

Photocatalytic activities and specific surface area of TiO₂ films prepared by CVD and sol-gel method

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Abstract—The photocatalytic activity of CVD grown films shows significant, non-linear (sigmoid-like) dependency on the film thickness. However, the photocatalytic activity of sol-gel grown film is almost independent of the film thickness. The specific surface area of sol-gel grown films is very small, regardless of the film thickness. Conversely, the specific surface area of CVD grown films indicates significant thickness dependency. The specific area and photocatalytic activity were found to show very similar dependencies on the film thickness.

Key words: TiO₂ Film, Chemical Vapor Deposition Method, Sol-Gel Method, Specific Surface Area, Photocatalytic Activity

INTRODUCTION

Heterogeneous photocatalysis has been widely accepted as a promising method for the treatment of trace organic compounds in both water and air. Due to its unique feature of the complete mineralization of pollutants, without causing secondary pollution, heterogeneous photocatalysis has been extensively studied [1]. TiO₂ photocatalysts have been applied to environmental applications, such as for the treatment of air and wastewaters and as deodorizers, because of their strong oxidizing power, high photocatalytic activity, self-cleaning function, and bactericidal and detoxification activities [2-4]. In principle, the specific surface area is one of the important factors that decides the photocatalytic activity, because photocatalytic reactions occur on the surface where electrons and holes are produced under UV irradiation [5]. Quantitative analyses of the specific surface areas for various TiO₂ photocatalyst powders have been proposed [6]. However, in most cases, measuring the very small specific surface area of a TiO₂ photocatalyst film coated onto a substrate can be very difficult [7].

In a previous paper [8], the activity of CVD grown TiO₂ photocatalyst films was shown to have a very strong non-linear dependency on the film thickness (the film thickness was varied by changing the CVD deposition time). At that time, the specific surface area was not measured. However, the photocatalytic activity was suggested to be dependent on the surface area, based on SEM observation of the film surfaces, which indicated that the surface roughness increased with increasing of film thickness.

In this study, the surface areas of TiO₂ photocatalyst films with different thicknesses prepared by both CVD and sol-gel methods were successfully measured by using a highly sensitive BET adsorption apparatus. The correlation between the surface area and photocatalytic activity was also tested.

EXPERIMENTAL

1. Preparation of CVD Grown TiO₂ Photocatalyst Films

For the analysis of the specific surface areas, TiO₂ photocatalyst films were grown on small glass beads (2 mm in diameter) and also on alumina balls (8 mm of diameter), by using a low pressure chemical vapor deposition (LPCVD) apparatus with titanium tetraisopropoxide (Ti[OCH(CH₃)₂]₄, TTIP) as a reagent. Details of the apparatus have been described in our previous paper [9]. Argon gas was fed to a bubbler containing liquid TTIP, heated at 323 K, to carry the TTIP vapor to the reactor. The gas was further diluted at the inlet of the reactor tube with Argon and oxygen. Mass-flow controllers were used to modulate the flow rates of argon and oxygen gases. The system was evacuated by a rotary oil vacuum pump, with the operating pressure measured by a pressure transducer at the outlet of the reactor tube. The gas lines were heated to prevent condensation of TTIP vapor. The LPCVD conditions used for the preparation of TiO₂ films were as follows: total flow rate of gas fed to the reactor, 1,500 sccm; oxygen concentration at the reactor inlet, 50 mol%; operating pressure, 1 Torr; deposition temperature, 773 K. The morphology of the films grown on the quartz glass substrate (20 mm×20 mm) was observed by using an FESEM (Hitachi, S-4700).

