

## Photocatalytic Decomposition of Gaseous Ozone over TiO<sub>2</sub> Thin Film

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### Abstract

The characteristics of heterogeneous photocatalytic decomposition were investigated at low concentration level of O<sub>3</sub> on TiO<sub>2</sub> for various operating parameters such as: loaded catalyst weight (0 ~ 4 mg/cm<sup>2</sup>), initial concentration of O<sub>3</sub> (0.06 ~ 10.0 ppm), gas flow rate (1.0 ~ 2.5 l/min), and relative humidity (0 ~ 80%). This study was conducted using a flow-type reactor at room temperature. Three kinds of pure TiO<sub>2</sub> (P25, ST-01, and E-23) were employed as photocatalysts. It was found that O<sub>3</sub> removal ratio was identical, regardless of the loaded TiO<sub>2</sub> weight in the range from 0.5 to 4.0 mg/cm<sup>2</sup>. It was also found that higher initial ozone concentration results in greater oxidation rate of ozone and experimental data show kinetically a good agreement with Langmuir-Hinshelwood kinetic model. We also observed that the removal ratio of O<sub>3</sub> decreases linearly with the increasing flow rate and also with the increasing relative humidity for each catalyst.

**Key words** : Photocatalyst, Langmuir-Hinshelwood, Kinetic model, Flow-type reactor

### 1. INTRODUCTION

Ozone (O<sub>3</sub>) has both beneficial and harmful role to human body. O<sub>3</sub> protects us from harmful UV radiation in the stratosphere but is a pollutant with high toxicity in the troposphere.

There is an increasing demand for utilization of O<sub>3</sub> as a markedly effective gaseous oxidizing agent: for example water purification, decolorization, and deodor-

ization etc. For environmental protection, the decomposition of the remaining unreacted O<sub>3</sub> in the exhaust from the O<sub>3</sub> treatment apparatus is very important. Furthermore, lowering concentration of O<sub>3</sub> in indoor and outdoor air will be demanded in near future.

The decomposition of O<sub>3</sub> is an environmentally significant reaction and has attracted considerable attention. But, only a limited number of reports for the interaction of O<sub>3</sub> with solid surfaces are available (Oyama, 2000; Li *et al.*, 1998; Imamura *et al.*, 1991). Among many proposed processes for O<sub>3</sub> decomposition, adsorption and reaction with activated charcoal and catalytic

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decomposition over metal and/or metal oxide catalysts are available methods for industrial application (Dhandapani and Oyama, 1995; Rakitskaya *et al.*, 1994; Calderbank and Lewis, 1976; Deitz and Bitner, 1973). But, for these methods, undesirable consumption of charcoal and additive energy is usually required.

Titanium dioxide ( $\text{TiO}_2$ ) has been extensively used as a photocatalyst for various redox reactions as well as a catalyst for thermal reactions. Ohtani *et al.* (1992) studied the dark and photo  $\text{O}_3$  decomposition at room temperature over 80 ppm of initial concentration of ozone and clarified the fundamental chemical feature of the photo-reaction. Bulanin *et al.* (1995) studied the low-temperature  $\text{O}_3$  adsorption on  $\text{TiO}_2$  using infrared (IR) spectroscopy. Pichat *et al.* (2000) investigated the decomposition of  $\text{O}_3$  (50~2000 ppm) on  $\text{TiO}_2$  in the temperature range of 248~358 K.

No results, however, for the decomposition of  $\text{O}_3$  of the ambient air concentration level (< 1 ppm) on  $\text{TiO}_2$  photocatalyst or any influences of environmental factors such as humidity, flow rate, and temperature etc. on the reaction have been published. The purpose of the present work is to investigate the characteristics of heterogeneous photocatalytic decomposition of low concentration level of  $\text{O}_3$  on  $\text{TiO}_2$ . The effect of operating parameters such as loaded catalyst weight, initial concentration of  $\text{O}_3$ , gas flow rate, and water vapor concentration was evaluated at room temperature on various  $\text{TiO}_2$  catalysts.

## 2. EXPERIMENTAL

Three kinds of  $\text{TiO}_2$  were employed: P25 (Nippon Aerosil Ltd., 80% anatase, crystallite size of 25 nm, specific surface area of  $50 \text{ m}^2/\text{g}$ ), ST-01 (Ishihara Sangyo Ltd., 100% anatase, crystallite size of 7 nm, specific surface area of  $300 \text{ m}^2/\text{g}$ ), and E-23 (Eco-device Ltd. 100% anatase, crystallite size of 100 nm, specific surface area of  $140 \text{ m}^2/\text{g}$ ).

