

Detection of H₂O₂ Released from TiO₂ Photocatalyst to Air

Wakana KUBO and Tetsu TATSUMA

Institute of Industrial Science, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8505, Japan

H₂O₂ generated and released from TiO₂ photocatalysts to the gas phase was detected. A flow-through cell packed with TiO₂-coated glass beads was irradiated with UV light, and the gas flowing out of the cell was flushed through a collecting solution containing 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) and peroxidase. Oxidative coloration of ABTS was observed only in the absence of catalase, indicating the presence of H₂O₂ in the gas. The quantum yield of the H₂O₂ generation was estimated to be $>1 \times 10^{-7}$. The detected amount of H₂O₂ decreased as the TiO₂ thickness decreased. H₂O₂ was not detected when dry air or nitrogen was used.

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TiO₂ photocatalysts have been studied extensively for the last few decades, from elucidation of the mechanisms to applications.¹ On the basis of their strong oxidizing ability, various TiO₂-based products including self-cleaning tiles and deodorizing filters have been developed.¹ Photocatalytic reactions involve not only photo-excited holes and electrons, but also oxidatively or reductively generated active oxygen species such as ·OH, O₂⁻, and H₂O₂.^{2,3} However, their behavior has not yet been fully understood, especially in the gas phase. If some of the active oxygen species desorb from the TiO₂ surface and diffuse in the gas phase, we would be concerned with their toxicity. In view of this, we have examined the behavior of photocatalytically generated active species in the gas phase, and we have found photocatalytic remote oxidation, in which a solid surface that is not in contact with TiO₂ is oxidized and decomposed.^{4,5} We have also reported modification and patterning of solid surfaces (photocatalytic lithography) on the basis of such remote oxidation.^{6,7}

In the remote oxidation, some kinds of chemical species generated at the TiO₂ surface may be transported in the gas phase and attack the substrates. Since both aliphatic and aromatic compounds as well as diamond surfaces are oxidized in the remote oxidation, it is likely that the chemical species reacting with the substrates directly is a very strong oxidant like ·OH.⁵⁻⁷ In addition, we have verified involvement of a double excitation scheme in the remote oxidation, in which not only TiO₂ but also the substrate to be oxidized or a diffusing chemical species must be excited by UV irradiation.⁷ On the basis of these results, we proposed possible mechanisms of the remote oxidation in which photocatalytically generated H₂O₂ diffuses *via* the gas phase and is photo-decomposed into ·OH, and the generated ·OH attacks the substrate. However, H₂O₂ generated on TiO₂ has never been detected in the gas phase, while the detection in liquids has been reported.^{8,9}

Therefore, to examine the safety of TiO₂ and to elucidate the mechanism of the remote oxidation, we investigated release of H₂O₂ from TiO₂ photocatalyst to air. In the previous paper, we reported preliminary result of the detection of a peroxide in air.⁷ In the present work, the detected peroxide was identified to be H₂O₂, and effects of the TiO₂ film thickness, humidity, and O₂ were investigated.

Experimental

A flow-through cell as shown in Fig. 1 was prepared with a test tube (inside diameter, 3 cm), inlet and outlet glass tubes, a silicone plug and Teflon tubes. TiO₂-coated glass beads (diameter, 2.5 mm; TiO₂ coating thickness, 1 μm (BL2.5DX) or 0.25 μm (BL2.5A); Photo-catalytic Materials Inc., Japan) or bare glass beads were packed in the cell. Humidity-regulated gas was flowed through the cell (100 mL min⁻¹) and the cell was irradiated with light using a Hg-Xe lamp (HB-25103BY, Ushio, Japan) through a cold mirror filter, unless otherwise noted. The light intensity was 30 mW cm⁻² when the cold mirror was not attached, and the irradiated area was 3 × 5 cm². Air that flowed through the cell was flushed through a glass flit into a 2 mL collecting solution containing 0.09 mM 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt solution (C₁₈H₁₆N₄O₆S₄(NH₄)₂, ABTS) and 20 mg L⁻¹ peroxidase (POD, from horseradish, Sigma) in a glass vessel. If necessary, catalase (from bovine liver, Sigma) was added to the collecting solution. Absorption spectra were collected by using a UV-visible spectrophotometer MCPD-3000 with MC-2530 (Otsuka Electronics Co., Ltd., Japan).