2. Preparation of Sol-gel Grown TiO₂ Photocatalyst Films

TiO₂ films were also prepared by the sol-gel method. TiO₂ sol

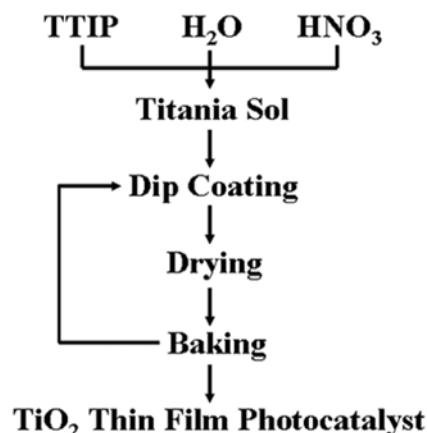


Fig. 1. Preparation of TiO₂ film by the sol-gel method.

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was prepared by using H₂O, HNO₃ and TTIP. An aqueous solution (150 ml of H₂O: 15 ml of TTIP: 1 ml of HNO₃) was refluxed at 353 K for 1 day. The sol was transparent and very stable in air. The TiO₂ film was prepared by the procedure indicated in Fig. 1. The sol was dip-coated, air dried and then heat-treated in an electric furnace at 773 K for 24 hours to obtain anatase film. The three-step process (dipping, drying, and heat-treatment) was repeated to obtain films of the desired thickness. Two types of sol-gel grown films were prepared, i.e., coated onto alumina balls (8 mm of diameter), which were used for evaluation of the activity, and coated onto small glass beads (2 mm of diameter), which was used for the BET analysis.

3. Evaluation of Photocatalytic Activity

The photocatalytic activities of the TiO₂ films were evaluated by the photodecomposition of an aqueous solution of methylene blue in a re-circulation type annular tube photo-reactor. Details of the photo-reactor have been described in our previous paper [9]. The photocatalyst balls were filled into the annular space of the reactor. A UV-A lamp (Philips, TL4W/05, with most intense power at 365 nm) was used as the light source. To conduct re-circulating flow experiments, 500 cm³ of a methylene blue solution was prepared, and circulated in the annular space of the reactor, with a flow rate of 50 cm³/min with a roller pump. The decomposition rate was evaluated as a function of the irradiation time from the change in the methylene blue concentration at the reactor outlet. The concentration of methylene blue was measured by the absorbance at $\lambda=580$ nm, with a spectrophotometer (UV-1601, Shimadzu). The initial methylene blue concentration was about 8.6×10^{-6} mol/liter, with 500 cm³ of solution circulated in the reactor at a flow rate of 200 cm³/min.

4. Specific Surface Area Measurement

The specific surface area of the TiO₂ films was very small, so it was measured with a BET adsorption apparatus with a symmetrically designed differential tensiometer (Belsorp-18plus, BEL Japan Inc.) at the temperature of liquid nitrogen by adsorbing krypton gas (99.995%) onto the film. Films with different thicknesses, grown on 1 gram of the small glass beads, were pretreated by heating the

samples under vacuum to 383 K for 2 hour in flowing helium gas (99.9999%).

RESULTS AND DISCUSSION

1. The Crystal Morphologies of the TiO₂ Films Prepared by the CVD and Sol-Gel Methods

Fig. 2 shows the cross-section and surface morphology of the TiO₂ films prepared by both the CVD and sol-gel methods with an FESEM. The cross-section of the TiO₂ film prepared by the CVD method shows many columnar crystals, with a prismatic top structure growing perpendicular to the substrate. On the contrary, the TiO₂ film prepared by the sol-gel method does not show any distinguishable crystal form. The surface morphology of the CVD grown films was rough and that of the sol-gel grown films was smooth. Although not quantitative, this figure shows that the TiO₂ film prepared by the CVD method has a relatively larger specific surface area compared to that prepared by the sol-gel method.

2. The Photocatalytic Activities of the TiO₂ Films Prepared by the CVD and Sol-Gel Methods

Fig. 3 shows plots of the methylene blue composition at the outlet of the reactor, as a function of the irradiation time, for TiO₂ coated photocatalyst films with different thicknesses prepared by the sol-gel method. These results indicate that the decomposition of methylene blue via the photocatalytic reaction in the presence of the TiO₂ catalyst approximated to a pseudo first order reaction model

$$C/C_0 = \exp(-kt) = \exp(-k'A t/V) \quad (1)$$

where C is the methylene blue concentration at time t ; C_0 , the initial concentration; k , the over-all rate constant; k' , the pseudo first order reaction rate constant; A , the total superficial surface area of photocatalyst balls installed in the reactor ($A=382$ cm²), and V , the total volume of the solution ($V=500$ cm³).

