

# Solid Phase Photocatalytic Reaction on the Soot/TiO<sub>2</sub> Interface: The Role of Migrating OH Radicals

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The photocatalytic degradation of flame-deposited hexane soot on TiO<sub>2</sub> films was carried out under UV illumination ( $\lambda > 300$  nm) in air in order to investigate the behavior of photooxidants at the solid/solid (soot/TiO<sub>2</sub>) interface. The photodegradation of the immobile soot layer on TiO<sub>2</sub> film was monitored by performing soot weight loss measurement, scanning electron microscopic (SEM) analysis, and gas-chromatographic CO<sub>2</sub> production measurement. The bulk of soot layer with  $\sim 2$   $\mu\text{m}$  thickness was completely oxidized to CO<sub>2</sub> over 30 h irradiation. The presence of O<sub>2</sub> was essential in the photocatalytic soot oxidation. The SEM images of the irradiated soot films revealed that the gap distance between the edges of soot on glass and TiO<sub>2</sub> domains continuously increased with UV illumination up to 80  $\mu\text{m}$ , implying that the active oxidants generated on the TiO<sub>2</sub> surface migrated across the gap into a remote soot domain to initiate the photocatalytic oxidation. The apparent activation energy for the photocatalytic soot oxidation was estimated to be 18.7 kJ/mol, which is largely ascribed to the diffusional activation of active oxidants because the reactant (soot) is immobile. Introducing water or 2-propanol vapor efficiently enhanced or reduced the photooxidation rate of soot since water or 2-propanol was the precursor or the scavenger of the main oxidant species, OH radical, respectively. The migrating nature of photooxidants (including OH radicals) should be taken into account in quantitative understanding of photocatalytic reaction mechanisms in all media (gas, liquid, and solid phases) in general.

## Introduction

TiO<sub>2</sub> photocatalysis has been extensively studied for its application to environmental remediation processes.<sup>1–4</sup> Most of the remediation power of TiO<sub>2</sub> photocatalysts is mainly attributed to the strong oxidation potential of the OH radicals that are generated on the UV-illuminated TiO<sub>2</sub> surface. The valence band (VB) holes react with surface hydroxyl groups or water molecules to produce OH radicals, which are usually considered to remain bound to the surface and react with the substrate molecule diffusing onto the surface. However, the possibility that the OH radicals desorb from the surface and diffuse into the bulk medium has been often raised.<sup>5</sup>

Recently, a few examples of diffusing OH radicals on illuminated TiO<sub>2</sub> have been reported from different studies. Tatsuma et al.<sup>6,7</sup> observed a remote oxidation of organic dye or film that was separated from a TiO<sub>2</sub>-coated glass plate by a small gap, which was ascribed to the action of active oxygen species (most likely OH radicals) that were generated on the TiO<sub>2</sub> surface and transported through the gas phase. They claimed that OH radicals traveled a distance up to 2.2 mm in air to react with remote substrates. Cho and Choi<sup>8</sup> reported that the photodegradation of TiO<sub>2</sub>-blended PVC film developed cavities around the imbedded TiO<sub>2</sub> particles where the cavity boundary was well separated by 1–2  $\mu\text{m}$  from the particle boundary, which was also attributed to diffusing OH radicals. Haick and Paz<sup>9</sup> observed a remote photodegradation of self-assembled monolayers of aliphatic chains anchored to an inert silicon surface whereas the chains were located as far as 20

$\mu\text{m}$  away from the TiO<sub>2</sub> microdomains. This also demonstrated the diffusing action of oxidizing species on the TiO<sub>2</sub> surface. On the other hand, the presence of diffusing OH radicals in an aqueous suspension of TiO<sub>2</sub> was recently suggested from a study of photocatalytic degradation of tetramethylammonium ions.<sup>10</sup>

Unlike the photocatalytic reactions at the solid/liquid and solid/gas interface where the reactants diffuse onto the illuminated surface site, the photocatalytic reaction at the solid/solid interface is unique in that the reactants are immobile. Therefore, the solid-phase photocatalytic reactions should be mostly mediated by diffusing oxidants species.<sup>8</sup> Little is known about the mechanisms and the role of diffusing OH radicals in solid-phase photocatalytic reactions. In this study, we investigated the solid-phase photocatalytic degradation reaction of black carbon soot deposited on TiO<sub>2</sub> film and demonstrated that the OH radicals generated on the TiO<sub>2</sub> surface migrated beyond 80  $\mu\text{m}$  to mediate the solid-phase photocatalytic oxidation of carbon soot. Mechanistic details and the role of migrating OH radicals in the solid-phase photocatalytic reaction are discussed in detail.