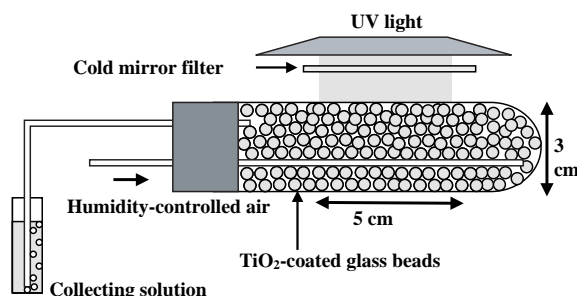


Fig. 1 Experimental setup for the detection of H₂O₂ released from TiO₂ to air. The flow-through cell was packed with TiO₂-coated glass beads, and irradiated with UV light through a cold mirror filter. Humidity-controlled air was flushed through the cell into the collecting solution containing ABTS and POD.

Table 1 Amounts of H₂O₂ detected under various conditions (relative humidity, 60%)

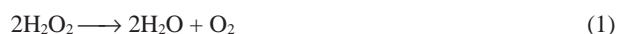
TiO ₂ thickness on glass beads/μm	Filter	Irradiation time/h	Detected H ₂ O ₂ (mean ± standard error)/mol
1.0	Cold mirror	1	(6.3 ± 1.2) × 10 ⁻¹⁰ (n = 9)
1.0	Cold mirror	2	(19 ± 8) × 10 ⁻¹⁰ (n = 5)
1.0	None	1	(8.6 ± 1.2) × 10 ⁻¹⁰ (n = 6)
0.25	Cold mirror	1	(1.3 ± 0.8) × 10 ⁻¹⁰ (n = 3)
0 (bare)	Cold mirror	1	< 1.0 × 10 ⁻¹⁰ (n = 4)
0 (bare)	Cold mirror	2	(3.0 ± 2.2) × 10 ⁻¹⁰ (n = 6)
0 (bare)	None	1	(1.9 ± 0.8) × 10 ⁻¹⁰ (n = 4)

Results and Discussion

Release of H₂O₂ from TiO₂

When the flow-through cell was packed with glass beads coated with 1 μm thick TiO₂ (BL2.5DX) and irradiated for 1 h, (6.3 ± 1.2) × 10⁻¹⁰ mol (mean ± standard error, n = 9) of a peroxide (a substrate of POD) was detected (Table 1). The detection was based on oxidative coloration of ABTS catalyzed by POD, and no coloration was observed in the absence of POD. Under dark conditions, ABTS was not colored, indicating that the amount of collected peroxide was smaller than the error of the present experiment, 1 × 10⁻¹⁰ mol. When the flow-through cell was packed with bare glass beads, peroxide was not detected. In the case of glass beads coated with thinner TiO₂ (0.25 μm, BL2.5A), a smaller amount of H₂O₂ ((1.3 ± 0.8) × 10⁻¹⁰ mol (n = 3), Table 1) was detected after irradiation for 1 h.

When catalase was added to the collecting solution prior to irradiation, no coloration was observed. It is known that catalase decomposes H₂O₂ (Eq. (1)), but does not react with organic peroxides.^{8,11}



Therefore, we concluded that the detected peroxide was not an organic peroxide but H₂O₂. H₂O₂ may be generated directly (Eq. (2)) or indirectly (Eq. (3) → (4)) by reduction of O₂, or indirectly by the oxidation of water (Eq. (5) → (6)).



Although it has been reported that H₂O₂ generated on TiO₂ reacts immediately with the TiO₂ surface,¹⁰ if the surface is saturated, H₂O₂ should be released.