Figure 1(a) shows a schematic flow diagram of the reaction system. Decomposition of  $\text{O}_3$  was conducted

in the flow-type photochemical reactor (Figure 1(b)) designed and fabricated in our laboratory (5 cm in width, 30 cm in length and 0.5 cm in height). Three 10 W black light lamps (300~400 nm, FL10NBL, Toshiba Ltd.) were used as a light source. The area of glass plate is  $50 \text{ cm}^2$  (5 cm width and 10 cm in length), and the  $\text{TiO}_2$  powder of 0.05 g was coated on it. Namely, a paste-like mixture of  $\text{TiO}_2$  (0.05 g) and distilled water (3 ml) was applied onto the surface of glass plate ( $1 \text{ mg}/\text{cm}^2$ ) and dried overnight at 383 K.

$\text{O}_3$  decomposition was carried out at room temperature (293~298 K) and atmospheric pressure. For analysis of  $\text{O}_3$ , a system (ML 9811, Monitor Labs, Inc., U.S.A.) composed of  $\text{O}_3$  generator and analyzer was used. The measurement method is UV absorption using a single glass measurement cell and is based on the Beer-Lambert relationship to calculate the ozone concentration.  $\text{O}_3$  concentration was continuously monitored every 10 seconds. In the experiment, air was purified using air purification apparatus (SGPU-22, STEC Ltd., JAPAN). To prepare humidified air, the purified

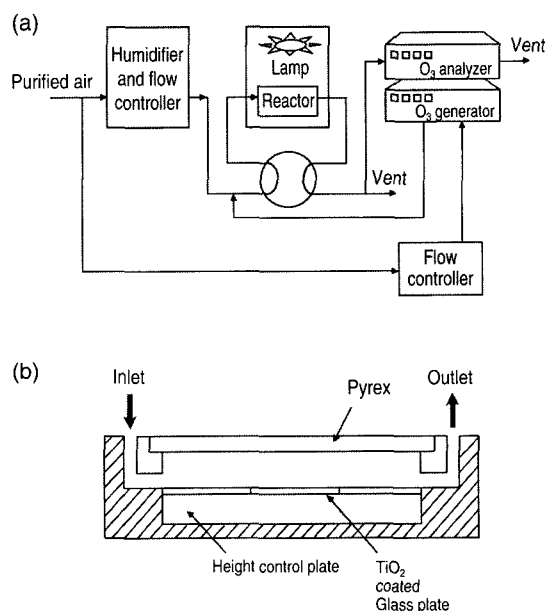


Fig. 1. Schematic depiction of the flow-type photochemical reaction system. (a) flow diagram, (b) detailed picture of reactor.

air was flown through purified water.

### 3. RESULTS AND DISCUSSION

#### 3.1 Photolytic decomposition of ozone and catalytic activity of TiO<sub>2</sub> (P25)

Figure 2 illustrates the time course for ozone decomposition. We tested O<sub>3</sub> decomposition under illumination without photocatalyst. The O<sub>3</sub> concentration and flow rate at the inlet of the reactor containing a bare glass plate (without TiO<sub>2</sub>) were 1.0 ppm and 1.0 l/min respectively and ultraviolet (UV) wavelength was 300 ~ 400 nm.

When only illumination was given, O<sub>3</sub> concentration was decreased by 3.1% with black light (300~400 nm). Ohtani *et al.* (1992) have reported that even in the absence of TiO<sub>2</sub>, irradiation of light with wavelengths > 200 nm induced the O<sub>3</sub> decomposition of 8%. However, irradiation of light with wavelengths > 290 nm did not induce O<sub>3</sub> decomposition. Therefore, decomposition corresponds to the photolysis of gaseous O<sub>3</sub> in the wavelength region of 200~290 nm (Griggs, 1968). As the spectrum of the black light lamp used in this experiment showed weak emission in UV region (< 290 nm), it seems that photolytic decomposition of gaseous ozone occurs under our experimental condition.