## Experimental Section

**Materials and Sample Preparation.** The photocatalyst used was Degussa P-25 TiO<sub>2</sub> with a crystalline structure of primarily anatase (80% anatase, 20% rutile), a B.E.T. surface area of  $\sim 50$  m<sup>2</sup>/g, and an average particle diameter of about 30 nm. The TiO<sub>2</sub> film was deposited on glass plates (area 0.55 or 3.24 cm<sup>2</sup>) using a dip-coating technique. A well-dispersed suspension (5 wt %) of TiO<sub>2</sub> was prepared in distilled water and stirred for 2 h. A substrate glass plate was coated with TiO<sub>2</sub> by dipping it in

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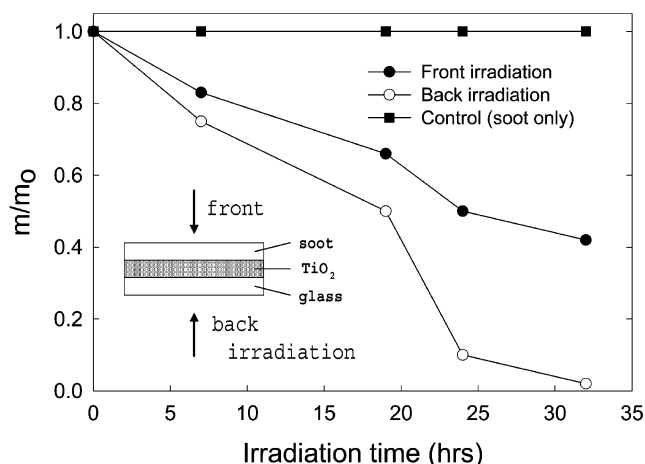
the TiO<sub>2</sub> suspension, dried under air, and then heated at 400 °C for 30 min. The dip-coating procedure was repeated several times until the thickness of the TiO<sub>2</sub> film was approximately  $\sim 1\ \mu\text{m}$ . One side of the TiO<sub>2</sub>-coated glass plate was cautiously wiped out. Black carbon soot film ( $\sim 2\ \mu\text{m}$  thickness) was directly flame-deposited on the TiO<sub>2</sub>-coated glass plate by burning *n*-hexane. The apparent UV absorption coefficient ( $\epsilon_\lambda$ ) of the hexane-soot film was estimated by measuring the absorbance (or transmittance) of a soot-coated glass plate as a function of the thickness of the soot film. The  $\epsilon_\lambda$  value of soot was determined to be approximately  $2 \times 10^4\ \text{cm}^{-1}$  at 350 nm.

**Photolysis and Analysis of Soot.** The soot photolysis experiments were carried out under ambient air. When we needed to monitor the CO<sub>2</sub> generation from the photodegrading soot on TiO<sub>2</sub>, a closed circulation reactor was used. It consisted of a Teflon reactor (volume 21 cm<sup>3</sup>) with a quartz window (area 7 cm<sup>2</sup>) and a magnetically driven circulation pump (Takatsuki Co., SPP-3EBS) connected to the reactor. The air circulation rate was about 200 cm<sup>3</sup> min<sup>-1</sup>. Light illumination was carried out using a 200-W mercury lamp. The soot-deposited TiO<sub>2</sub> film/glass was irradiated through a Pyrex glass cover to transmit light with  $\lambda > 300\ \text{nm}$  only. The light was incident on either the soot-coated side (front irradiation) or the uncoated glass side (back irradiation). The distance between the sample and the lamp was 22 cm. The light flux onto the sample surface was measured to be 1.5 mW/cm<sup>2</sup> ( $300\ \text{nm} < \lambda < 400\ \text{nm}$ ) using a power meter (Newport 1815-C with a 818-UV silicon diode detector). All the photolysis experiments were performed under air in a lamp-housing box (35 cm  $\times$  30 cm  $\times$  35 cm) where the temperature was maintained at 43–45 °C during irradiation. When the effect of oxygen was investigated, the photolysis was carried out under pure oxygen or helium atmospheres. A set of duplicate or triplicate samples was tested under each experimental condition. For the control experiment, the soot layer deposited directly on a glass plate without TiO<sub>2</sub> coating was irradiated to compare its direct photodegradation with the photocatalytic degradation of soot on TiO<sub>2</sub>. The loss of soot mass due to photodegradation was monitored by weighing the soot-coated glass plate before and after UV irradiation.