Generation of H₂O₂ in the absence of TiO₂

Next, 2 h irradiation was conducted (Table 1). In the case of TiO₂-coated glass beads (BL2.5DX; TiO₂ thickness, 1 μm) (19 ± 8) × 10⁻¹⁰ mol (n = 5) of H₂O₂ was detected. The amount of released H₂O₂ might be proportional to the irradiation time. On the other hand, when bare glass beads were used, (3.0 ± 2.2) ×

10⁻¹⁰ mol (n = 6) of H₂O₂ was detected. Incidentally, ABTS was not colored by flushing the collecting solution for 2 h without irradiation. It is known that H₂O₂ could be generated by photolysis of water (Eq. (7) → (6)).¹²



The excitation wavelength is 200 nm or shorter. Although light beams of such short wavelengths were mostly cut off by the cold mirror, the photolysis might have been driven by stray UV light.

Then the experiments were conducted without the cold mirror. As a result, (1.9 ± 0.8) × 10⁻¹⁰ mol (n = 4) of H₂O₂ was detected even for bare glass beads irradiated for only 1 h (Table 1); the photolysis of water was promoted as expected. However, it was also revealed that the H₂O₂ generation from TiO₂ was not increased remarkably (Table 1). The reaction might not be limited by the number of incident photons even when the cold mirror was used.

Quantum yield and estimation of safety

In the case of the direct irradiation (without the cold mirror), the apparent quantum yield for the release of H₂O₂ from TiO₂ (= 2 × the number of H₂O₂ molecules detected/the number of incident photons) was estimated to be (1.4 ± 0.3) × 10⁻⁷ (n = 6). This is in good agreement with the value reported previously,⁷ 1.8 × 10⁻⁷, for a flow-through cell filled with TiO₂ powder. These values are two orders of magnitude lower than the quantum yield of remote oxidation, >10^{-5.5}. Since the absorption edge of H₂O₂ is around 360 nm,^{13,14} a portion of the released H₂O₂ molecules must have been decomposed by UV irradiation (Eq. (8)) before reaching the collecting solution.



Moreover, some of the H₂O₂ molecules that reached the collecting solution might not dissolve in the solution. For these reasons, it would be expected that the actual quantum yield is larger than that of the estimated one.

On the basis of the apparent quantum yield, we estimated how much H₂O₂ could be concentrated in a certain room. We assumed that all the walls, the ceiling and the floor of a room of which size was 5 × 5 × 3 m (75 m³), were fully covered with TiO₂ films (110 m²). If the films were irradiated with 360 nm UV of which the intensity was 1 mW cm⁻², the H₂O₂ generation rate was estimated to be 3.3 × 10⁻¹⁰ mol s⁻¹. Hence, the increment of H₂O₂ concentration per hour would be 5.4 × 10⁻⁴ mg h⁻¹ m⁻³ in the room if one assumes no loss of H₂O₂ by ventilation or catalytic decomposition. The threshold limit value of H₂O₂, 1.4 mg m⁻³, which has been reported by the American Conference of Governmental Industrial Hygienists (ACGIH),¹⁵ would be reached in 110 days. Thus, we can conclude that H₂O₂ released from TiO₂ to air would not be harmful to our health.

Effects of oxygen and humidity

Next, N₂ gas was employed instead of air to flush the cell. Consequently, no significant release of H₂O₂ was observed. This reflects that O₂ contributes to the photocatalysis as the electron acceptor (Eqs. (2) and (3)).

The experiments were also conducted at different humidities. When the relative humidity was 20%, only a negligible amount of H₂O₂, (0.6 ± 0.3) × 10⁻¹⁰ mol (n = 4), was detected. Besides, when dry air that contains < 40 ppm of water was employed, H₂O₂ was not detected. These results suggest that water

contributes to the photocatalysis as the electron donor for the photo-generated holes (Eqs. (5) and (9)).



Although we also examined the effects of humidity at above 80%, we could not obtain reliable data because some dewdrops were observed in the cell. H_2O_2 generated on TiO_2 might be trapped in the dewdrops and decomposed by UV light.

Detection of H_2O_2 generated and released from TiO_2 to air was reported. Both water and O_2 were necessary for the generation of H_2O_2 . The apparent quantum yield was estimated to be $(1.4 \pm 0.3) \times 10^{-7}$ ($n = 6$). Although, H_2O_2 released to air might play an important role in the photocatalytic remote oxidation, it may not be harmful to human health.

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