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Remote Photocatalytic Oxidation Mediated by Active Oxygen Species Penetrating and Diffusing through Polymer Membrane over Surface Fluorinated TiO_2

Jong Sung Park and Wonyong Choi*
School of Environmental Science and Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea

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Active oxygen species desorbed from the illuminated TiO_2 surface can penetrate through organic polymer membrane with degrading dye substrates loaded within the pores, and their permeating action into the membrane was dramatically enhanced with surface fluorinated TiO_2.

The successful performance of TiO_2 as an environmental photocatalyst is mainly ascribed to the generation of highly reactive radical species such as OH radicals.[1] The traditional view on the mechanistic behavior of oxidant radicals involved in photocatalysis was that the photogenerated radicals remain immobile at the surface sites and react with substrates that are preadsorbed or diffusing onto the surface. However, recent studies revealed that the oxidant radicals generated on the illuminated TiO_2 not only diffuse laterally on the surface but also desorb from the surface into the air to initiate photocatalytic reactions at a remote site.[2–8] Such remote photocatalytic oxidation (PCO) effects have been confirmed in various systems and now the mobile nature of oxidant species generated on the UV-illuminated TiO_2 surface is well recognized. On the other hand, the identity of migrating oxidant species in remote PCO is in dispute and several different species such as OH, HO_2, H_2O_2, $^1O_2$ have been considered.[2–8] This group recently found that the surface-fluorinated TiO_2 (F-TiO_2; reaction 1) enhances the remote PCO activity in the ambient air condition and concluded that the air-borne oxidants that are mostly responsible for the remote PCO are OH radicals: the surface fluorination enhances the desorption of OH radicals generated on TiO_2 into the air (reaction 2).[6] The surface fluorination of TiO_2 promotes the desorption of OH radicals not only at the TiO_2/water interface[9,10] but also at the TiO_2/air interface.[6]

$$\equiv\text{Ti–OH} + \text{F}^- \rightleftharpoons \equiv\text{Ti–F} + \text{OH}^-, \qquad (1)$$

$$\equiv\text{Ti–F} + \text{H}_2\text{O}_{ad} + \text{h}_{vb}^+ \rightarrow \equiv\text{Ti–F} + \bullet\text{OH (air-borne)} + \text{H}^+. \qquad (2)$$

In this study, we found that the oxidants desorbed from the illuminated TiO_2 surface diffuse through organic polymer membrane (≈120 µm thick) with degrading dye substrates loaded within the pores. The permeating action of the oxidants into the membrane was dramatically enhanced with F-TiO_2.

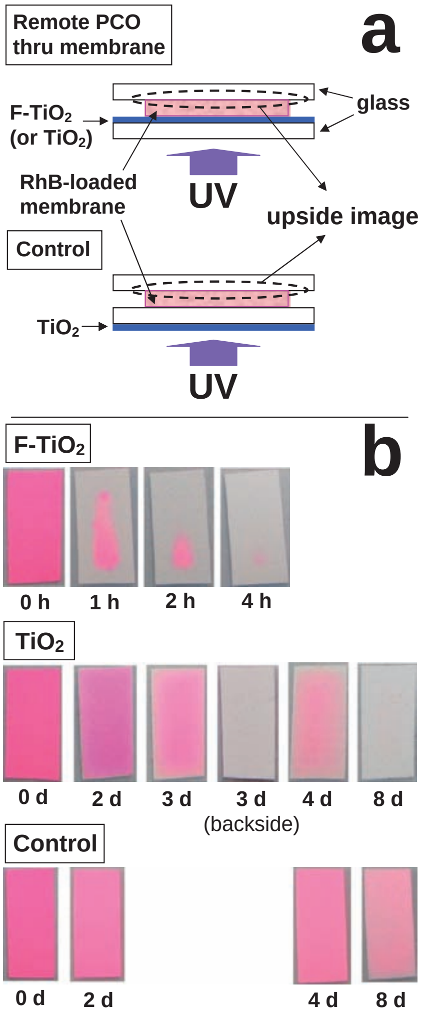

Figure 1. (a) Schematic illustration for the remote photocatalytic bleaching of RhB loaded within the pores of PVDF membrane and the control experiment. (b) The remote photocatalytic bleaching (color change) of the RhB-loaded membrane over the irradiated F-TiO_2 and pure TiO_2 film. The direct photolytic bleaching (control) is compared as well. All photo images show the upside of the membrane except one that shows the backside of the membrane (TiO_2, 3 day irradiated).

The experimental setup was schematically illustrated in Figure 1a. A dye-loaded polymer membrane was sandwiched between a TiO_2-coated glass plate and a blank glass plate to make a close contact with the surface of TiO_2. The TiO_2 film was coated onto a slide glass (Corning No. 2948, USA) from an aqueous suspension (5 wt %) of TiO_2 (Degussa P25) and then calcined at 400 °C for 30 min. The coating procedure was repeated five times. To fluorinate the TiO_2 surface (via reaction 1), the TiO_2-coated glass plate was soaked in a NaF solution (50 mM, pH 3.5) for 30 min and then dried under air. A disc-type polyvinylidene fluoride (PVDF) membrane [$–(CH_2CF_2)_n–$; pore size 0.45 µm; average thickness 120 µm; Pall Corp.] was employed and its cross-sectional image obtained with a scanning electron micrograph (SEM) is shown in Figure 2a. Rhodamine B (RhB, Aldrich) was used as a probe substrate to test the activity of remote PCO. The PVDF membrane ($0.5 \times 1\ cm^2$) was immersed into 50 µM RhB solution for 5 min and then dried under ambient air. The RhB-loaded PVDF membrane and the TiO_2 (or F-TiO_2)-

