

Enhanced photocatalytic oxidation properties in Pt-TiO₂ thin films by grounding

Wooseok Nam, Jong Hyeok Park, and Gui Young Han[†]

Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea
(Received 26 March 2008 • accepted 18 September 2008)

Abstract—The rates of formaldehyde and toluene photocatalytic oxidation with different initial concentrations over a Pt-TiO₂ film were analyzed at both the grounded and non-grounded states. The photocatalytic oxidation rates at the grounded states were faster than in the non-grounded states under similar reaction conditions. The enhanced photocatalytic oxidation rates in the grounded state were attributed to the effective splitting of the electron-hole pairs as a result of the scavenging of photoexcited electrons through the ITO (indium tin oxide) glass to earth. The pseudo first order model showed good agreement with the experimentally obtained heterogeneous photocatalytic oxidation rates of formaldehyde and toluene.

Key words: Pt-TiO₂, Sputtering, Scavenging, Toluene, Formaldehyde

INTRODUCTION

Indoor air pollutants, which mainly include nitrogen oxides (NO_x) and volatile organic compounds (VOCs), have carcinogenic potential [1]. In particular, toluene and formaldehyde are well-known components of VOCs, which are widespread and persistent in both the indoor and outdoor environment. The carcinogenic potential of VOCs has led to research on the development of various technologies for air cleaning systems, which are common methods for controlling air pollution [1], and using air purifiers such as filtering methods to remove particulate matter. However, these techniques simply transfer the problem to other places, resulting in the need for additional disposal or handling steps.

An alternative remediation technology is the use of photocatalytic oxidation methods (PCO). PCO might be more effective than other conventional techniques such as activated carbon adsorption and chemical scrubbers because semiconductors are inexpensive and are capable of effectively oxidizing most organic compounds to CO₂ and H₂O without significant energy input [2-4]. The photocatalytic oxidation of environmental contaminants has been studied over the past three decades. Recent developments in the field of photocatalytic oxidation have led to the remarkable elimination of aliphatic and aromatic pollutants decomposed in the air and water environment. TiO₂ powder is a well-known photocatalyst that has been studied extensively. It is often immobilized on inorganic materials in order to adsorb trace contaminants as well as to increase photocatalytic efficiency [5-7]. TiO₂ has an indirect bandgap (3.2 eV) between the valence and conduction bands. Under UV illumination, the valence band electrons are photoexcited to the conduction band, creating highly reactive electron-hole pairs, which can participate in charge-transfer reactions with contaminants adsorbed on catalyst surface. These holes and electrons are quite mobile; the electrons participate in reduction reactions and the holes participate in oxidation reactions. A great deal of research has been focused

on increasing the photocatalytic activity of TiO₂ by controlling the rate of electron/hole recombination.

The photocatalytic ability is lost if these electron/hole pairs recombine before they can be used for photocatalysis. Therefore, the photocatalytic activity can be remarkably improved if the electron-hole recombination in the photocatalytic reaction can be effectively eliminated [8]. Accordingly, many researchers have examined charge separation in nanocrystalline films using an electrolyte and additional potential [9-13]. The main objective of this study is to investigate the possibility of scavenging photoinduced electrons from a Pt-TiO₂ film to improve the photocatalytic ability by simple ground method. Fig. 1 shows the concept of photoinduced electron scavenging using ITO glass by grounding. We investigated the scavenging effect of photoexcited electrons by a grounding method on photocatalytic removal of two gas-phase organic pollutants (formaldehyde and toluene). In addition, a kinetic study using pseudo first order kinetic equation was carried out to determine the effect of the thickness of the Pt and spin-coated TiO₂ film on the photocatalytic decomposition reaction rates.