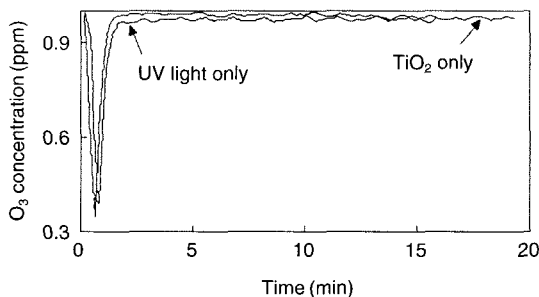


Fig. 2. Representative time course of ozone decomposition in the presence of TiO<sub>2</sub> only or UV light only (initial ozone conc.: 1.0 ppm, flow rate: 1.0SLPM, lamp: black lamp (300~400 nm), relative humidity: 0%, TiO<sub>2</sub> coated on glass plate: 1.0 mg/cm<sup>2</sup>).

A heterogeneous catalytic reaction consists of the following processes: 1) mass transfer of reactants to the catalyst surface, 2) adsorption of reactants on the surface, 3) chemical reaction on the surface, 4) desorption of products from the surface, and 5) mass transfer of products from the surface into the bulk of the fluid.

#### 3.2 Influence of loaded TiO<sub>2</sub> (P25) weight on photocatalytic decomposition of O<sub>3</sub>

Figure 3 shows the relation between O<sub>3</sub> removal ratio and loaded weight of catalyst for a selected reaction condition at the same irradiation condition when P25 was used as photocatalyst. Under fixed light intensity (0.49 mW/cm<sup>2</sup> at 300~400 nm), almost the same removal ratio was obtained regardless of the amount of TiO<sub>2</sub> in the range from 0.5 mg/cm<sup>2</sup> to 4 mg/cm<sup>2</sup>, indicating that a feature of the reaction rate above 0.5 mg/cm<sup>2</sup> is constant regardless of the loaded weight of photocatalyst. This is thought to be due to the fact that the number of photon adsorbed by photocatalyst is limited because light could penetrate into only certain depth of photocatalyst. Ohtani *et al.* (1992) suggested that the photocatalytic activities of TiO<sub>2</sub> powder are independent of their surface area. As shown by data below 0.5 mg/cm<sup>2</sup> in Figure 3, a loaded weight of photocatalyst becomes smaller, so does ozone removal ratio. Therefore, in this study, the amount of photocatalyst loaded on glass plate was fixed to 1.0 mg/cm<sup>2</sup> for each experiment.

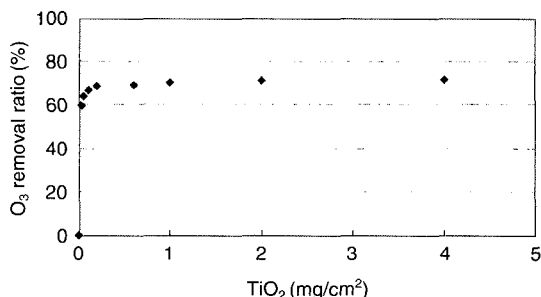
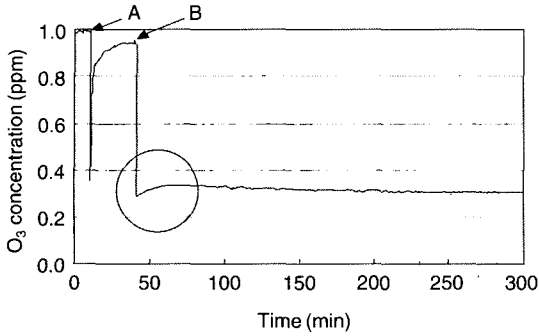


Fig. 3. The relation between ozone removal ratio and loaded amount of photocatalyst (initial ozone conc.: 1.0 ppm, flow rate: 1.0SLPM, lamp: black light (300~400 nm), relative humidity: 0%).