The overall rate constant, k , was determined from the slopes of the lines in Fig. 3 by regression analysis. The results as a function of the film thickness (d) are shown in Fig. 4. The overall rate constants of the CVD-grown catalyst films are also plotted in this figure. CVD-grown films exhibit steep increases in the over-all rate constants in small d regions, but become saturated at $d > 5$ μ m, as pre-

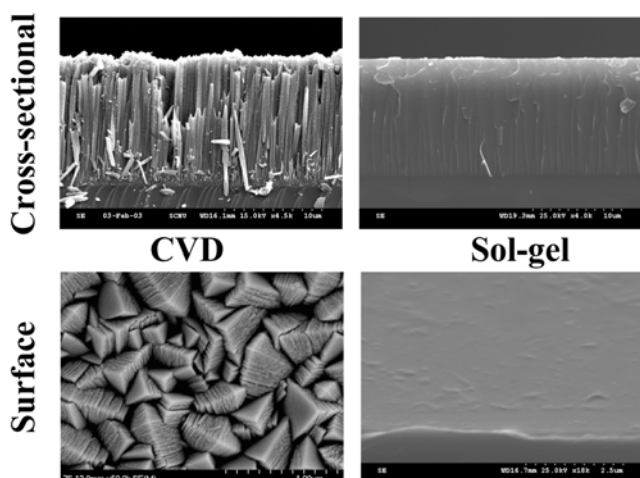


Fig. 2. Cross-sectional and surface morphologies of the TiO₂ films prepared by the CVD and sol-gel methods. CVD deposition time; 8 hours, film thickness; 15 μ m. Sol-Gel growth conditions: dipped 5 times, film thickness; 12.5 μ m.

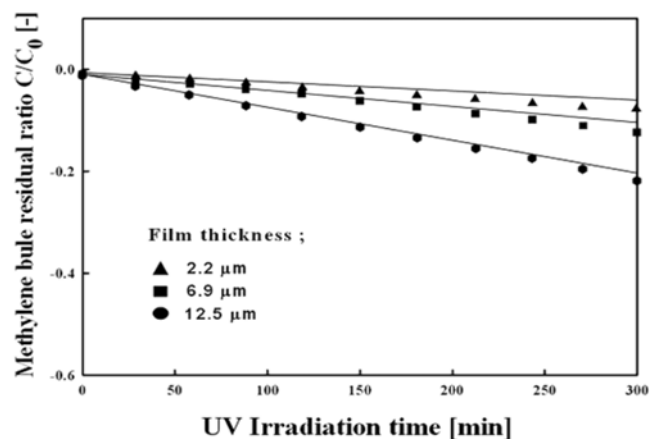


Fig. 3. Photodecomposition of methylene blue on the sol-gel grown TiO₂ film catalysts with different thicknesses.

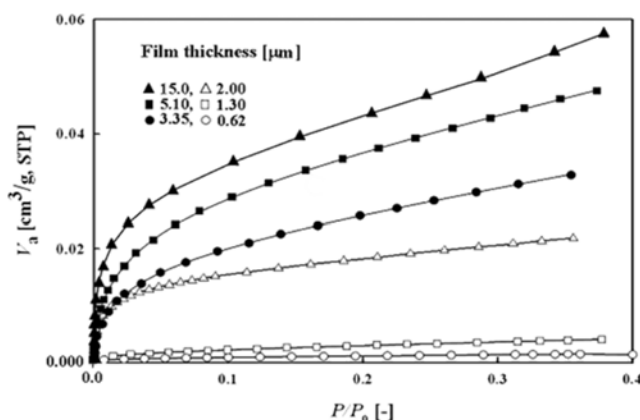


Fig. 4. Effect of TiO_2 film thickness on the apparent first order rate constant, k , and specific surface area.