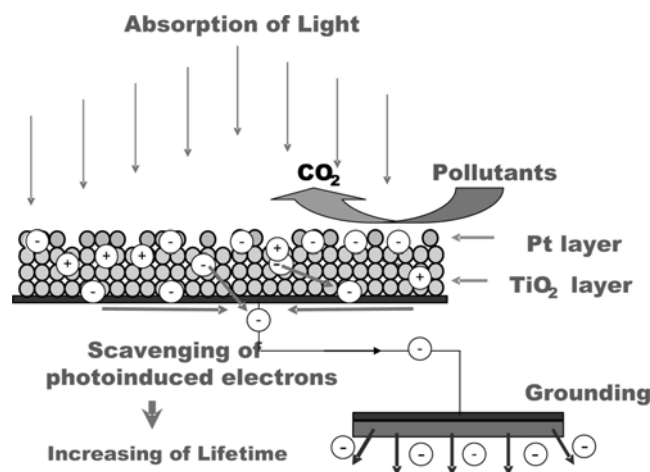


Fig. 1. Basic concept of photoinduced electron scavenging by grounding.

[†]To whom correspondence should be addressed.
E-mail: gyhan@skku.ac.kr

EXPERIMENTAL

1. Preparation of TiO₂ Film on the ITO Glass

Titanium tetraisopropoxide (TTIP, 98.0% Junsei) was used as the TiO₂ precursor. The alkoxide precursor was hydrolyzed in excess water with an acid catalyst. TTIP 1.0 mol was dissolved in 60 mL of absolute ethanol. The alcohol solution was vigorously stirred for 2 hr, and 10.0 mol of H₂O and 5.0 mol of HCl were then added in a N₂ atmosphere. The resulting alkoxide solution was stirred continuously for 12 hr at room temperature during the hydrolysis and condensation of the titanium alkoxide.

Transparent indium tin oxide (ITO) coated glass of 8.0×8.0 cm² in size was prepared as the photoinduced electron scavenging substrates. The above solution (~0.5 cm³) was added dropwise and spin-coated at 3,000 rpm for 1 min. After drying at 110 °C for 1 h, the coated layer was heated to 500 °C at a rate of 10 °C·min⁻¹ in ambient conditions and was maintained at that temperature for 1 h for calcination. The film thickness was controlled by the number of spin-coatings and calcinations at 500 °C.

2. Pt Sputtering on the TiO₂ Film

Pure platinum was sputtered by using an e-beam evaporator on the TiO₂ layer. After thermal annealing at 300 °C for 30 minutes, a chemical cleaning process was performed by using alcohol and acetone. Before each deposition, the sputter chamber was evacuated to a base pressure of approximately 2×10⁻⁵ mbar. For all samples, deposition was done in Ar plasma. The operation pressure was approximately 6×10⁻¹ mbar. The substrate temperature was kept at 573 K during Pt deposition. The properties of the Pt-TiO₂ films were investigated by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) attached to the SEM instrument and X-ray photoelectron spectroscopy (XPS). The SEM and EDX measurements were performed with a Phillips model XL30 scanning electron microscope equipped with a Phillips EDX probe. The XPS data were obtained with a Mg (K α , h ν =1253.6 eV, 1 eV=1.603×10⁻¹⁹ J) X-ray source on an ESCA2000 (VG Microtech) instrument.

3. Photocatalytic Reaction

The photocatalytic oxidation experiment in the module reactor was performed in a quartz glass vessel. The photocatalyst was immobilized on the ITO glass substrate and placed at the bottom of the reactor. Aqueous formaldehyde or toluene was used as the representative VOC. An appropriate concentration of formaldehyde or toluene was injected into the vessel with a microsyringe. UV irradiation from a 400 W metal halide lamp was used to trigger the photocatalytic degradation reaction. The electrode with photocatalyst film was grounded by using a copper line attached to the bottom of the stainless steel reactor with silver paste. The volume of the photocatalytic reactor was approximately 0.2 L. The photocatalyst was exposed to UV-light with an average quantum rate of 10 mmol·sec⁻¹·m⁻². The concentration of the reactants gas (the initial concentrations of formaldehyde and toluene were approximately 500 ppm) was analyzed by gas chromatography every 30 minutes. During each experiment, approximately 100 L of the reactant samples was collected at the designated times by using a gas-tight syringe. The collected sample gases were analyzed by gas chromatography (Model M600D, Yonglin Co., Korea) with a multi packed column (molecular sieve, Haysep-Q and Carboxen 1004) and TCD.

