Photocatalytic soot oxidation on TiO$_2$ microstructured substrate

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Highlights

- Photocatalytic soot oxidation using TiO$_2$ microstructured substrates was proposed.
- Photon absorption in TiO$_2$ substrate to generate electron-hole pairs was analyzed.
- Soot oxidation rate on plain TiO$_2$ substrates increased with substrate thickness.
- Micropillar substrate showed enhanced soot oxidation rate.
- Multiscale phenomena presented here can be optimized for further improvement.

Abstract

Photocatalytic soot oxidation was investigated using TiO$_2$ microstructured substrates. Plain and micropillar substrates of sintered TiO$_2$ nanoparticles were prepared using a soft lithography process. Photon absorption analysis revealed substantial photon transmission for plain substrate within the current substrate thickness range (<2.5 $\mu$m). The porous structure of substrate was confirmed by electron microscopy and by dimensional changes due to sintering, allowing gaseous species and radicals to diffuse across micrometer-thick substrates. It was found that the soot oxidation rate increased with the thickness of the plain TiO$_2$ substrate; this was related to the increase in electron-hole pair generation associated with increased photon absorption. The soot oxidation rate increased further with the use of TiO$_2$ micropillars, enhancing photon absorption through multiple scattering. These multiscale phenomena in the photocatalytic soot oxidation on TiO$_2$ microstructured substrates were analyzed.

1. Introduction

Soot is a fine solid particulate matter of carbon generated in various incomplete combustion processes of hydrocarbons and is considered an environmental pollutant when emitted into the atmosphere [1]. It is oxidized to carbon dioxide at high temperature often with the help of an oxidation catalyst (e.g., platinum), which indicates that soot removal is an energy-consuming process [2]. Techniques based on renewable energy and using inexpensive materials are desirable for oxidizing soot. Photocatalysis using TiO$_2$ offers a potential pathway with the direct use of sunlight in this endeavor [3].

Photocatalytic soot oxidation has been studied using TiO$_2$ photocatalyst [4–7]. Lee et al. reported that the radicals generated by TiO$_2$ migrated tens of micrometers to oxidize soot [4], which was also confirmed later by another group [5]. Using infrared spectroscopy, Mills et al. revealed that photocatalytic soot oxidation exclusively yielded carbon dioxide as the product [6]. Smits et al.
studied self-cleaning building materials and examined soot oxidation on mortar coated with TiO$_2$ [7]. These previous studies examined some fundamental aspects of soot oxidation using plain TiO$_2$ films with thicknesses of approximately 1 µm [4] and 0.9 µm [6]; however, there appears to be no report on the attempt to improve the efficiency of photocatalytic soot oxidation from the viewpoint of photocatalyst substrate structure.

The efficiency of photocatalytic soot oxidation depends on several factors. Soot is a strong absorber of ultraviolet (UV) rays, so the amount of photons generating electron-hole pairs is reduced when soot covers the TiO$_2$ substrate [4,8]. The recombination of the generated electron-hole pairs occurs while the carriers diffuse in TiO$_2$. The diffusion length of the carriers, or the characteristic length of carrier diffusion $l_c$, for anatase TiO$_2$ is found to be only about 3 nm [9]. In contrast, the characteristic length of radical diffusion $l_r$ is tens of micrometers [4]. Considering the large gap between the characteristic lengths ($l_c \ll l_r$), one possible strategy to minimize the carrier loss is to use TiO$_2$ nanoparticles for allowing the carriers to diffuse only a few nanometers to the solid–gas interface and letting the produced radicals diffuse across the micrometer-thick substrate. The characteristic length of photon penetration in a TiO$_2$ substrate is also important when optimizing the thickness of TiO$_2$ substrate.

In the present study, we investigate the effect of TiO$_2$ substrate microstructure on photocatalytic soot oxidation. First, we analyze photon absorption in a TiO$_2$ substrate. Subsequently, we show the fabricated TiO$_2$ substrates of sintered nanoparticles and the dependence of soot oxidation rate on the TiO$_2$ substrate microstructure. The underlying mechanism is presented to interpret the experimental results.