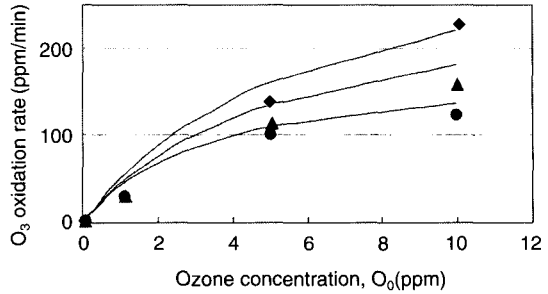
**Fig. 4. Representative time course of photocatalytic decomposition of ozone in the presence of TiO<sub>2</sub> (initial ozone conc.: 1.0 ppm, flow rate: 1.0SLPM, lamp: black lamp (300~400 nm), relative humidity: 0%, TiO<sub>2</sub> coated on glass plate: 1.0 mg/cm<sup>2</sup>, A: reaction start, B: UV irradiation start).**

Figure 4 illustrates the typical time course for photocatalytic decomposition of O<sub>3</sub> on TiO<sub>2</sub> in this study. At first, in the presence of TiO<sub>2</sub> catalyst, a decrease in O<sub>3</sub> concentration was observed in the dark. However, this may not be due to the decomposition in the dark but due to the adsorption by TiO<sub>2</sub>. When the outlet O<sub>3</sub> concentration becomes about 90% of initial one, UV light was irradiated (titled B in Fig. 4). As shown in Figure 4, O<sub>3</sub> was removed by UV irradiation quickly. We found that outlet O<sub>3</sub> concentration gradually rose after a rapid decrease and then stabilized as shown in circle in Figure 4. A desorption rate of O<sub>3</sub> adsorbed in TiO<sub>2</sub> in the dark may be higher than the rate of O<sub>3</sub> photocatalytic decomposition at the beginning of irradiation.

**3. 3 Influence of initial concentration on photocatalytic decomposition of O<sub>3</sub>**

The influence of O<sub>3</sub> concentration on the kinetic oxidation rate of O<sub>3</sub> over TiO<sub>2</sub> is shown in Figure 5. As the initial O<sub>3</sub> concentration becomes higher, the O<sub>3</sub> oxidation rate becomes higher.

In general, for gas–solid reaction, the kinetics would follow the Langmuir–Hinshelwood (L–H) model, in which the reaction rate varies proportionally with the surface coverage ( $\theta$ ) as:



**Fig. 5. Influence of initial ozone concentration on the ozone oxidation rate over TiO<sub>2</sub> (flow rate: 1.0SLPM, lamp: black light (300~400 nm), relative humidity: 0%, the amount of TiO<sub>2</sub> coated on glass plate: 1.0 mg/cm<sup>2</sup>, photocatalysts: P25 (diamond), ST-01 (circle), E-23 (triangle up).**

$$r = k\theta = \frac{kKC}{(1 + KC)} \tag{3}$$

Where  $k$  is the rate constant, related to the limiting rate of reaction at maximum coverage for the experimental conditions;  $K$  is the adsorption equilibrium constant and reflects the proportion of solute molecules which adhere to the catalyst surface; and  $C$  is the concentration of the O<sub>3</sub>. Since the rate expression (Eq. 3) is nonlinear, least-squares optimization was used to determine values for the constants. The results of the optimization are given in Table 1. The rates from Eq. (3) are in good agreement with the measured data as seen in Figure 5.

After substituting this rate expression into a mass balance on a plug flow reactor, the following expression is obtained (Zhang *et al.*, 1994):

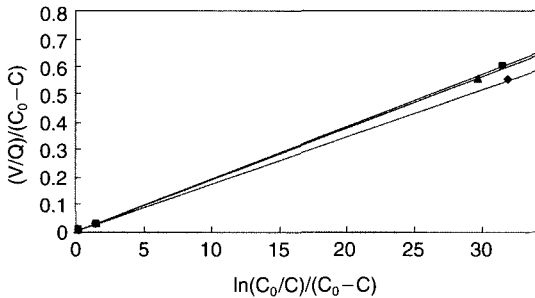
$$\frac{V}{Q} = \frac{1}{kK} \ln\left(\frac{C_0}{C}\right) + \frac{1}{k} (C_0 - C) \tag{4}$$

Where  $V$  is the volume of the reactor,  $Q$  is the flow rate through the photoreactor and  $C_0$  is the initial concentration of O<sub>3</sub>. The quantity,  $V/Q$  is known as the contact time (residence time) for the reaction or average time that a molecule passes through the reactor.

