased from 12.59 nm without acetyl acetone to 20.15 nm with the ratio 1:0 of titanium butoxide(IV):acetyl acetone. The experimental work carried out here suggests that acetyl acetone tends to induce the crystallite growth and yield the bigger size of nanoparticle than the original crystallite size in the absence of acetyl acetone. This effect of acetyl acetone is expected to have influence on photocatalytic activity as well, due to the fact that the active surface area for the reaction might be reduced with the bigger size of nanoparticle.

Table 1. Crystallite size of TiO_2 films prepared from different molar ratio of acetyl acetone.

Titanium(IV) butoxide : acetyl acetone	Crystallite Size (nm)
1:0	12.59
1:1	16.12
1:2	20.15

Photocatalytic activity

On the basis of thin film photoactivity studies, further investigations were performed to obtain the effect of acetyl acetone on the photocatalytic performance. Figure 3 shows the effect of acetyl acetone in thin film preparation on the fraction of Cr(VI) remaining in the water as a function of time. The reaction rates were found to follow the zero-order kinetic models, of which the reaction rate constants were determined by fitting statistically with the experimental data. The calculated reaction rate constants were 0.1930, 0.1659 and 0.1634 for the thin film obtained from the different molar ratio of acetyl acetone, as shown in Table 2.

Apparently, the rate constants were slightly decreased as acetyl acetone 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 surface area that serves as active sites decreases.

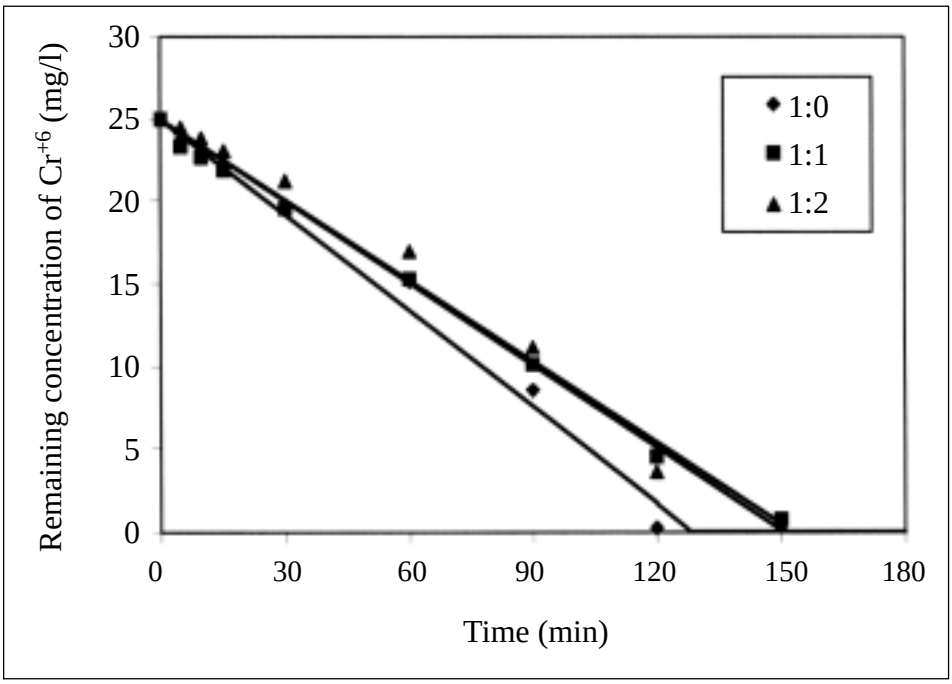

Figure 3. Photocatalytic reduction of Cr(VI) on TiO_2 thin film derived from different molar ratio of acetyl acetone.

Table 2. Reaction rate constants for Cr(VI) photocatalytic removal using thin film TiO_2 derived from different molar ratio of acetyl acetone.

Titanium(IV) butoxide : acetyl acetone	Rate constant (k, mg/l-min)	Coefficient Determination (r^2)
1:0	0.1930	0.9877
1:1	0.1659	0.9957
1:2	0.1634	0.9884

CONCLUSION

This paper has shown that acetyl acetone plays an important role on the properties of TiO_2 thin film. Addition of acetyl acetone to the sol solutions significantly enhances the adherence property and smoothness of the film surface. On the contrary, acetyl acetone exerted less effect on the crystal structure of TiO_2 film and increased nanoparticle size of TiO_2 which results in the decrease of photocatalytic activity of the film.

ACKNOWLEDGEMENTS

This work was supported in part by National Research Center for Environmental and Hazardous Waste Management, Chulalongkorn University, Thailand and the National Metal and Materials Technology Center under grant no.MT-B-47-MET-20Ð158G.

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