2. Experimental

2.1. Fabrication of TiO$_2$ structured substrates

We fabricated two types of TiO$_2$ microstructured substrates: plain and micropillar substrates of sintered nanoparticles. The micropillar substrate comprised a periodic array of cylindrical pillars. Micrometer-scale surface structure was controlled via a soft lithography process wherein TiO$_2$ nanoparticles were assembled using a polydimethylsiloxane (PDMS) stamp. The outline of soft lithography processes is schematically shown in Fig. 1. A flat glass plate and a patterned photoresist master were prepared as a master for the plain and micropillar TiO$_2$ substrates, respectively. A room-temperature-vulcanizing silicone rubber, ELASTOSIL® RT601 (Wacker Asahikasei Silicon, Japan), was used to prepare the PDMS stamp. A TiO$_2$ nanoparticle suspension (Sakai Chemical Industry, Japan), in which TiO$_2$ nanoparticles were dispersed in methanol, was used in the process. The concentration of TiO$_2$ particles was 15.4 wt%. The crystal phase of the TiO$_2$ nanoparticles was anatase. The mean diameter of the TiO$_2$ nanoparticles was 3.7 nm, which was measured using a dynamic light-scattering instrument and supported by transmission electron microscopy [10]. After the TiO$_2$ suspension was dropped onto a glass plate, the PDMS stamp was placed on the suspension. Drying of the suspension due to methanol evaporation and particle compaction proceeded at room temperature. Then, the PDMS stamp was released and the sintering of particles to obtain the final form of TiO$_2$ substrate was performed at 600°C for 20 min in an electric furnace. In our previous research, we confirmed that the anatase phase of the TiO$_2$ particles was maintained under this sintering condition [10].

The microscale structure of the obtained TiO$_2$ substrates was characterized prior to soot oxidation experiments. First, we analyze photon absorption in a TiO$_2$ substrate. Subsequently, we show the fabricated TiO$_2$ substrates of sintered TiO$_2$ nanoparticles and the dependence of soot oxidation rate on the TiO$_2$ substrate microstructure. The underlying mechanism is presented to interpret the experimental results.

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coated the sample with osmium using a Neoc coater (Meiwafosis, Japan). When acquiring the top view images, this coating was unnecessary and we used the bare samples. The micropillar substrates were also evaluated using these techniques.

2.2. Soot oxidation experiment

We setup a stable candle flame for sampling soot particles. Plume-loaded soot was thermophoretically deposited on a substrate above the flame. We used a near-UV (NUV) lamp, FPL27BLB (Sankyo Denki, Japan), to supply NUV rays to the TiO2 substrate. The light intensity was approximately 4 mW/cm²; this value was obtained using a UV light meter UV-340C (Custom, Japan). Soot oxidation under UV irradiation was performed at approximately 22°C and at a relative humidity of 25%. In addition, optical transmission measurements in the visible (V) range and SEM observation were performed to evaluate the amount of soot on the TiO2 substrates.

3. Results and discussion

3.1. Photon absorption analysis

We first estimate the photon absorption characteristics of the TiO2 substrate in our experimental conditions considering the UV light source and photocatalyst materials. The spectral intensity of the UV lamp I\text{in} is shown in Fig. 2(a), which is normalized by its maximum value at 366 nm. We use the complex refractive index found in the literature for anatase TiO2 (n = 3.2 eV) as a function of photon wavelength [13]. The spectral absorption coefficient κ is calculated by the extinction coefficient k as

\[ \kappa = k \frac{4\pi}{\lambda}. \]

where \( \lambda \) is the photon wavelength in a vacuum. Fig. 2(b) shows the spectral absorption coefficient of anatase TiO2. The bandgap of anatase TiO2 is 3.2 eV, which corresponds to the wavelength of 388 nm, and therefore the absorption coefficient at wavelengths longer than 388 nm vanishes. The absorption coefficient increases as the wavelength becomes shorter. The present data ends at 320 nm in the short wavelength range; nevertheless, we can continue the analysis because the incident intensity of the UV lamp is negligible at wavelengths shorter than 330 nm. To evaluate the total (i.e., spectrally integrated) absorption behavior, we use the Planck mean absorption coefficient \( \kappa_p \), which is expressed as follows [14]:

\[ \kappa_p = \frac{\int_0^\infty I_k \kappa d\lambda}{\int_0^\infty I_k d\lambda}, \]

and we obtain \( \kappa_p = 0.27 \mu m^{-1} \). The integrand of the numerator in the right-hand side of Eq. (2) is shown in Fig. 2(c) in a normalized form. The wavelength range around 358 nm dominates in terms of the amount of energy, and thus, the Planck mean value is much smaller than the spectral values at wavelengths less than about 340 nm.

Next we examine how deeply the incident photon penetrates into the TiO2 substrate. When the TiO2 substrate is assumed to have the porosity \( \varepsilon \), the variation of photon intensity in the substrate is calculated as follows:

\[ \frac{I(x)}{I(0)} = \exp[-\kappa_p(1-\varepsilon)x], \]

where x is the penetrating distance from the substrate surface, \( I(x) \) is the photon intensity at the distance x inside the TiO2 substrate, and \( I(0) \) is the photon intensity at the substrate surface (x = 0). Fig. 3 shows \( I(x)/I(0) \) as a function of x. The substrate porosity of 0.4 is assumed here because the porosity of randomly packed uniformly-sized spheres ranges from 0.38 to 0.41 [15]. The non-porous case is also plotted in Fig. 3 for comparison. We note that more than 60% of the energy remains unabsorbed for the porous case when the substrate thickness is less than 3 \mu m. As described later, the thickness of plain TiO2 substrates ranges from 0.5 to 2.5 \mu m in the present study; thus, we anticipate that a substantial amount of photon energy is not utilized to generate electron-hole pairs.

3.2. Sintering process

TiO2 substrates comprising nanoparticles are considered to have a porous structure. As mentioned above, we assume that

Fig. 2. (a) Normalized spectral intensity of the UV lamp used in the soot oxidation experiment. (b) Spectral absorption coefficient of anatase TiO2. (c) Normalized product of the UV lamp spectral intensity and TiO2 spectral absorption coefficient used in Planck mean absorption calculation.

Fig. 3. Decay of incident light in a porous anatase TiO2 substrate as a function of penetrating distance x.
the porosity of the TiO$_2$ substrate before sintering is approximately 0.4. The sintering of the TiO$_2$ particles was performed at 600°C for 20 min to maintain the anatase phase of TiO$_2$ [10]. Sintering treatment enhances particle packing; thereby reducing the porosity. Fig. 4(a) shows an SEM image of the cross section of a TiO$_2$ substrate. It can be observed from the figure that the fine-particle structure remains and submicron pores exist in the substrate. Pores at size scale that is considerably lower than that of the observed pores may exist; however, it is difficult to confirm this because of the limited resolution of SEM images. To confirm that the porous structure did not vanish, the thickness of a plain TiO$_2$ substrate was measured before and after the sintering treatment. Fig. 4(b) shows the dimensional change of plain TiO$_2$ substrates due to sintering as a function of substrate thickness. Herein, we approximated the effective refractive index ($n_e$) of the TiO$_2$ substrate to obtain the first estimation of the substrate thickness. Later, this estimation was improved by considering the change in $n_e$ due to sintering (see Supporting Information). A line with a slope of unity is drawn for reference. Experimental data are fitted by a line passing through the origin, and the slope is 0.95. The subsequent analysis indicates that the volume of TiO$_2$ substrate reduced by 11% due to sintering. Because we have assumed that the porosity of TiO$_2$ substrate before sintering is about 0.4, the porosity after sintering is estimated to be 0.33. We will use this porosity in the following discussion.

