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Mechanisms of Photocatalytic Remote Oxidation

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Since the Honda−Fujishima effect[1] was reported, the TiO_2 photocatalyst has been applied to self-cleaning glasses, antibacterial tiles, and so on, because it has strong oxidizing power to decompose most organic compounds to CO_2.[2,3] However, the mechanisms of this photocatalysis have not yet been elucidated completely, because the photocatalysis involves direct reactions of a substrate with photoexcited electrons and holes and indirect reactions with various active oxygen species,[2,3] and it is difficult to monitor their behavior independently. Recently, we separated the indirect reactions from the direct ones by separating the photocatalyst from a substrate.[4] In the photocatalytic remote oxidation, a chemical species generated on the photocatalyst is transported in air to an organic or inorganic substrate, which it then oxidizes. This process is important not only as a partial reaction model extracted from the conventional photocatalysis. We have applied it to modification and patterning of solid surfaces as a means of photocatalytic lithography,[5] which other groups have also used.[6]

We have concluded that the species that attacks the substrates directly should be an active species as strong as $^{\bullet}OH$, on the basis of the fact that aliphatic and aromatic hydrocarbons are oxidized to CO_2 in the remote oxidation[4b] and the comparison of the remote oxidation with Fenton and H_2O_2−UV reactions,[4c] which generate $^{\bullet}OH$. We also revealed that the remote oxidation involves excitation of not only TiO_2 but also a substrate and/or a species diffusing from TiO_2 (double excitation mechanism).[5b] On the basis of these findings, we proposed a possible mechanism in which photocatalytically generated H_2O_2 is transported in air and then photocleaved into $^{\bullet}OH$ by UV light (H_2O_2−UV reaction) in the vicinity of the substrate, which the $^{\bullet}OH$ oxidizes (Figure 1). Actually, we detected H_2O_2 that diffused from TiO_2 to air.[7] Although there is another possibility that ozone is the diffusing species, photocatalytic generation of ozone on TiO_2 has never been reported,[8] to the best of our knowledge. In this study, the remote oxidation was compared with the H_2O_2−UV reaction in further detail, and it was revealed that the H_2O_2−UV reaction is essential in the remote oxidation (Figure 1).

Here we employed several different TiO_2 photocatalysts and examined the relationship between the remote oxidation ability and H_2O_2 generation ability using a photocatalyst flow cell, as shown in Figure 2A. Two glass plates (12 × 5 cm) were coated with anatase TiO_2 (A, 4 wt % sol, average particle size = 20 nm, STS-21; B, 30 wt % sol, average particle size = 7 nm, STS-01; both from Ishihara Sangyo, Japan) by a spin-coating technique and calcined at 400 °C for 1 h.[4c] The film thickness was about 1 μm. If necessary, the TiO_2 film was loaded with Pt (1.0 wt %) or Ag (0.0055 wt %) by a photocatalytic means.[4c] The two identical photocatalyst films faced each other with an intervening gap of 8 mm, and the sides were sealed with glass plates and silicone, except for inlet and outlet tubes. An octadecyltriethoxysilane (ODS)-coated glass plate was used as the probe for the remote oxidation. The ODS probe, irradiated with a Hg−Xe lamp (100 mW cm^{-2}), was sprayed with purified and humidified air that passed through the photocatalyst cell and was irradiated with another Hg−Xe lamp ($\lambda > 300$ nm, 30 mW cm^{-2}) for 15 h. The water contact angle of the ODS probe surface was measured before and after the experiment. It has been shown that oxidative removal of the alkyl group of the ODS layer results in an increase in the hydrophilicity of the ODS probe surface and a decrease in the water contact angle.[4b] Therefore, the rate of decrease of the water contact angle can be an index of the remote oxidation ability.[4b,c,5] The relative humidity (RH) of the outflowing gas was 60%. The outflowing gas from the irradiated cell was bubbled into a collecting water for 30 min, and the amount of H_2O_2 was determined by a colorimetric method using peroxidase,[7] before and after the remote oxidation experiment.

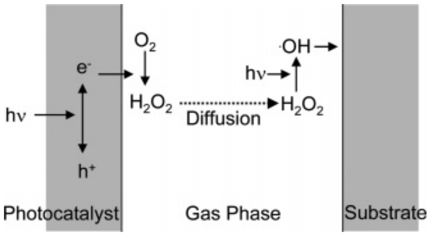

Figure 1. Possible mechanism of the remote oxidation.

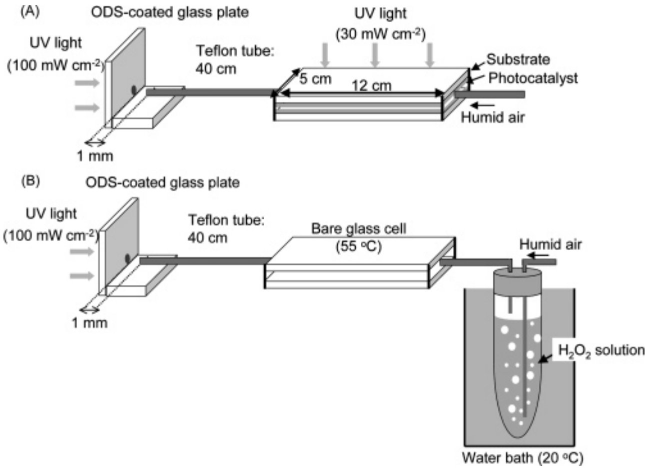

Figure 2. Experimental setups for (A) the remote oxidation and (B) the H_2O_2−UV reaction.