The CO<sub>2</sub> generated in the UV-illuminated reactor was quantified using an on-line connected gas chromatograph (GC Hewlett-Packard 6890) that was equipped with a flame ionization detector (FID), a Porapak column, a CO<sub>2</sub> methanizer (HP G2747A), and a gas sampling valve. Images of the soot layer on TiO<sub>2</sub> film were obtained before and at regular time intervals during UV illumination by using SEM (Hitach, S-2460N). The cross-section of the soot/TiO<sub>2</sub> film was imaged to measure the soot thickness. The samples were coated in gold using a sputter coater before SEM analysis. Raman spectroscopic analysis (using a Renishaw system 3000 with an excitation wavelength of 632.8 nm) of the flame-deposited black carbon soot showed the presence of graphitic carbons.

## Results and Discussion

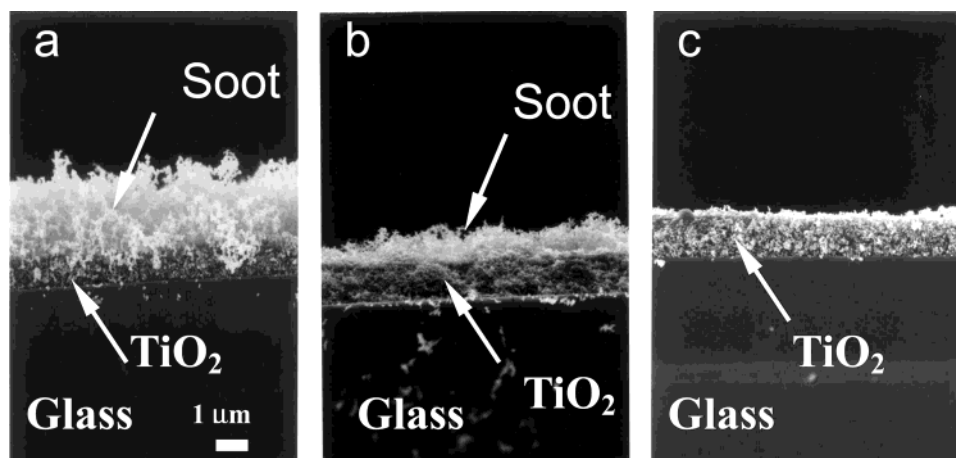
**Photocatalytic Degradation of Soot on TiO<sub>2</sub>.** Figure 1 compares the time-dependent profiles of soot degradation between the front and back irradiation modes under air. Direct photolytic degradation of soot without TiO<sub>2</sub> was not observed at all. The soot degraded slower under the front irradiation than the back irradiation. This is due to the fact that the soot layer blocked some fraction of incident UV in the front irradiation mode with fewer photons reaching the underlying TiO<sub>2</sub> surface. On the other hand, the back irradiation provided unattenuated light intensity onto the TiO<sub>2</sub> film and generated more oxidants