3.3. Soot oxidation on plain substrate

We collected soot particles on a prepared plain TiO$_2$ substrate to investigate the effect of the TiO$_2$ substrate microstructure on photocatalytic soot oxidation. The soot exposure and deposition on the TiO$_2$ substrate were monitored to avoid thick soot layers and uncertainties in the reaction rate evaluation (described later). To examine the soot deposition state, we conducted SEM observations. Fig. 5 shows the top view image of a soot-deposited plain TiO$_2$ substrate with low [Fig. 5(a)] and high [Fig. 5(b)] magnifications. We can observe the TiO$_2$ substrate surface through the thin soot layer in Fig. 5(a). In the following reaction experiments, we illuminated the TiO$_2$ substrate with NUV rays from the soot-deposited side (i.e., the front irradiation mode [4,8]). Under an initial thick-soot coverage of the substrate, the NUV intensity at the substrate surface would significantly change as the soot decomposes (under front irradiation). To minimize this effect, we used a coarse soot coverage. The size difference between soot and TiO$_2$ particles is confirmed in Fig. 5(b). Since the pores between TiO$_2$ particles were much smaller than the soot particles, we consider that soot particles did not penetrate into the TiO$_2$ substrate and that soot oxidation progresses on the TiO$_2$ substrate surface.

The amount of soot on a TiO$_2$ substrate was evaluated by measuring the transmission of visible light. The transmittance of the soot-loaded substrate is lower than that of a clean substrate because of light absorption by soot.
\[ T = T_{\text{clean}} \exp(-\kappa_{\text{soot}} \delta_{\text{soot}}), \]

where \( T \) is the transmittance of the soot-loaded substrate, \( T_{\text{clean}} \) is the transmittance of the substrate before depositing soot, \( \kappa_{\text{soot}} \) is the absorption coefficient of soot layer, and \( \delta_{\text{soot}} \) is the thickness of soot layer. In the case of particle dispersions, the absorption coefficient \( \kappa \) is given as \[ \kappa = N C_{\text{abs}}. \]

where \( N \) is the number density of particles and \( C_{\text{abs}} \) is the absorption cross section of a single particle. Photocatalytic soot oxidation may reduce any of \( N, C_{\text{abs}}, \) and \( \delta_{\text{soot}} \); however, these details are not required for conducting this study. We therefore introduce \( \delta_{\text{soot}} = \delta_{\text{soot}}(t) \) to express the amount of soot remaining on the TiO\(_2\) substrate surface. The amount of soot decreases with the reaction time \( t \), and therefore it is a function of time: \( \delta_{\text{soot}} = \delta_{\text{soot}}(t) \). Considering that the transmittance is also a function of time, we obtain the soot oxidation rate \( r_T \) as

\[ r_T = \frac{\delta_{\text{soot}}(0) - \delta_{\text{soot}}(t)}{t} = \frac{1}{t} \ln \frac{T(t)}{T(0)}, \]

where the subscript \( T \) is used to emphasize that the soot oxidation rate is evaluated by the optical transmittance measurement (see Supporting Information). When collecting soot from a candle flame, volatile hydrocarbons can also deposit on the TiO\(_2\) substrate. Because (a) the oxidation rate of such volatile species is generally much higher than that of the soot particles and (b) the light absorption by soot controls the reaction rate, the influence of the volatile component is considered to be negligible.

We prepared plain TiO\(_2\) substrates with different thicknesses and compared their soot oxidation rates; the results of which are summarized in Fig. 6. Furthermore, we estimated the change in the NUV intensity at the TiO\(_2\) surface based on the changes in the V transmittance caused by the soot removal (instead of using a direct measurement due to spectrometer limitations). This estimate has uncertainty, as indicated by error bars in Fig. 6. We did not observe a dependence of the oxidation rate on the reaction time, and the results for \( t = 37 \) and 72 h are plotted to show this aspect. We found that the soot oxidation rate increased with the substrate thickness. The thickness-dependent photocatalytic reactivity was also reported by Luttrell et al. \[9\] with a different mechanism. They used thin films of non-porous TiO\(_2\) \(<15 \text{ nm}\) for organic dye decomposition and observed that the activity increased with the film thickness only up to the diffusion length of the excited carriers \( \sim 3.2 \text{ nm} \) for anatase. In our case, the increasing activity was observed with the substrate thickness over a much larger range \( \sim 1 \text{ µm} \) because our TiO\(_2\) substrates had a porous structure and the produced radicals were able to migrate within them. Hence, the amount of produced carriers or absorbed photons in TiO\(_2\) substrates is important to interpret the increasing soot oxidation rate with substrate thickness. To estimate the increase in the absorbed photon amounts with TiO\(_2\) substrate thickness, the absorbed light intensity relative to the incident intensity \( I_{\text{abs}}/I_{\text{inc}} \) was calculated on the basis of Eq. (3) and plotted in Fig. 6. As expected in the above photon absorption analysis (Section 3.1), the soot oxidation rate appears to be proportional to the amount of absorbed photons in the TiO\(_2\) substrate as follows:

