Photoactive TiO_2 Containing Paper: Preparation and Its Photocatalytic Activity under Weak UV Light Illumination

Hirokazu Matsubara,[†,††] Makoto Takada,[††] Shinichi Koyama,[††] Kazuhito Hashimoto,[†] and Akira Fujishima[†]
[†]*Department of Applied Chemistry, Faculty of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113*
[††]*Gifu Prefectural Paper Research Institute, 777 Maeno, Mino, Gufu 501-37*

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TiO_2-containing papers with highly photocatalytic activity have been prepared. Their photocatalytic activity was investigated by measuring the decomposition of gaseous acetaldehyde under illumination from a weak UV light source such as a conventional white fluorescent light bulb. It was found that the photocatalytic efficiency of the TiO_2-containing papers was higher than that of Degussa P-25, one of the most efficient commercial TiO_2 powders, indicating that paper pulp serves as a good matrix for highly efficient TiO_2 photocatalysts.

It is well known that semiconducting TiO_2 has a strong oxidation power when it absorbs photons with energies greater than its band gap. There has been much research on TiO_2 photocatalysis for the removal of harmful organic materials from the environment.[1-11] We have developed several photocatalytic systems, showing deodorizing, antibacterial and self-cleaning functions under room light illumination, by coating photoactive TiO_2 thin *films* on various materials such as a ceramic tile[12] and window glass.[13] Here we report on photoactive paper in which TiO_2 *powder* photocatalystic material is dispersed.

The TiO_2-containing paper was prepared by the following method. A mixture of a softwood kraft pulp (NBKP) and TiO_2 aqueous sol (STS-01: 7 nm in diameter, Ishihara Sangyo Kaisha, Ltd.), coagulated on $Al(OH)_3$ in an aqueous suspension, was flocculated with polyacrylamide and polyamine binder. The amount of added TiO_2 was from 2 to 10 wt% based on the weight of the pulp. The TiO_2-containing paper sheets were made using a Tappi standard sheet machine. The sheets were dried by press-drying at 115 °C for 3 min. The basis weight of the pulp was 100 g/m^2.

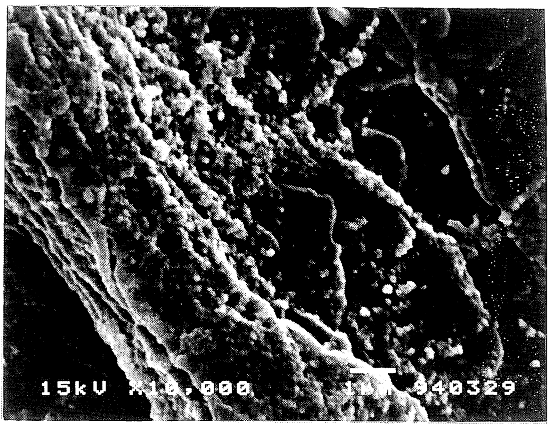

Figure 1. SEM photomicrograph of the surface of the TiO_2-containing (5 wt%) sheet.

Figure 1 shows a SEM photomicrograph of the surface of TiO_2-containing (5 wt%) sheet. It is seen that TiO_2 aggregates ca. 0.1 μm in size were randomly distributed on the pulp. By increasing the amount of TiO_2 contained, the number of the aggregates increased, but the size of the aggregates did not change drastically.

The photocatalytic decomposition of gaseous acetaldehyde with the various TiO_2-containing papers was carried out under weak UV illumination from a conventional white fluorescent light bulb (Mitsubishi/Osram; neolumisuper FL10W, UV intensity; 0.08 mW/cm^2). The volume of the reaction glass vessel was ca. 1600 mL. The size of the TiO_2-containing sheet was 10 cm x 10 cm. The acetaldehyde concentration was measured using a gas chromatograph, Ohkura Model C-103, equipped with a 2 m TCP column and a flame ionization detector, with helium as the carrier gas.