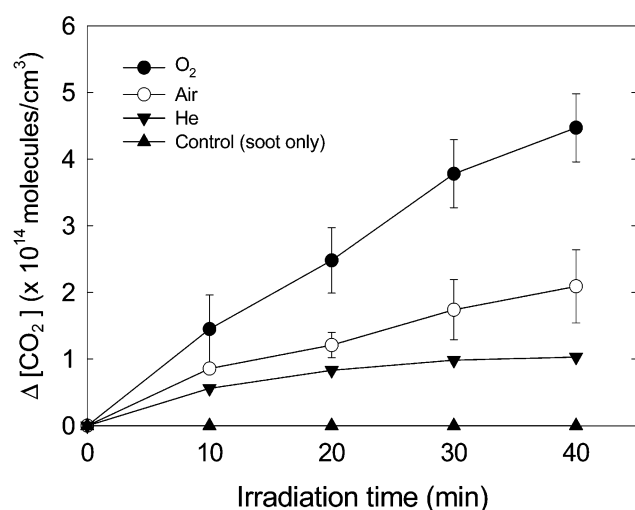
**Figure 1.** Decrease of soot mass on TiO<sub>2</sub> film as a function of UV irradiation time. Two different modes of illumination (front vs back) are compared for their degradation efficiencies. The initial soot thickness was  $\sim 2.2\ \mu\text{m}$ .

that initiated soot degradation. After more than 30 h of back irradiation, the soot layer was completely oxidized, with the black color of the soot-coated TiO<sub>2</sub> film turning into white. The cross-sectional SEM images of the soot layer on TiO<sub>2</sub> film (Figure 2) exhibit the progressive degradation of soot as the irradiation time increases. The image shows that the soot layer of  $\sim 2\ \mu\text{m}$  thickness completely disappeared after 32 h irradiation, which corresponds to a soot oxidation rate of  $\sim 65\ \text{nm/h}$ . The hexane soot layer shows very porous structure and has been reported to have a B.E.T. surface area of 46 m<sup>2</sup>/g,<sup>11</sup> which is very similar to that of P25 TiO<sub>2</sub> used in this study. An ellipsometric study by Remillard et al.<sup>12</sup> reported that solid stearic acid films (one or two layers with  $\sim 30\ \text{\AA}$  thickness) on TiO<sub>2</sub> degraded with a removal rate of  $\sim 22\ \text{nm/h}$  under UV illumination in air. Considering that the stearic acid films should be much denser than the porous soot film, the photocatalytic removal rates of the two different films are quite comparable even though their thickness differs by a factor of 1000. Although the oxidants should be produced on the surface of the TiO<sub>2</sub> film, a strict two-dimensional surface reaction at the soot/TiO<sub>2</sub> interface cannot account for the complete degradation of the soot bulk layer. This implies that the active oxidants generated on the TiO<sub>2</sub> surface desorbed and migrated into the bulk of the soot layer. We believe that the migrating photooxidants played a similar role in the photocatalytic degradation of stearic acid layers on TiO<sub>2</sub> films.<sup>12</sup>

The oxidation of soot produced CO<sub>2</sub> as shown in Figure 3. The rates of CO<sub>2</sub> production (or the soot oxidation rates) were much higher under oxygen than air or helium, indicating that the presence of O<sub>2</sub> was essential for the soot oxidation. Under the helium atmosphere, the CO<sub>2</sub> generation proceeded until the steady state was reached at about 30 min, which implied that the trace oxygen that was adsorbed or trapped in the pore of soot layer was depleted and further oxidation was inhibited. In accordance with the mass monitoring experiment of Figure 1, the soot layer directly deposited on the glass plate without TiO<sub>2</sub> did not emit any CO<sub>2</sub> at all under air and UV irradiation. The CO<sub>2</sub> production rates (Figure 3) decelerated gradually over time, which seemed to be ascribed to depleting water vapor (or adsorbed water) concentration in a close circulation reactor. The presence of water vapor was essential for the efficient photo-oxidation of soot (vide infra: Figure 8). In Figure 4, the rates of CO<sub>2</sub> production from three soot samples having different thickness are compared between the front and back irradiation



**Figure 2.** Cross-sectional SEM images of soot-coated  $\text{TiO}_2$  films on a glass plate. The UV light was illuminated from the backside. (a) Before illumination; (b) 18 h illuminated; (c) 32 h illuminated.

