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# Remote Bleaching of Methylene Blue by UV-Irradiated TiO<sub>2</sub> in the Gas Phase

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## LETTERS

### Remote Bleaching of Methylene Blue by UV-Irradiated TiO<sub>2</sub> in the Gas Phase

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The remote bleaching of a dye, methylene blue, by UV-irradiated TiO<sub>2</sub> was studied in the gas phase. A TiO<sub>2</sub>-coated glass plate was faced to a glass plate coated with methylene blue, separated by a small gap (12.5 to 500  $\mu\text{m}$ ), and the TiO<sub>2</sub> coating was irradiated with UV light from the back. As a result, methylene blue was bleached in the gas phase containing oxygen, although it was inhibited by ethanol vapor. The remote bleaching is not a simple reduction of methylene blue to its leuco form; methylene blue is probably oxygenated or decomposed. The bleaching process may be caused by active oxygen species that are generated at the TiO<sub>2</sub> surface and transported to the methylene blue layer.

#### Introduction

TiO<sub>2</sub>, as a powerful photocatalyst,<sup>1,2</sup> is now a very important material for the improvement of our quality of life. It is being applied to glass, tile, filters, and many other materials that possess self-cleaning, deodorizing, self-sterilizing, anti-fogging, and air-cleaning functions.<sup>2–4</sup> Some of these characteristics are based on the photocatalytic generation of active oxygen species, which may include hydroxyl radical (HO $\cdot$ ), superoxide anion (O<sub>2</sub> $^{\cdot-}$ ), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and singlet oxygen (<sup>1</sup>O<sub>2</sub>). It is known that some of the active oxygen species generated on TiO<sub>2</sub> surfaces in the gas phase<sup>5–7</sup> diffuse two-dimensionally at the TiO<sub>2</sub> surface<sup>7</sup> and react with organic (and inorganic) substrates adsorbed on the surface. However, to the best of our knowledge, it has not been determined whether the active oxygen species is desorbed from the TiO<sub>2</sub> surface and is transported in the gas phase. In the present work, we report the remote bleaching of a dye, methylene blue, by UV-irradiated TiO<sub>2</sub> in air and several other gas atmospheres. A TiO<sub>2</sub>-coated glass plate was faced to a glass plate coated with methylene

blue, separated by a small gap (12.5 to 500  $\mu\text{m}$ ), and the TiO<sub>2</sub> coating was irradiated with UV light from the back (Figure 1a,b). Thus observed bleaching of methylene blue may be caused by active oxygen species that are generated at the TiO<sub>2</sub> surface and transported in the gas phase. In any event, the information obtained should be important from the viewpoint of the safety of TiO<sub>2</sub>-based materials. Additionally, this information would be of significance with respect to the catalytic efficiency of TiO<sub>2</sub> in air, because not only substrates adsorbed on the TiO<sub>2</sub> surfaces but also those in the gas phase in the vicinity of the TiO<sub>2</sub> may react during UV-light irradiation.

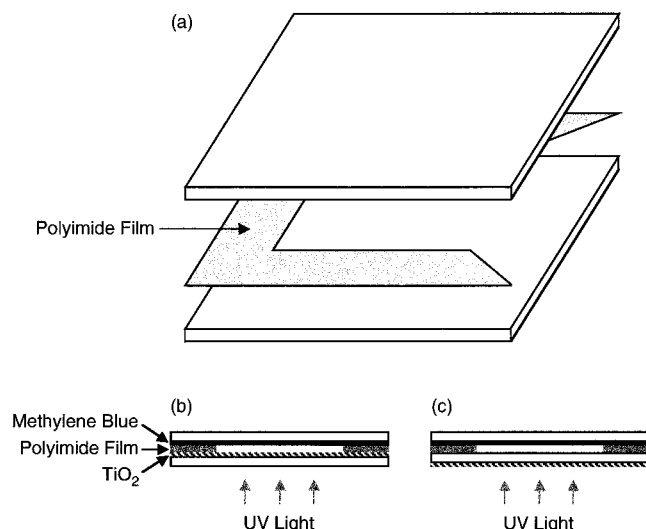
#### Experimental Section

An anatase TiO<sub>2</sub> aqueous sol STS-21 (Ishihara Sangyo, Japan) was diluted with water (80 vol %), then sonicated for 1 h, and coated on a Pyrex glass plate (5 cm  $\times$  5 cm) by spin-coating at  $\sim$ 2000 rpm for 10 s. The glass was calcined at 450  $^{\circ}\text{C}$  for 30 min to obtain a TiO<sub>2</sub>-coated glass plate. The resulting TiO<sub>2</sub> coating was irradiated with a black-light-type lamp ( $\sim$ 300–400 nm,  $\sim$ 1.8 mW/cm<sup>2</sup>) overnight before each experiment to clean the surface.