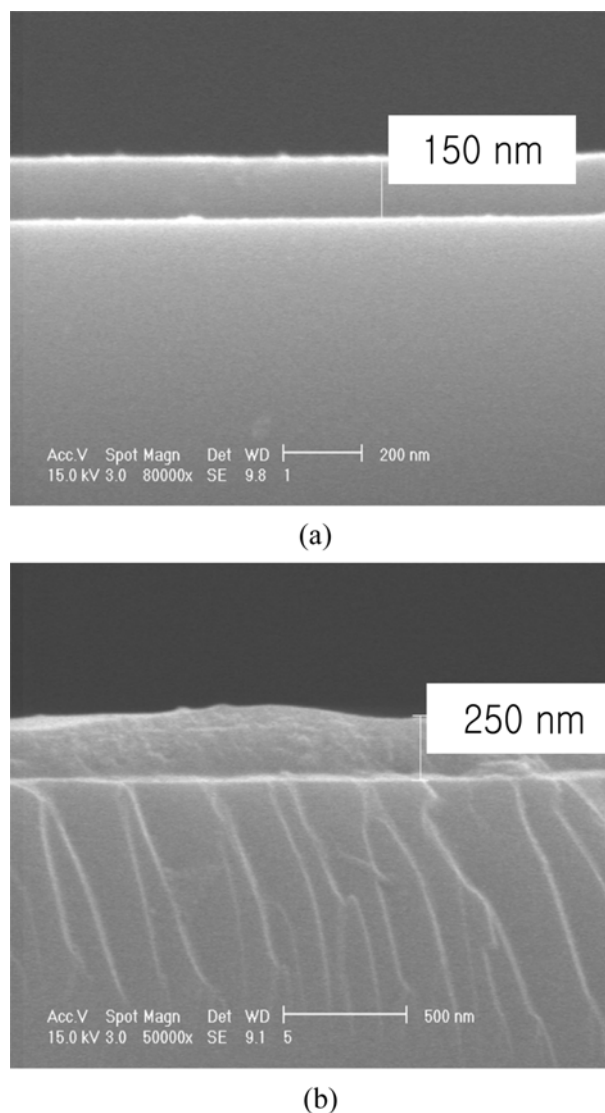


Fig. 2. SEM images of the TiO₂ films (top layer) on ITO glass (bottom layer) by spin-coat-annealing process at 3,000 rpm, 500 °C; (a) 150 nm thickness and (b) 250 nm thickness.

RESULTS AND DISCUSSION

The spin-coating method was found to give a well-controlled thin overlayer of TiO₂. Fig. 2(a) and (b) show SEM images of TiO₂ films at different thickness prepared by spin-coat-annealing methods. The relative photocatalyst film thickness vs. UV-light absorption ability was investigated by the simple current-voltage (I-V) curves of TiO₂/ITO samples in the UV-irradiation and dark condition (Fig. 3). Fig. 3 shows that the photocurrent increases with increasing TiO₂ film thickness, indicating good absorption of UV light. The I-V curves corresponding to these samples showed almost linear characteristics, indicating that these TiO₂/ITO samples have good ohmic characteristics. However, the I-V curves were almost the same when the photocatalyst film thickness exceeded approximately 150 nm. This suggests a limit of penetration of UV-light of approximately 150 nm under these reaction conditions. At a higher photocatalyst loading, the screening effect of UV-light occurred as a result of the