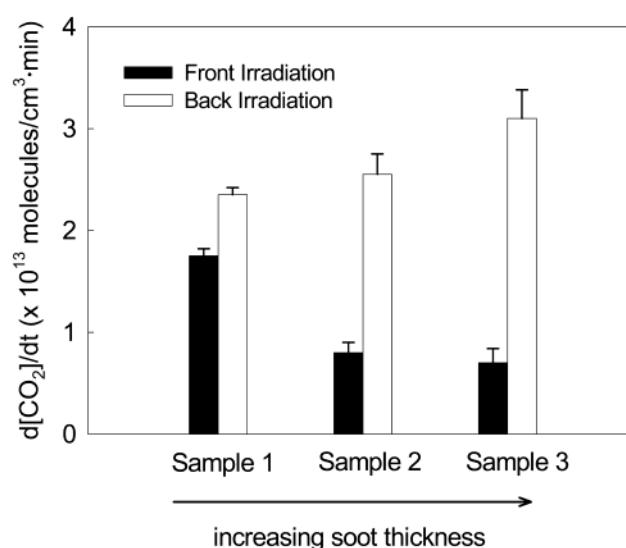


**Figure 3.**  $\text{CO}_2$  evolution from the photocatalytic degradation of soot as a function of the illumination time (front irradiation mode). The photocatalytic  $\text{CO}_2$  generation rates under air, oxygen, and helium atmospheres are compared. The soot area was  $0.55 \text{ cm}^2$ , and its thickness was  $\sim 2.4 \mu\text{m}$ .

modes. Front irradiation produced less  $\text{CO}_2$  than the back irradiation, which is consistent with the weight loss data of Figure 1. It should be noted that the  $\text{CO}_2$  production rates exhibited opposite dependences on the soot thickness between the two different irradiation modes. Under the front irradiation, a thicker soot layer blocked more UV light with a reduced rate of  $\text{CO}_2$  production. However, the fact that the back irradiation generated more  $\text{CO}_2$  with thicker soot coating cannot be explained provided that the soot oxidation occurred only at the soot/ $\text{TiO}_2$  interface. The amount of soot in direct contact with the  $\text{TiO}_2$  surface should be independent of the soot thickness. This can be accounted for only by assuming that the soot oxidation proceeded both at the soot/ $\text{TiO}_2$  interface and in the bulk of soot layer. Photooxidants generated on the  $\text{TiO}_2$  film surface should diffuse into the porous soot layer where more  $\text{CO}_2$  was produced in a thicker soot layer. Since  $d[\text{CO}_2]/dt$  continuously increased with increasing soot thickness up to  $\sim 4 \mu\text{m}$  under the back irradiation, the oxidants (most likely OH radicals) should migrate beyond this thickness.

#### Evidence for Migration of OH Radicals and Their Role.

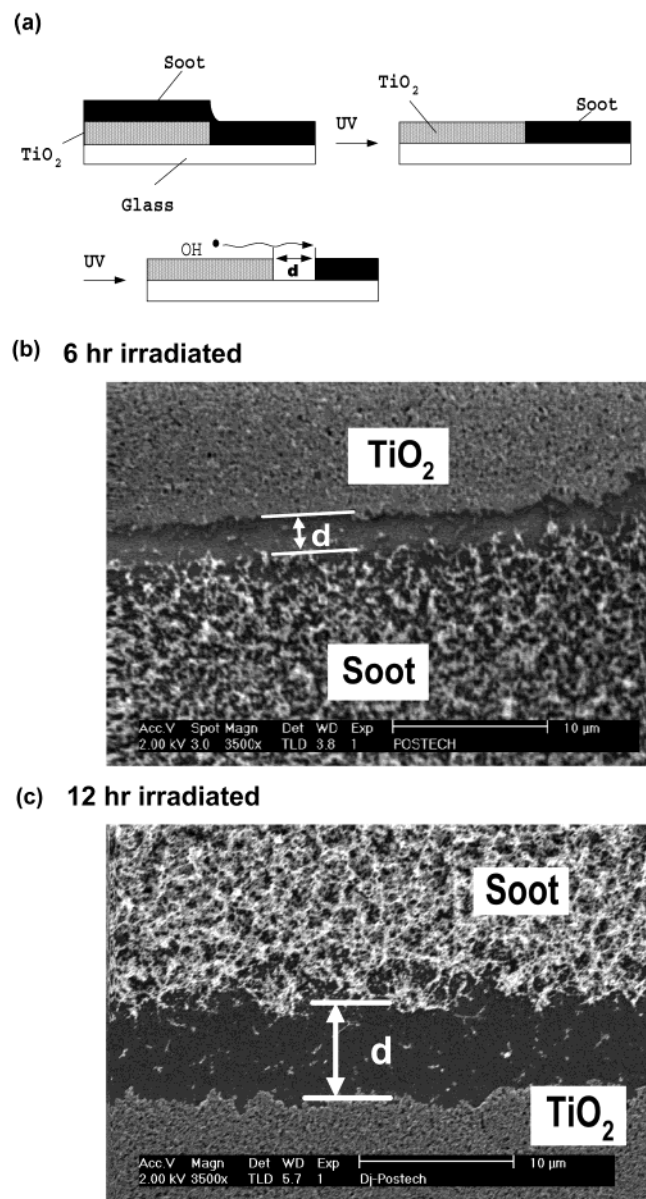
To assess how far the oxidants migrate away from the  $\text{TiO}_2$  surface, the photocatalytic degradation of a soot layer near the edge of  $\text{TiO}_2$  film was monitored by taking a series of SEM