The linear characteristic of Eq. (4) was used for fitting the experimental data after changing the form as

**Table 1. Langmuir–Hinshelwood parameters obtained for the photocatalytic decomposition of gaseous ozone**

Catalysts	<i>k</i> (ppm/min)	<i>K</i> (1/ppm)	<i>kK</i> (1/min)
P25	357.14	0.16	58.14
ST-01	277.78	0.19	52.63
E-23	185.19	0.29	53.76

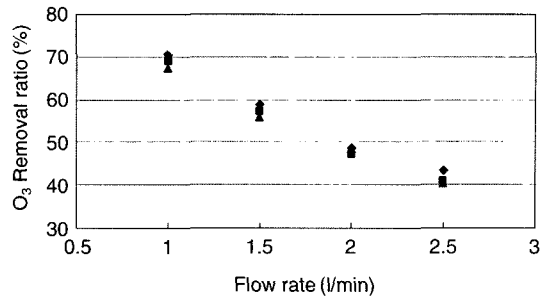


**Fig. 6. Langmuir–Hinshelwood plots for ozone decomposition (TiO<sub>2</sub>: P25 (diamond), ST-01 (square), E-23 (triangle up)).**

follows;

$$\frac{V/Q}{(C_0 - C)} = \frac{1}{k} + \frac{1}{kK} \frac{\ln(C_0/C)}{(C_0 - C)} \quad (5)$$

If one assumes that L-H kinetics hold for a plug flow reactor, then a plot of  $(V/Q)(C_0 - C)^{-1}$  vs.  $\ln(C_0/C)(C_0 - C)^{-1}$  should be linear. Eq. (5) can be tested using different values of  $C_0$  and  $C$ . Here the initial concentration of O<sub>3</sub> was varied. Figure 6 shows the experimental data obtained for O<sub>3</sub>, which are in good agreements with this integral rate-law analysis. The kinetic parameters,  $k$  and  $K$  were obtained using linear least squares analysis. Table 1 summarizes the kinetic parameters of photocatalytic decomposition for O<sub>3</sub> under the identical conditions. It is interesting to note that the photocatalytic degradation rate is related to  $k$  and  $K$ ; therefore, a higher adsorption constant does not always result in a higher reaction rate. Although it could be thought that a high rate constant leads to a rapid reaction, the reaction rate based on the L-H kinetic model



**Fig. 7. The influence of flow rate on photocatalytic decomposition of gaseous ozone (initial ozone concentration: 1.0 ppm, lamp: black light (300~400 nm), relative humidity: 0%, the amount of TiO<sub>2</sub> coated on glass plate: 1.0 mg/cm<sup>2</sup>, TiO<sub>2</sub>: P25 (diamond), ST-01 (square), E-23 (triangle up)).**

depends simultaneously on  $k$  and  $K$ . In our experiment, the rate constant did increase in the order of P25, ST-01 and E-23, but the multiplied products of  $k$  and  $K$  did increase in the order of P25, E-23 and ST-01.

### 3. 4 Influence of flow rate on photocatalytic decomposition of O<sub>3</sub>

Figure 7 shows that the removal ratio of O<sub>3</sub> decreases linearly with the increasing flow rate for each catalyst. This is expected because a better gas–solid contact can be obtained with lower flow rate.

The photocatalytic reactor used in this study has negligible intraparticle transport resistance due to its non-porous catalyst configuration. Thus, only the bulk fluid-to-catalyst diffusion mass transfer is available. The effect of external mass transfer limitations which may occur in transfer of the gas from bulk to the exterior surface of the TiO<sub>2</sub> was investigated using different flow rates of the gas.

Figure 8 shows the dependency of O<sub>3</sub> reaction rate on the gas flow rate for each catalyst under the relative humidity of 0%. For the system used in this study, gas velocity at each flow rate is as follows; 0.067 m/s (1 l/min), 0.1 m/s (1.5 l/min), 0.133 m/s (2 l/min) and 0.167 m/s (2.5 l/min). The results in Figure 8 show that the reaction rate increases with the flow rate.

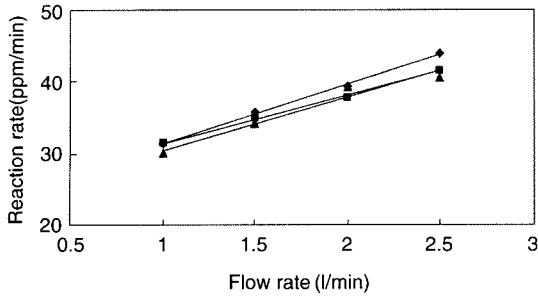


Fig. 8. The influence of flow rate on photocatalytic oxidation rate of ozone over  $\text{TiO}_2$  (initial concentration: 1.0 ppm, lamp: black light (300~400 nm), relative humidity: 0%,  $\text{TiO}_2$ : P25 (diamond), ST-01 (square), E-23 (triangle up)).