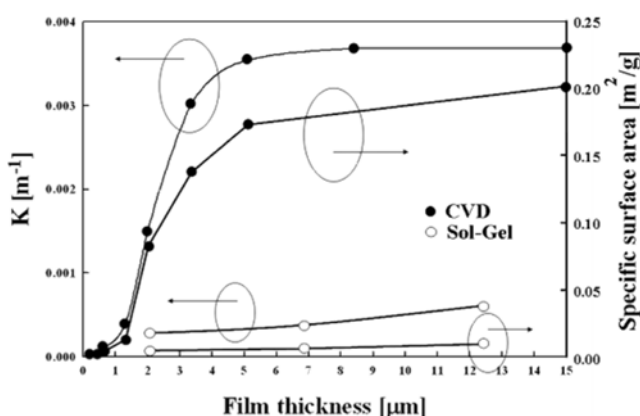


Fig. 5. Adsorption isotherm of krypton on the CVD grown TiO_2 films with different thickness.

viously reported [8]. However, the overall rate constants of the sol-gel grown films are much smaller, and show less film thickness dependency than that of CVD grown films.

3. Specific Surface Area of TiO_2 Films

Fig. 5 shows the amounts of krypton adsorbed onto one gram of glass beads coated with the CVD-grown TiO_2 film as a function of the relative pressure. The mass of the coated films was too small to obtain a reliable weight. Therefore, the G_s values in the present measurements should only be used for a relative comparison. The results indicated that the surface area was strongly dependent on film thickness.

For very thin films, the specific surface area could not be measured with the present BET apparatus, as the amount of krypton absorbed was too small.

The measured specific surface areas of the TiO_2 films with different thicknesses, prepared by both the CVD and sol-gel methods, are plotted in Fig. 4 and summarized in Table 1. From the A_s seen in Fig. 4, the specific surface area of the CVD grown photocatalysts film increases significantly with increasing thickness, but becomes saturated at $d > 5 \mu\text{m}$. The specific surface area of the sol-gel grown films does not show any significant thickness dependency. These behaviors resemble those of the overall rate constant, k , as seen from Fig. 4.

Table 1. The over-all rate constant, k , and specific surface area at different TiO_2 film thickness

Method	Thickness [μm]	k [min^{-1}]	A_s [m^2/g]	k/A_s
CVD	0.11	0.000017	-	-
CVD	0.43	0.000030	-	-
CVD	0.62	0.000105	0.0046	0.0228
CVD	1.30	0.000379	0.0134	0.0283
CVD	2.00	0.001499	0.0825	0.0182
CVD	3.35	0.003013	0.1373	0.0219
CVD	5.10	0.003545	0.1725	0.0206
CVD	8.40	0.003683	-	-
CVD	15.0	0.003685	0.2010	0.0183
Sol-Gel	2.20	0.000324	0.0084	0.0385
Sol-Gel	6.90	0.000422	0.0112	0.0377
Sol-Gel	12.5	0.000674	0.0183	0.0368

In Table 1, the k/A_s values for each film are presented. These values indicate a measure of the photocatalytic activity per unit surface area, as measured by the BET method. Films grown by the CVD method show similar k/A_s values. Films grown by the sol-gel method show slightly larger k/A_s values than those of the CVD grown films. On the basis of the overall rate constant, k , the CVD grown films appear to be higher than that of sol-gel grown films. However, from the activity based on the BET surface area that of the sol-gel grown films was slightly higher.

CONCLUSION

Our results indicate that CVD-grown TiO_2 films show significant increases in both catalytic activity and BET surface area with increases in film thickness for a range of very small film thicknesses, and become saturated at thicknesses greater than 3-5 μm . However, the sol-gel grown TiO_2 films show smaller overall rate constant and BET surface area values than those of CVD-grown films. However, the photocatalytic activity per unit BET area was almost independent of the film thickness. Sol-gel grown films show slightly larger photocatalytic activity values per unit BET area than those of CVD-grown films.

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