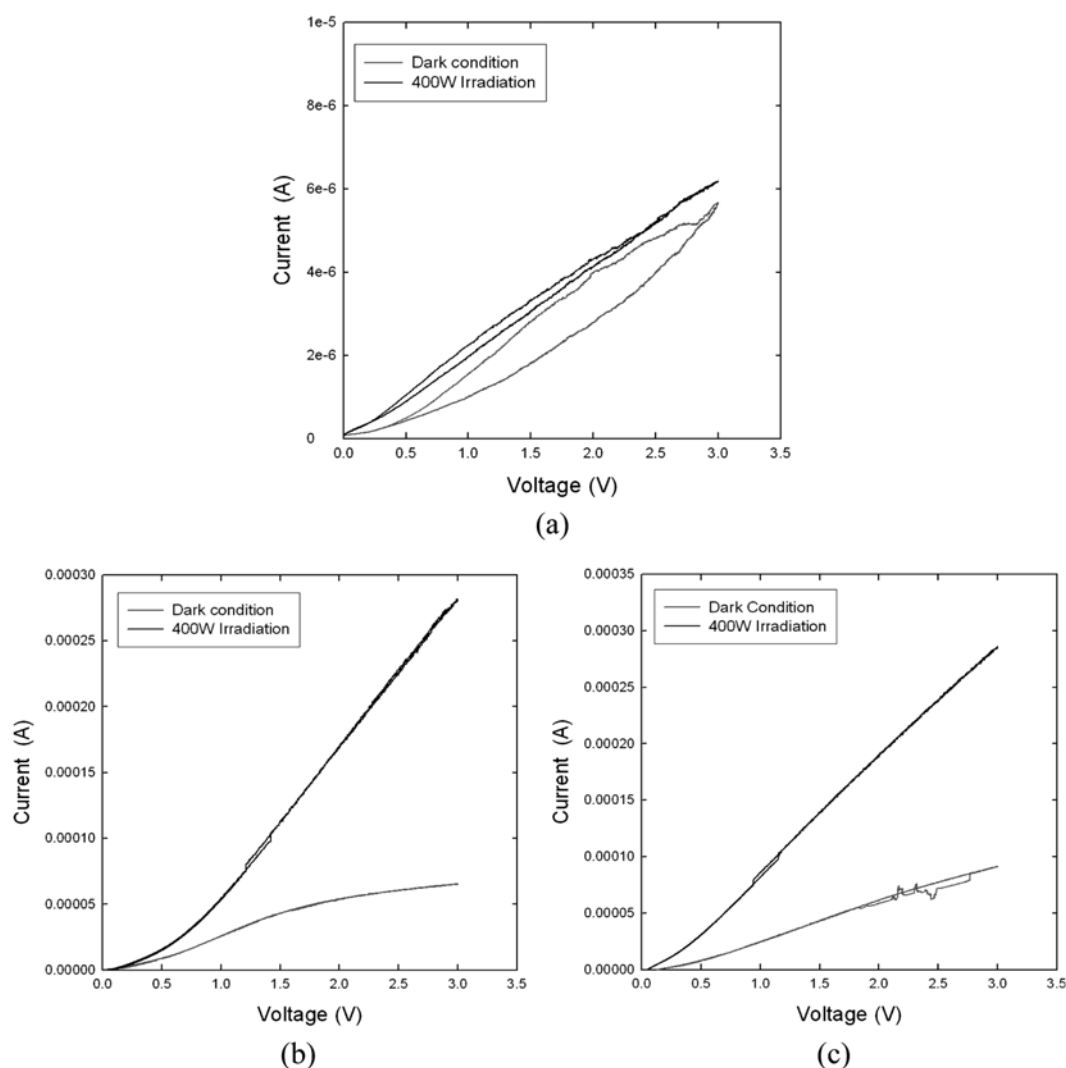


Fig. 3. Current-voltage curves in the dark and UV-irradiation conditions (a) 50 nm thickness, (b) 150 nm thickness, and (c) 250 nm thickness.

thick film thickness. In addition, the thick film provides large resistance to the photocurrent. Therefore, 150 nm was chosen as the TiO_2 photocatalyst film thickness on the ITO glass. Fig. 4(a) shows the EDX spectra of the Pt on the TiO_2 films. The typical electron energy was 10 keV and the acquisition time for the EDX measurements was 150 sec. From the EDX analysis, the level of Pt on the surface was approximately 1.0% after 8 min deposition condition. Fig. 4(b) shows an XPS plot of the Pt on the TiO_2 films at various deposition times under the same experimental conditions. The binding energies of the core electrons of Pt metal (Pt^0 , $4f_{7/2}$ (71.2 eV)) on the TiO_2 films were observed, but there were no PtO_2 ($4f_{5/2}$ (75 eV)) peaks present. However, a very small amount of PtO ($4f_{5/2}$ (74.2 eV)) peaks was observed. Therefore, Pt was well attached to the TiO_2 film but was not chemically bonded to Ti or O. However, there was a rapid decrease in transparency with increasing amount of Pt deposited over 8 minutes. This decrease in transparency would prevent light from reaching the TiO_2 catalyst and impede the photocatalytic reaction.