\[ r_T \propto I_{\text{abs}} = I_{\text{inc}} \{1 - \exp[-r_T(1 - e)\delta_{\text{soot}}]\}, \]

where \( \delta_{\text{soot}} \) is the thickness of the TiO\(_2\) substrate.

Incident photons with an energy \( (\hbar \omega_{\text{ph}}) \) larger than the TiO\(_2\) bandgap \( \Delta E_g \) are absorbed in TiO\(_2\) substrate, and electron-hole pairs are produced \[16\]. Since photons penetrate across a TiO\(_2\) substrate as discussed in Section 3.1, carriers are produced in the whole volume of the TiO\(_2\) substrate. Carrier diffusion takes place in TiO\(_2\) crystal having a characteristic length \( l_c \) of approximately 3 nm \[9\]. At the solid–gas interface, radicals are produced by the reaction of adsorbed gas molecules with carriers. These radicals migrate in the TiO\(_2\) substrate due to surface diffusion, which has a characteristic length of tens of micrometers \[4\]. Since the characteristic lengths of photon penetration \( l_{\text{ph}} \) and radical diffusion \( l_r \) are longer than the substrate thickness \( \delta_{\text{soot}} \) \( (l_r > l_{\text{ph}}) \), the soot oxidation rate monotonically increases with substrate thickness under the present experimental conditions. According to the photon absorption analysis in Section 3.1, the unabsorbed photons transmitting through the TiO\(_2\) substrate at this range of substrate thickness exist. Therefore, the soot oxidation rate has a potential to further increase by enhancing photon absorption.

### 3.4. Soot oxidation on micropillar substrate

We next examined the soot oxidation rate on a micropillar TiO\(_2\) substrate. Fig. 7 shows the perspective view of the micropillar substrate. The base TiO\(_2\) layer exists between the glass plate and the micropillars. The pillar diameter \( d \) was 2.4 µm, the pillar height \( h \) was 5.4 µm, the pitch of the pillars \( p \) was 7.6 µm, and the thickness of the base layer \( \delta_b \) was 2.3 µm. We deposited soot particles on the micropillar substrate, and the resulting surface conditions were observed using an SEM as shown in Fig. 8. While soot particles on the base layer appeared to be in a density that was similar to that for a plain substrate \[Fig. 5(a)\], three-dimensional accumulation of soot was observed at the top of each pillar. In addition,
the soot particle density on the side surface of each pillar was relatively small.

In Section 3.3, we found that the thickness of TiO₂ was critical for photon absorption, i.e., for electron-hole pair production. We use the volume of TiO₂ per unit projected area for the plain and micropillar substrate for comparison, and the volume per projected area \( V/A_p \) can be expressed as follows:

\[
V/A_p = \begin{cases} 
\delta_{\text{sub}} & \text{(flat substrate)} \\
\delta_{\text{b}} + \frac{\pi d^2 h}{4p^2} & \text{(micropillar substrate)}
\end{cases}
\]

It is obvious from the above definition that \( V/A_p \) can also be interpreted as an equivalent plane thickness of the micropillar substrate. Using the sizes of the micropillar substrate, \( V/A_p = 2.7 \text{ μm}^3/\text{μm}^2 \) in the present case.