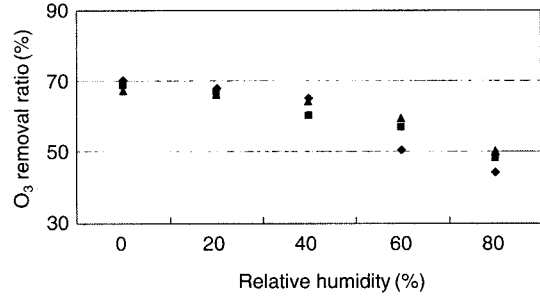


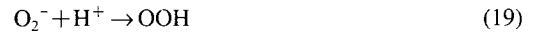
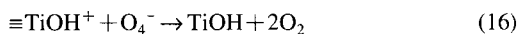
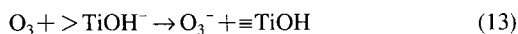
Fig. 9. The influence of relative humidity to photocatalytic decomposition of gaseous ozone (flow rate: 1.0SLPM, initial ozone concentration: 1.0 ppm, lamp: black light (300~400 nm),  $\text{TiO}_2$ : P25 (diamond), ST-01 (square), E-23 (triangle up)).

### 3. 5 Influence of relative humidity

In aqueous solution, water molecule takes part in the radical chain reaction as follows:



That is, water molecule enhances the consumption of  $\text{O}_3$ . But, for gaseous  $\text{O}_3$  decomposition, the experimental result (Figure 9) shows that water molecule decreases the  $\text{O}_3$  decomposition percentage for each photocatalyst because higher humidity evokes low decomposition percentage. It has been reported that during  $\text{O}_3$  decomposition over  $\text{TiO}_2$ ,  $\text{O}_3^-$  and  $\text{O}_4^-$  were detected as intermediates (Gonzalez-Elipse *et al.*, 1981). Hoffmann *et al.* (1995) and Ohtani *et al.* (1992) reported that the following reaction sequence may occur on the surface of  $\text{TiO}_2$ :



Equations (11)~(16) depict the decomposition reactions for  $\text{O}_3$ , and Equations (17)~(21) depict the processes in which water molecule scavenges  $\text{e}^-$  (exited electron) and  $\text{h}^+$  (positive hole). It is obvious that water molecule competes with  $\text{O}_3$  for scavenging exited electron and positive hole on the surface of  $\text{TiO}_2$ . So the humidity decreases the  $\text{O}_3$  removal ratio. This is proved by our experimental results shown in Figure 9.

## 4. CONCLUSIONS

In this study, the characteristics of heterogeneous photocatalytic decomposition of low concentration level of  $\text{O}_3$  over  $\text{TiO}_2$  were investigated for various operating parameters. The conclusions from the present work can be summarized as follows:

1. Under fixed light intensity, flow rate, initial  $\text{O}_3$  concentration, and  $\text{TiO}_2$  loaded amount in the range from  $0.5 \text{ mg/cm}^2$  to  $4 \text{ mg/cm}^2$  gained almost the same  $\text{O}_3$  removal ratio and the ratio became constant for more amount of catalysts in this reactor.
2. For the influence of initial  $\text{O}_3$  concentration to the photocatalytic decomposition of gaseous  $\text{O}_3$ , higher

initial O<sub>3</sub> concentration resulted in greater oxidation rate of O<sub>3</sub>, and the experimental data was kinetically in good agreement with Langmuir–Hinshelwood kinetic model.

3. The decomposition of O<sub>3</sub> decreased with the increasing flow rate. This is expected because a better gas–solid contact can be obtained with lower flow rate.

4. It was observed that water molecule competes with O<sub>3</sub> for scavenging exited electron and positive hole on the surface of TiO<sub>2</sub> catalyst. Therefore, the O<sub>3</sub> removal ratio was decreased with increasing relative humidity.

According to our results, photocatalytic decomposition of gaseous O<sub>3</sub> over TiO<sub>2</sub> thin film has the high potential to be used for purification of vent gases from industrial process and indoor/outdoor air.

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