**Figure 4.** Comparison of the initial photocatalytic soot oxidation (or  $\text{CO}_2$  generation) rates with the front or back illumination mode. The samples 1, 2, and 3 (in this order) have a successively thicker coating of soot ( $1.7$ ,  $2.3$ , and  $3.9 \mu\text{m}$ , respectively) on the same  $\text{TiO}_2$ -coated glass plate. The soot area was  $0.55 \text{ cm}^2$ .

images. Figure 5a illustrates the process of a gap ( $d$ ) development by migrating oxidants (e.g., OH radicals) between the edges of  $\text{TiO}_2$  and soot domains on a glass plate. The SEM images in Figure 5b,c show that the photodegradation of the soot layer on an inert glass surface started from the  $\text{TiO}_2$ /soot interface and continued to penetrate into the soot/glass domain with increasing gap distance,  $d$ . As shown in Figure 6, the gap distance between the edges of soot and  $\text{TiO}_2$  domains continuously increased with UV irradiation beyond  $80 \mu\text{m}$ . This result clearly verifies that the active oxidant species formed on the irradiated  $\text{TiO}_2$  surface desorbed and migrated across the glass surface to reach the soot domain. The rate of the gap distance development seemed to gradually decelerate with time, which indicated that the number of photooxidants that reached the soot domain through migration decreased with increasing  $d$ . Our observation is quite similar to that reported by Haick and Paz,<sup>9</sup> who could photodegrade octadecyltrichlorosilane chains on a silicon surface in the presence of adjacent  $\text{TiO}_2$  microdomains. Both observations confirm that the surface diffusion of active oxidants on  $\text{TiO}_2$  is an efficient mechanism through which photocatalytic reactions proceed. It should also be considered that the diffusion of active oxidants through the air<sup>6,7</sup> could play