As shown in Figure 3 (◆), a positive correlation was observed between the remote oxidation ability and the H_2O_2 generation ability. It was verified that the detected species was not an organic peroxide but H_2O_2 by an experiment using catalase.[7] The detected H_2O_2 was generated at an irradiated photocatalyst because H_2O_2 was not detected at all when a bare glass cell was used or a photocatalyst cell was used that was not irradiated with UV light. Photocatalytic reduction of O_2 was most likely responsible for the H_2O_2 generation ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$).

When a non-irradiated photocatalyst cell or a bare glass cell was used in the remote oxidation experiment, changes in the water contact angle of the ODS-coated glass surface were almost

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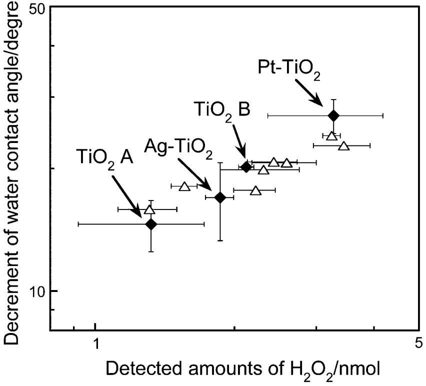

Figure 3. Correlations between the remote oxidation ability and the H_2O_2 generation ability for various photocatalysts (◆) (measured as shown in Figure 2A). The correlation between the oxidation ability and the H_2O_2 amount for the H_2O_2−UV reaction is also shown (△) (measured as shown in Figure 2B). In both experiments, the water contact angle of the ODS probe surface and the amount of H_2O_2 in the gas flowing out of the cell were measured before and after each experiment (15 h), and the decrement of the water contact angle was plotted as an index of an oxidation ability as a function of the amount of H_2O_2. The remote oxidation experiments were repeated 4−6 times with each photocatalyst except, for TiO_2 B ($n = 1$). The H_2O_2 concentration was measured three or four times before and after each experiment. Each data point for the H_2O_2−UV experiment corresponds to a single measurement, and the H_2O_2 concentration was measured three or four times before and after each experiment.

negligible (<5°). In the case where the ODS probe was not irradiated while the photocatalyst cell was irradiated, the decrease in the water contact angle of the probe surface was not negligible only when Ag−TiO_2 was used (10 ± 1.8°). This indicates the possibility that a strong oxidizing species like $^{\bullet}OH$, which is able to oxidize ODS even in the dark,[4b] diffuses from the photocatalysts. However, greater changes were obtained when both the ODS and the photocatalysts were irradiated with UV light.

Next, a remote oxidation experiment was carried out with monochromatic light ($\lambda = 365$ nm, 5.5 mW cm^{-2}, full width at half-maximum = 10 nm) for the ODS irradiation. The light does not excite C−C and C−H bonds in alkyl chains.[9] A Pt−TiO_2 cell with relatively high activity was used for this experiment. As a result, the water contact angle of the ODS probe surface decreased by about 14° during 7 h of irradiation, whereas the decrease was negligible in the case of a bare glass cell. These results indicate that the irradiation of ODS is necessary not for the excitation of ODS but for that of the species diffusing from the photocatalyst.

A H_2O_2−UV experiment was also performed with monochromatic light. H_2O_2 is known to exhibit weak absorption, even at 365 nm,[10] and to dissociate into $^{\bullet}OH$ at 351 nm.[11] The ODS-coated glass plate was mounted onto the window of a glass cell that was filled with H_2O_2-saturated air (25 °C). The ODS layer exposed to H_2O_2 was irradiated from its back with monochromatic light (365 nm). The water contact angle of the ODS probe surface decreased by ca. 50° during 8 h of irradiation. In addition, the decrement increased gradually as the wavelength was decreased to 280 nm. This tendency, which was also observed for the remote oxidation, was in good agreement with the wavelength dependence for UV absorption of H_2O_2. All these results are consistent with our hypothesis that the H_2O_2−UV reaction participates in the remote oxidation.

If the remote oxidation is based on the photolysis of the diffusing H_2O_2 into $^{\bullet}OH$, the oxidizing ability of the remote oxidation should be in accord with that of the H_2O_2−UV reaction at the same H_2O_2 concentration as that for the gas flowing out of the photocatalyst cell. To examine this, the surface of the ODS probe irradiated with the Hg−Xe lamp (100 mW cm^{-2}) was sprayed with humid air (RH = 60%) containing H_2O_2 vapor for 15 h (Figure 2B). The H_2O_2-containing gas was passed through a non-irradiated bare glass cell that was kept at 55 °C, which was the average temperature of the irradiated photocatalyst flow cells (50−60 °C), during the remote oxidation experiment. The water contact angle at the ODS probe surface and the amount of H_2O_2 in the outflowing gas were measured before and after the experiment. The results are shown in Figure 3 (△). Changes in the water contact angle for the H_2O_2−UV reaction were in close agreement with those for the remote oxidation. When the ODS probe was not irradiated with UV light, the decrement of the water contact angle was negligible, indicating that H_2O_2 can remove ODS at 55 °C only with the aid of UV light. These results suggest that the H_2O_2−UV reaction plays an essential role in the remote oxidation.

The mechanisms of photocatalytic remote oxidation elucidated in this work should contribute to acceleration of the development of photocatalytic lithography. In addition, conventional photocatalysis might also involve this process. A chemical species that is hardly adsorbed by a photocatalyst could be decomposed photocatalytically by exploiting the remote oxidation.

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