We repeated the soot oxidation experiment on the micropillar substrate, and the mean value of the soot oxidation rate with its standard deviation is plotted against \( V/A_p \) in Fig. 9, along with the fitted curve for the plain substrate from Fig. 6. Despite the dispersion in the soot oxidation rate for the micropillar substrate, the soot oxidation rate of the micropillar substrate is nearly twice that of the plain substrate for the same \( V/A_p \). The difference in the soot oxidation rate between the plain and micropillar substrates cannot be solely explained from the volume of TiO₂. Thus, we consider that there must be another mechanism to enhance the photon absorption (i.e., electron-hole pair production) for a micropillar substrate.

If the irradiated surface is not optically smooth but rough or structured at the micrometer scale, then multiple scattering of incident light occurs. For example, the application of a scattering mechanism was reported to enhance the light absorption in an optically thin medium [17]. As mentioned in Section 3.1, a substantial amount of photon energy transmits through the plain TiO₂ substrate with the thickness less than 5 μm. Multiple scattering of the incident photons by the micropillar structure enhances the overall photon absorption.

Fig. 9 shows the soot oxidation rate estimated under ideal photon absorption condition in the TiO₂ substrate using the optical constant of TiO₂ at 358 nm, where the photon absorption is maximum [Fig. 2(c)]. The refractive index of TiO₂ is 3.27 and the effective medium approximation gives a value of 2.5 for the porous substrate, which results in the normal reflectivity \( R_n \) of 0.18 at the TiO₂ substrate surface. Assuming the Planck mean absorption coefficient \( k_P \) [Eq. (2)] and the equivalent plane thickness \( V/A_p \) as well as neglecting the multiple reflection of the TiO₂ substrate, the absorbed portion of incident light can be expressed as follows:

\[
I_{\text{abs}} = I_{\text{inc}}(1 - R_n)[1 - \exp(-k_P V/A_p)];
\]

Fig. 10. Schematic of the multiscale phenomena occurring in photocatalytic soot oxidation on a TiO₂ microstructured substrate. There are nano-, submicron-, and micron-scale interactions involving photons, charges, gaseous species, and nanoparticle-based porous microstructures.
where $I_{\text{abs}}$ is the intensity of the absorbed light and $I_{\text{inc}}$ is the intensity of the incident light. The value of $I_{\text{inc}}/I_{\text{abs}}$ is 3.34, and this multiples the soot oxidation rate of the plain substrate, giving the ideal photon absorption shown in Fig. 9. It is clear that there is large photon transmission when the TiO2 substrate is thin. By enhancing the photon absorption, we can increase the soot oxidation rate until other rate-limiting processes appear to dominate (e.g., radicals and other species diffusion).

Fig. 10 illustrates the multiscale phenomena occurring in the photocatalytic soot oxidation on the TiO2 microstructured substrate. At the nanometer scale, the incident photons $h\nu\rho_{\text{ph}}$ ($>\Delta E_g$) generate electron-hole pairs and they diffuse in TiO2 nanoparticles to produce radical species at the TiO2 surface. At the submicron scale, the radical and other species diffusion and the photon penetration occur. At the micrometer scale, the incident light is scattered by the micropillar structure and penetrates into the TiO2 substrate. As part of our future work, we can optimize the photocatalyst structure on the basis of these established multiscale phenomena.

4. Conclusions

We investigated photocatalytic soot oxidation using TiO2 microstructured permeable substrates for enhancing the oxidation rate. The photon absorption analysis indicated a non-linear increase of electron-hole generation with substrate thickness, which was subsequently demonstrated in the soot oxidation experiment using plain TiO2 substrates. The presented analysis can be used for designing a photocatalyst system with different photon sources (e.g., solar radiation). Moreover, we demonstrated that the porous TiO2 micropillar-array substrate effectively enhances the soot oxidation rate due to improved electron-hole pair generation. The present results suggested that the nanoporous structure allows radial diffusion in the photocatalyst substrate, leading to an improved use of the generated carriers. Further analysis using photocatalysts with different microstructures would facilitate a comprehensive modeling of the multiscale phenomena addressed herein. Considering the characteristic lengths of carrier diffusion, radical diffusion, and photon penetration, optimizing the microstructure of photocatalyst substrate can lead to efficient utilization of the incident photons.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.06.094.

References