The photocatalytic oxidation rates of the organic contaminants over the irradiated TiO_2 were curve-fitted by using a pseudo first

order kinetic model [21-23]. Since the pseudo first order kinetic model equation is valid only for a single component and at the initial stage, it was assumed that there was a negligible intermediate concentration and the initial stage should be very short. In this study, the initial rates were calculated from the first half hour of the reaction. During the experiment, the temperature of the reactor increased slightly for the first half hour and then remained at a constant temperature of 40 °C. Based on this assumption, the following single-site pseudo first order kinetic model was introduced to evaluate the photocatalytic oxidation rates:

$$r = -\frac{dC_t}{dt} = \frac{kKC_i}{1 + KC_i} \quad (1)$$

Where r is the reaction rate ($\text{mol} \cdot \text{min}^{-1}$), t is the irradiation time (min), k is the pseudo kinetic constant ($\text{mol} \cdot \text{min}^{-1}$), K is the adsorption equilibrium constant (mol^{-1}), and C_i is the contaminant concentration at time t (mol). If $KC_i \ll 1$, the reaction can be fitted as a pseudo first-order reaction with a constant reaction rate coefficient. Hence, Eq. (1) can be rewritten as Eq. (2).

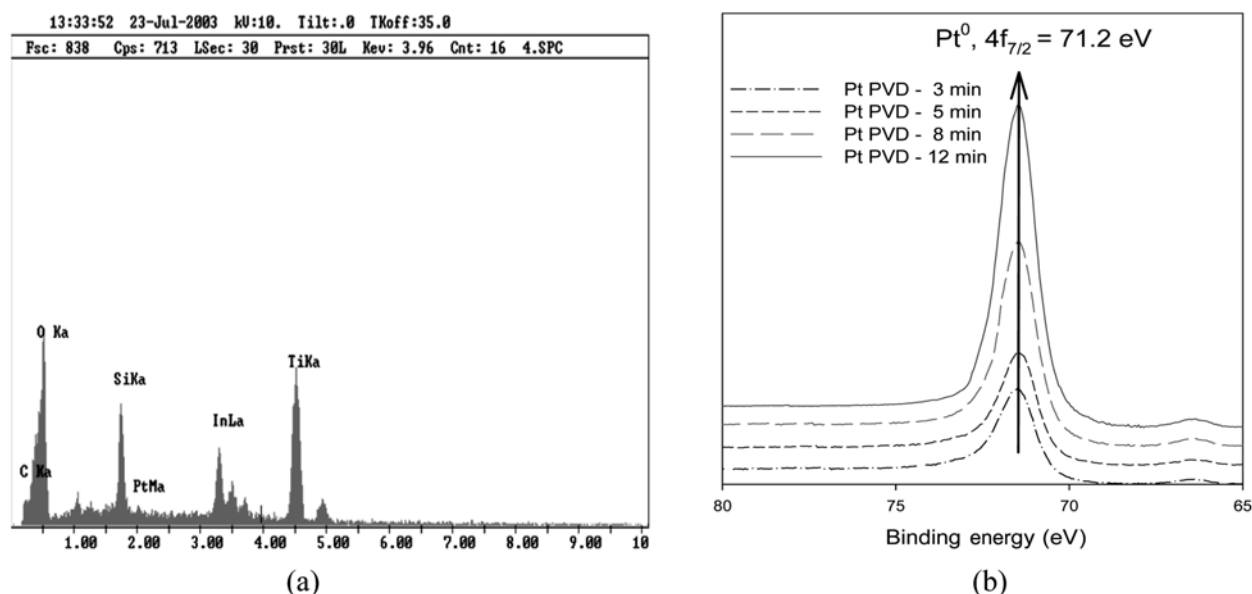


Fig. 4. EDX (a) and XPS (b) images of the Pt deposited TiO₂ films by spin-coat-annealing process at 2,000 rpm, 500 °C.