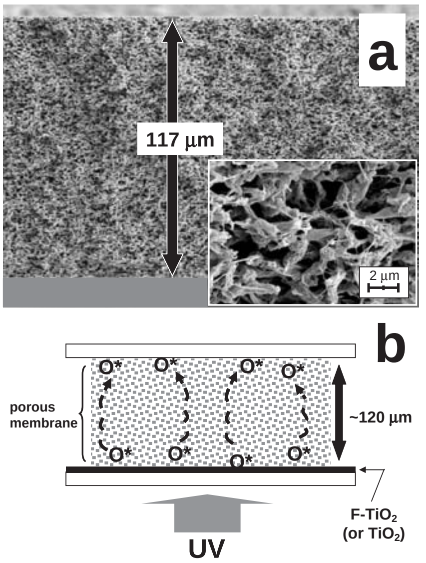

Figure 2. (a) The cross-sectional SEM image of the PVDF membrane within which RhB is loaded. (b) The illustration that shows that oxidant species (O*) desorbed from the illuminated F-TiO_2 (or TiO_2) surface can penetrate through the interconnected channels of membrane pores up to the other side of the membrane.

coated glass were faced each other and held together (Figure 1a). A black-light UV lamp (10 W, Sankyo Denki) irradiated the sample from the TiO_2-coated glass side. The UV intensity was 1.5 mW/cm^2. A control experiment was carried out with reversing the TiO_2-coated glass plate upside down as shown in Figure 1a. The bleaching of RhB under illumination was monitored by taking optical images of the RhB-loaded membrane using a digital camera. Both the upside (the side not in contact with the TiO_2 surface) and backside (the side in contact with the TiO_2 surface) images of the membrane were compared as a function of the irradiation time.

The photo images in Figure 1b show that the RhB-loaded membrane on the TiO_2 film was gradually bleached under UV irradiation in the ambient air condition. The control experiment shows that the direct photolytic bleaching of RhB loaded within the membrane was insignificant compared with the photocatalytic bleaching under the present irradiation condition and also confirms that the dye bleaching is not due to the diffusion of RhB itself. The photocatalytic bleaching started from the backside that is in direct contact with the TiO_2 surface and gradually reached the upside of the membrane. Compare the upside and backside images that were taken after 3 day irradiation on the pure TiO_2 film. By this time, the backside was almost completely bleached whereas the upside was only slightly discolored. Near complete bleaching of the upside of the membrane needed up to 8 days of irradiation. This observation clearly indicates that the photocatalytic bleaching should be mediated by oxidant species that are diffusing from the TiO_2 surface into the membrane pores and that the diffusing air-borne oxidants are able to penetrate through the 120 µm-thick membrane. The remote photocatalytic bleaching was remarkably enhanced over the F-TiO_2 film. The complete bleaching of the RhB-loaded membrane on F-TiO_2 took only 4 h or so whereas the bleaching on the pure TiO_2 film took about 8 days of irradiation. This indicates that the generation and the subsequent penetration of active oxidants into the membrane are highly enhanced on F-TiO_2. Figure 2b schematically illustrates the situation. The oxidants desorbed from the illuminated TiO_2 surface should migrate through the interconnected channels of membrane pores up to the other side of the membrane.

We do not have any experimental data to identify the diffusing oxidants but this observation is consistent with our previous claim the generation of air-borne OH radicals are highly enhanced over the F-TiO_2 surface.[6] The enhanced fluorination effect also implies that the dye is not bleached reductively because the surface fluorination of TiO_2 markedly inhibits the photocatalytic reduction reactions.[10] The surface fluoride species that is highly electronegative reduces the interfacial electron-transfer rate by tightly holding trapped electrons. Judging from the results of previous studies on remote PCO that have demonstrated strong oxidizing power for a wide variety of substrates,[2–8] the most probable candidate of the diffusing air-borne oxidant seems to be an OH radical although its presence has never been directly identified. On the other hand, H_2O_2 has been suggested as a diffusing oxidant species responsible for the remote PCO in a recent study.[7] However, this mechanism cannot be supported in this case because a control experiment that was carried out with H_2O_2 vapor alone in the absence of TiO_2 did not show any sign of photooxidation under the present irradiation (black light) condition.[6] It is highly likely that the diffusing oxidants that are acting in the conventional remote PCO and in the present membrane system are the same species. Hydroxyl radicals are transient species and react with most organic compounds with diffusion-limited rates. They should also react with the PVDF membrane, which has been confirmed in a recent remote PCO study.[8] However, the fact that OH radicals are able to react with PVDF does not necessarily mean that OH radicals cannot diffuse through the PVDF membrane. The concentration of OH radicals could be gradually extinguished with increasing the penetration depth.

In conclusion, this study clearly demonstrated that the oxidants desorbed from the illuminated TiO_2 surface can penetrate and diffuse through the polymer membrane. The surface fluorination of TiO_2 drastically enhances the permeating action of oxidants by promoting their desorption. Although OH radicals seem to be the probable diffusing oxidant, we cannot completely rule out other oxidants (e.g., HO_2, H_2O_2, $^1O_2$). Further studies are needed to address this issue.

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