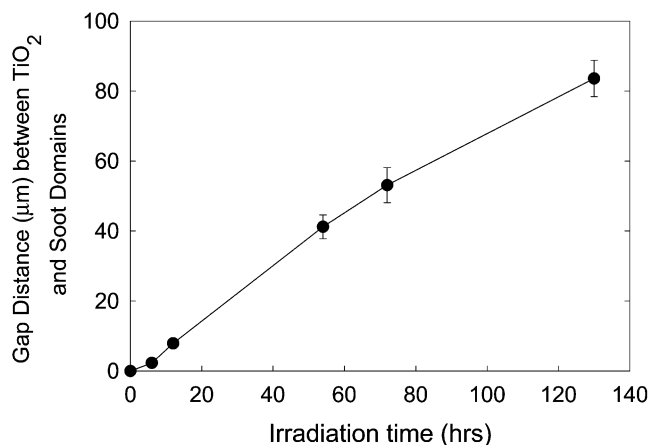




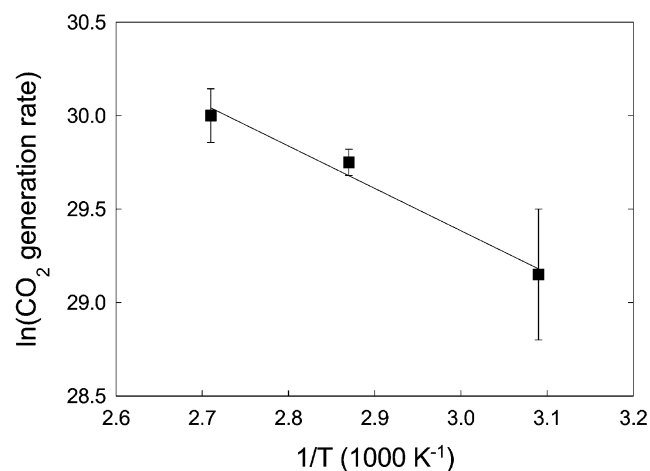
**Figure 5.** Remote photocatalytic degradation of soot near the edge of the  $\text{TiO}_2$  domain. (a) Schematic illustration of the photocatalytic degradation of the soot layer near the borderline of the soot and  $\text{TiO}_2$  domains where a gap distance  $d$  develops between the edges of  $\text{TiO}_2$  and the soot domain with illumination time. The SEM images show the developing gap at (b) 6 h and (c) 12 h irradiation. The initial soot thickness was  $\sim 0.7 \mu\text{m}$ , and the irradiation was from the front side.

a role in the oxidation of the soot layer. Although the through-air diffusion mechanism was shown to be far less contributing than the surface diffusion mechanism in the remote degradation of the aliphatic chain monolayer,<sup>9</sup> the degradation of the soot layer above the  $\text{TiO}_2$  film should be mediated by the diffusing oxidants into the pores of bulk soot layer. The through-air diffusion within the soot layer thickness (less than a few micrometers) could be an efficient mechanism as well.

The temperature effect on the soot photooxidation rate was investigated by measuring  $d[\text{CO}_2]/dt$  at the reactor temperature of 323, 348, and 368 K. By plotting the logarithm of the  $\text{CO}_2$  generation rate versus the reciprocal temperature (Figure 7), an apparent Arrhenius activation energy ( $E_a$ ) for the soot photooxidation was calculated to be 18.7 kJ/mol (or 0.19 eV). This value is comparable with typical activation energies of photocatalytic oxidation of organic molecules: 10 kJ/mol for phenol



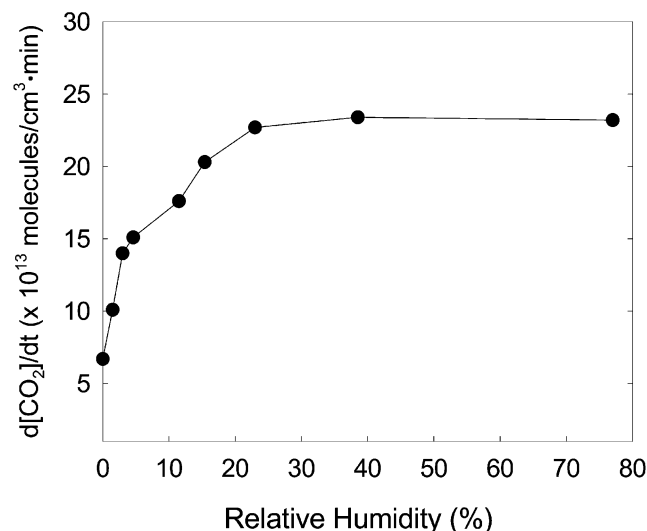
**Figure 6.** Increase of the gap distance  $d$  (see Figure 5a) as a function of UV irradiation time.