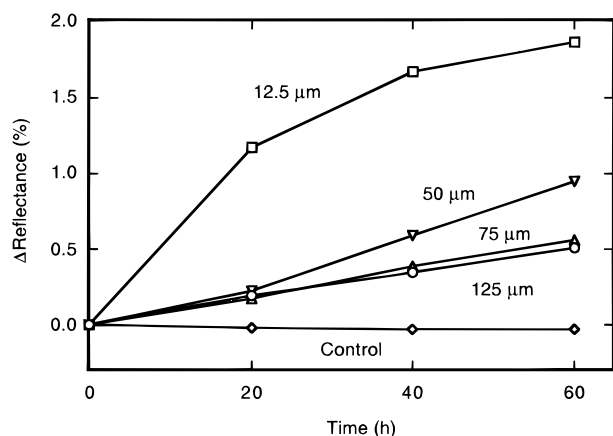
A frosted glass (5 cm  $\times$  5 cm; roughness scale observed by SEM,  $\sim$ 3  $\mu\text{m}$ ) was dipped in a 10 mM methylene blue aqueous

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**Figure 1.** Experimental setups for the remote bleaching experiment (a) and (b), and the control experiment (c).



**Figure 2.** Increases in the reflectance at 580 nm of the methylene blue coating during the remote bleaching experiment (gap between TiO<sub>2</sub> and methylene blue, 12.5 to 125 μm; UV irradiation time, 1 h).

solution for 1 h, and then rinsed with water. The methylene blue-coated glass plate thus obtained was faced to the TiO<sub>2</sub> coating with a small intervening gap (12.5 to 500 μm). The gap was controlled by use of polyimide films, as shown in Figure 1a,b. The TiO<sub>2</sub> coating was irradiated with the black-light lamp from the back. The reflectance of visible light (580 nm) at the methylene blue-coated glass plate (placed on a piece of white paper) was measured ex situ by use of a reflectance spectrophotometer, "Handy-Spec", GY-Gardner. The atmosphere during the UV-light irradiation was controlled as needed. Dry nitrogen, wet nitrogen (dry nitrogen sparged through water), dry oxygen, wet oxygen, or wet oxygen containing ethanol vapor [dry oxygen sparged through water + ethanol (1:1 by volume)] was used. A control experiment was carried out by mounting the TiO<sub>2</sub>-coated glass plate upside-down, as shown in Figure 1c.

## Results and Discussion

The reflectance of the bare frosted glass at 580 nm was decreased by ~12% by the methylene blue coating. In control experiments (Figure 1c; gap, 125 μm), no bleaching was observed during the UV-light irradiation for at least 1 h (Figure 2a). However, when the TiO<sub>2</sub> coating faced the methylene blue coating, the decrease in the reflectance was appreciable,

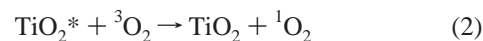
**TABLE 1: Increases in the Reflectance at 580 nm after the Remote Bleaching Experiment (distance, 50 μm; irradiation time, 1 h) in Various Atmospheres**

atmosphere	Δ reflectance (%)
nitrogen, dry	0.2
nitrogen, wet	0.3
oxygen, dry	1.4
oxygen, wet	1.4
oxygen, wet, ethanol	0.4

indicating that methylene blue was bleached. The bleaching rate was inversely dependent on the distance from the TiO<sub>2</sub> coating. These results suggest that some chemical species generated on the TiO<sub>2</sub> surface were transported to the methylene blue coating and bleached it. The bleaching was observed even when the gap was 500 μm.

Similar experiments were carried out in dry nitrogen, wet nitrogen, dry oxygen, wet oxygen, and wet oxygen containing ethanol vapor. The gap between the TiO<sub>2</sub> and methylene blue layers was 50 μm. Table 1 summarizes the results (errors are less than 0.2%). The bleaching was appreciable in the presence of oxygen. Although slight bleaching was observed in the absence of oxygen, this may be due to the difficulty in complete purging of oxygen. In contrast, ethanol inhibited the remote bleaching to a large extent.

If only oxygen is necessary for the remote bleaching, the actual chemical species involved in the bleaching may be singlet oxygen <sup>1</sup>O<sub>2</sub>. Indeed, it has recently been reported that singlet oxygen is generated from irradiated TiO<sub>2</sub>.<sup>8,9</sup>



The inhibition effect of ethanol on the remote bleaching might be explained in terms of the protic property; a protic solvent like ethanol shortens the lifetime of <sup>1</sup>O<sub>2</sub>. However, bleaching was not inhibited even in the presence of water, which is more protic than ethanol. Water and ethanol may also quench the excited TiO<sub>2</sub> by trapping holes. For example,



This overall reaction consists of the following two primary reactions:

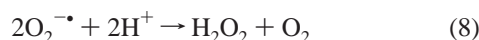


where e<sup>-</sup> and h<sup>+</sup> are electrons and holes generated at the excited TiO<sub>2</sub> surface.