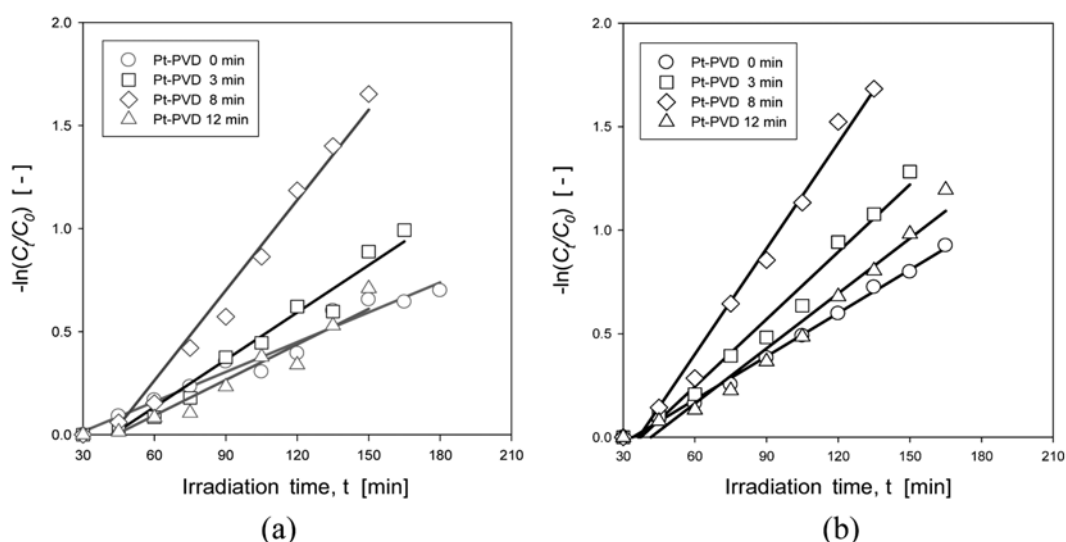


Fig. 5. Dependence of $-\ln(C_t/C_0)$ on t of formaldehyde under (a) non-grounding, and (b) grounding conditions.

$$r = -\frac{dC_t}{dt} = k_R C_t \quad (2)$$

Eq. (2) is expressed in an integrated form as Eq. (3).

$$C_t = C_0 e^{-k_R t} \quad (3)$$

Using a logarithmic function, Eq. (3) can be linearly expressed as Eq. (4):

$$\ln C_0 - \ln C_t = k_R t \quad (4)$$

Where k_R is the pseudo first-order reaction constant (min⁻¹). Eq. (4) is simplified to:

$$-\ln\left(\frac{C_t}{C_0}\right) = k_R t \quad (5)$$

The reactant residue (C_t/C_0) is a ratio of the instantaneous concentration of a gaseous reactant (C_t) at the actual irradiation time, t to the initial concentration (C_0). Eq. (5) shows that there is a strong linear relationship between $-\ln(C_t/C_0)$ and t during the photocatalytic reaction provided that $k_R C_t$ is $\ll 1$. The slope of the fitted straight line is equal to the pseudo first-order reaction coefficient, k_R [24]. Fig. 5(a) and (b) show the effect of the TiO₂ film thickness on the photocatalytic oxidation rate of toluene in the grounded and non-grounded state, respectively. The TiO₂ film thickness on the ITO glass was controlled by the number of spin-coating repetitions (from 1 to 5). The addition of Pt to this system strongly affected the rate of toluene decomposition. In addition, the conversion of toluene decomposition was higher in the grounded photocatalyst system. Fig. 6(a) and (b) show comparison plots of $-\ln(C_t/C_0)$ of the residual formaldehyde versus actual irradiation time, t on the non-grounded