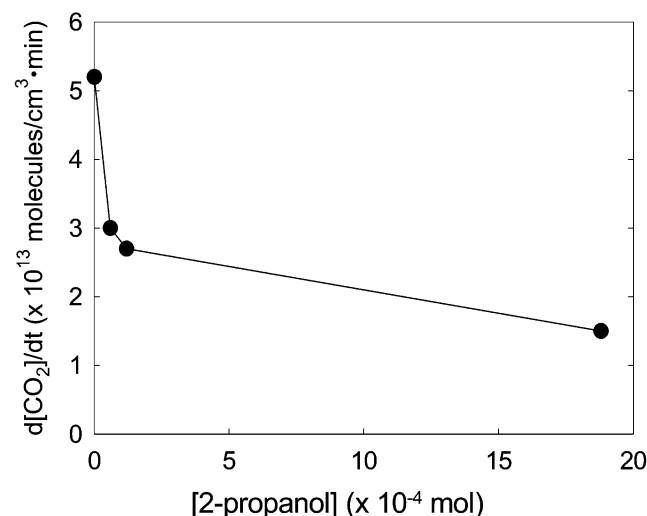
**Figure 7.** Arrhenius plot for the photocatalytic  $\text{CO}_2$  production from the degradation of soot on  $\text{TiO}_2$ . The soot area was  $0.55 \text{ cm}^2$ , and the irradiation was from the front side.

in water,<sup>13</sup> and 14.1 kJ/mol for ethylene in air.<sup>14</sup> Although the apparent activation energy in typical photocatalytic reactions is often ascribed to the adsorption/desorption process of reactants and products on the photocatalyst surface,<sup>15</sup> it is most probably due to the diffusion process of active oxidants in the present case. The immobile reactant (soot) and the easily desorbing product ( $\text{CO}_2$ ) should have negligible contribution to the apparent activation energy. A similar  $E_a$  value of 0.24 eV for the photocatalytic degradation of the aliphatic chain monolayer immobilized on  $\text{TiO}_2$  film has also been reported.<sup>9</sup>

Since the migrating active oxidants at the soot/ $\text{TiO}_2$  interface are most likely to be OH radicals as in other photocatalytic remediation systems,<sup>1-4</sup> the effect of water vapor, which is a precursor of hydroxyl radical, on the soot oxidation rate was investigated and is shown in Figure 8. The initial addition of water vapor rapidly increased the  $\text{CO}_2$  production rate, and the water content above 20% relative humidity was saturated with respect to the soot oxidation rate, which was a typical water-concentration dependence found among gas-phase photocatalytic oxidation reactions.<sup>16</sup> The reactivity of OH radicals can be quenched with the addition of hydroxyl radical scavengers.<sup>4d,10</sup> Since 2-propanol is an efficient OH radical scavenger,<sup>17</sup> the rates of soot photooxidation were rapidly reduced with the addition of 2-propanol vapor as shown in Figure 9. On the basis of the above results, we conclude that the migrating active photooxidants in the photocatalytic soot oxidation reaction are primarily OH radicals.



**Figure 8.** Effect of humidity on the photocatalytic oxidation rate of soot in the front irradiation mode. The soot area was 3.24 cm<sup>2</sup>.



**Figure 9.** Inhibition of the photocatalytic oxidation of soot with the addition of 2-propanol vapor. The relative humidity was 0%, and the irradiation was in the front mode. The soot area was 3.24 cm<sup>2</sup>.

## Conclusions

This study demonstrated that the photocatalytic degradation of soot at the solid/solid interface was mediated by migrating OH radicals. The active photooxidants were generated on the

TiO<sub>2</sub> surface and migrated across a gap of inert glass surface into a soot domain to initiate remote photocatalytic oxidation. The OH radicals were found to diffuse away as far as 80 μm from the TiO<sub>2</sub> domain. The photocatalytic oxidation of soot on TiO<sub>2</sub> led to the complete degradation of a soot layer with CO<sub>2</sub> production. Both surface diffusion and through-air diffusion should be operative in order to accomplish the photooxidation of the bulk of soot layer with a few micrometers thickness. Since the degradation of the immobile soot layer should be carried out by mobile oxidants, migrating OH radicals seem to be the dominant mechanism in solid-phase photocatalytic degradation reactions. This finding confirms the recent observations<sup>6–10</sup> of the migrating behavior of active photooxidants generated on TiO<sub>2</sub> and proposes that the diffusing nature of photooxidants should be taken into account in a quantitative understanding of photocatalytic reaction mechanisms in all media (gas, liquid, and solid).

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