Another explanation for the remote bleaching in dry oxygen is that residual water in the gas phase or adsorbed on the TiO<sub>2</sub> surface took part in reaction 3 and thus generated active oxygen species that bleached methylene blue. Electrostatically neutral active oxygen species which can be generated as a result of reaction 3 are HO<sup>•</sup>, HO<sub>2</sub><sup>•</sup>, and H<sub>2</sub>O<sub>2</sub>. HO<sub>2</sub><sup>•</sup> can be formed as a result of the protonation of O<sub>2</sub><sup>•-</sup>.



Also, H<sub>2</sub>O<sub>2</sub> can be generated from reactions involving HO<sup>•</sup> and O<sub>2</sub><sup>•-</sup>, for instance,

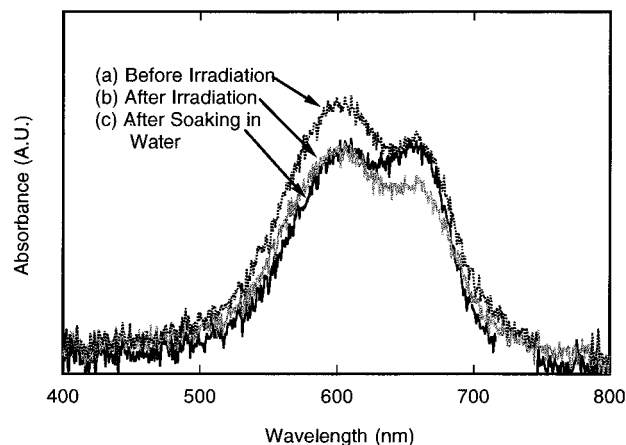


The deprotonated forms of these active oxygen species (i.e.,  $\text{O}^{\bullet -}$ ,  $\text{O}_2^{\bullet -}$ ,  $\text{HO}_2^{\bullet -}$ , and  $\text{O}_2^{2\bullet -}$ ) might also be transported as a result of electrostatic forces. In this case, the  $\text{TiO}_2$  coating would have to be negatively charged and/or the glass plate coated with methylene blue would have to be positively charged, although these possibilities may not be very plausible. Among those active oxygen species,  $\text{HO}^\bullet$  (and probably  $\text{O}^{\bullet -}$ ) are known to be scavenged by ethanol.

Additionally,  $\text{O}^+$  and  $\text{OH}^+$ , which are liberated from the surface of oxides including  $\text{TiO}_2$  by the photon-stimulated desorption (PSD),<sup>10</sup> could also be responsible for the remote bleaching, as a result of oxidation of methylene blue. However, since the photon energy in the present work is much lower than that necessary for PSD ( $\geq 18$  eV). Therefore, those species are not very likely to contribute to the remote bleaching.

There are two possible mechanisms for the bleaching of methylene blue: (1) simple reversible reduction of methylene blue to the leuco form (LMB), and (2) irreversible oxygenation or decomposition of methylene blue. If methylene blue is reversibly reduced to LMB,  $\text{HO}^\bullet$  and  $^1\text{O}_2$  should not be responsible for the remote bleaching, because these species are not known to reduce substances such as methylene blue. In view of this supposition, we examined the reversibility of the bleaching process. A bleaching experiment which is similar to that mentioned above was carried out (gap,  $12.5\ \mu\text{m}$ ; irradiation time, 2 h; ambient conditions). After the UV irradiation, the frosted glass coated with methylene blue (bleached to some extent) was left for 4 h in air in the dark, and finally the glass was soaked in air-saturated water for about 10 min and dried again. It is known that LMB generated by the reduction of methylene blue is oxidized again to methylene blue by oxygen dissolved in water.<sup>11</sup>

Figure 3 shows the changes in the visible absorbance spectrum of the methylene blue coating obtained by use of a conventional UV-visible spectrophotometer (since a frosted glass was used, quantitative analysis was difficult). As can be seen, the absorbance decreased as a result of UV irradiation. After leaving the plate in air, the absorbance peak at 630 nm recovered slightly, and much further recovery was observed after the soaking in air-saturated water. However, no appreciable change of the peak at 600 nm was observed even after the water treatment. Possible explanations for this behavior are as follows: (1) there were two different states of methylene blue—one of them is reversibly reduced to LMB, while the other is irreversibly oxygenated or decomposed during the remote bleaching; and (2) methylene blue is not reduced to LMB but



**Figure 3.** Spectra of the methylene blue coating on frosted glass before (a) and after (b) the remote bleaching experiment (gap between  $\text{TiO}_2$  and methylene blue,  $12.5\ \mu\text{m}$ ; irradiation time, 2 h). The partially bleached coating was left in air for 4 h and then immersed in air-saturated water for  $\sim 10$  min (c).

is oxygenated or decomposed to some extent, and the resulting product reacts with dissolved oxygen, causing the increase in the peak at 630 nm. Since the recovered peak at 630 nm is slightly narrower than the original peak, the former explanation may be less convincing. In either event, the reaction does not appear to be simply a process. Work is currently under way on quantitative analysis and elucidation of the bleaching mechanism.

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