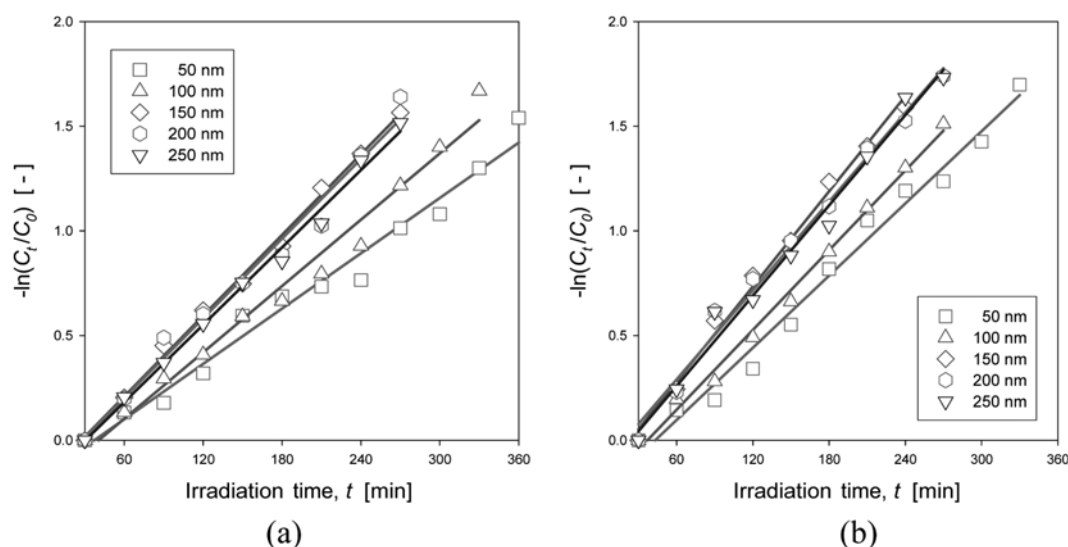


Fig. 6. Dependence of $-\ln(C_t/C_0)$ on t of toluene under (a) non-grounding and (b) grounding conditions. Pt-PVD time: platinum deposition time by e-beam evaporator.

Table 1. Kinetic data based on pseudo first order model

Reactant (500 ppm)	TiO ₂ film thickness (nm)	Pt PVD (min)	Grounded system		Non-grounded	
			K_R (h ⁻¹)	R^2	K_R (h ⁻¹)	R^2
Formaldehyde	150	0	0.0070	0.997	0.0048	0.961
	150	3	0.0108	0.980	0.0077	0.966
	150	8	0.0170	0.986	0.0146	0.974
	150	12	0.0089	0.973	0.0057	0.931
Toluene	50	8	0.0058	0.985	0.0044	0.978
	100	8	0.0064	0.994	0.0053	0.980
	150	8	0.0075	0.993	0.0064	0.996
	200	8	0.0071	0.988	0.0063	0.980
	250	8	0.0072	0.986	0.0062	0.993

and grounded systems at different platinum deposition times. The plots indicate that the slopes (the pseudo first-order reaction coefficients) of the fitted straight line by using the least-square method increase with increasing platinum sputtering time at a constant formaldehyde concentration. The decomposition performance for toluene increased significantly with increasing film thickness. However, the reaction rates were almost the same when the photocatalyst film thickness exceeded 150 nm. Pt can trap some of the photoexcited electrons from TiO₂ [25], but photoactivity is impeded if there is too much Pt. Table 1 summarizes the results of grounded and non-grounded systems. From the results, the scavenging of the photoinduced electrons improves the photocatalytic reaction rate compared with non-grounding conditions. In addition, it was confirmed that the grounded photocatalyst system was more useful in decomposing pollutants than the non-grounded photocatalytic system.

CONCLUSIONS

Pt-TiO₂ thin films were prepared with different thicknesses and amounts of Pt loading. Formaldehyde and toluene were well oxidized photocatalytically on the Pt-TiO₂ film surface. In addition,

the photoinduced electrons were easily scavenged by the grounded ITO glass via the ohmic contact. The pseudo first model showed good agreement with the experimentally obtained heterogeneous photocatalytic oxidation rates of formaldehyde and toluene. The effect of the scavenging of photoinduced electrons from Pt-TiO₂ film using the ohmic contact with ITO glass was experimentally observed and the scavenging of photoinduced electrons using a grounding method can be one of the effective ways for the photocatalytic oxidation of VOCs.

ACKNOWLEDGMENTS

This research was performed for the Hydrogen Energy R & D Center, one of the 21st Century Frontier R & D program, funded by the Ministry of Education, science and technology of Korea.

NOMENCLATURE

C_0 : initial concentration of the reactant [mol]
 C_t : contaminant concentration at time t [mol]
 k : pseudo kinetic constant [mol·min⁻¹]

- k_R : pseudo first-order reaction coefficient [min^{-1}]
 K : adsorption equilibrium constant [mol^{-1}]
 r : reaction rate [$\text{mol} \cdot \text{min}^{-1}$]
 t : irradiation time [min]

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