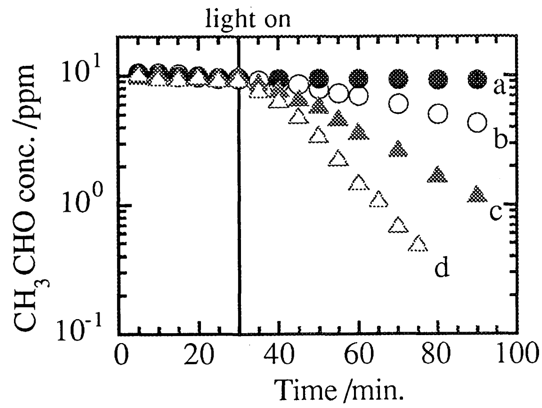

Figure 2. Decomposition of gaseous acetaldehyde under white fluorescent light irradiation (UV intensity; 0.08 mW/cm^2), for (a) TiO_2-free sheet, (b) TiO_2-containing (2 wt%) sheet, (c) TiO_2-containing (5 wt%) sheet, (d) TiO_2-containing (10 wt%) sheet.

Figure 2 shows the semilogarithmic plots of the concentration change of gaseous acetaldehyde vs. light irradiation time. The initial concentration of acetaldehyde was ca. 10 ppm. The concentration of acetaldehyde was constant with the TiO_2-free sheet. However, acetaldehyde degradation was clearly seen with the TiO_2-containing papers even under very weak UV irradiation. The reaction proceeded with first-order reaction kinetics. The decomposition rate increased with increasing amounts of TiO_2 contained in the paper. CO_2 was produced gradually only when acetaldehyde was injected into the reaction vessel.

The quantum yields for the TiO_2-containing papers were measured under 0.50 mW/cm^2 monochromatic illumination (360 nm) from a Hg-Xe lamp, with an initial acetaldehyde concentration of 1000 ppm. The TiO_2-containing sheet size was 3.4 cm x 3.2 cm in this case. The experiment was also done using commercially available TiO_2 powder (Degussa P-25, Nippon Aerosil Co., Ltd.), which is known to be one of the most photoactive TiO_2 powders. In this case, 0.14 g of TiO_2 powder was spread uniformly over a 3.4 cm x 3.2 cm area. We measured the amounts of CH_3CHO destroyed and the amounts of CO_2 produced. The CO_2 concentration was measured using a gas chromatograph, Ohkura Model 502 T, equipped with thermal conductivity detector, with helium as the carrier gas.

The results are listed in Table 1. Photogenerated electron reacts with O_2 producing $O_2{\cdot}^-$. The role of $O_2{\cdot}^-$ is not clear in the present reaction. Therefore the quantum yields were calculated under the assumption that CH_3COOH is the only stable reaction product and that the photogenerated holes in TiO_2 can only participate in the following successive reactions. The amount of CH_3COOH produced was estimated from those of CH_3COOH decreased and CO_2 produced.

$$CH_3CHO + H_2O + 2h^+ \rightarrow CH_3COOH + 2H^+ \quad (1)$$

$$CH_3COOH + 2H_2O + 8h^+ \rightarrow 2CO_2 + 8H^+ \quad (2)$$

Table 1. Quantum yields for the decomposition of gaseous acetaldehyde, using photocatalytic papers with various amounts of added TiO_2 , and P-25 powder

Sample	Quantum yield (%)		
	Φ_{CH_3COOH}	Φ_{CO_2}	Φ_{total}
TiO_2-containing (2 wt%) sheet	14	10	24
TiO_2-containing (5 wt%) sheet	15	27	42
TiO_2-containing (10 wt%) sheet	58	32	90
P-25 powder	37	6	43

UV intensity: 0.50 mW/cm^2; initial concentration of CH_3CHO: 1000 ppm.

Those experiments were done in air. Therefore, it is considered that water adsorbed on the photocatalyst takes part in the above reactions. The highest quantum yield obtained with TiO_2-containing paper was 90% and was ca. two times larger than that of P-25 (43%). The total amount of TiO_2 contained in the 3.4 cm x 3.2 cm 10 wt%-paper is only 0.014 g, which is 10 times less than that in a P-25 powder system. These data clearly indicate that paper pulp serves as a good matrix for a highly efficient TiO_2 photocatalyst.

We have shown that highly photoactive TiO_2-containing papers can be prepared by dispersing TiO_2 powder in paper pulp and that they can decompose 10 ppm gaseous acetaldehyde, a relatively high concentration of this noxious gas, even under illumination from a white fluorescent light bulb. It is well known that photo-irradiated TiO_2 can oxidize almost all organic compounds in addition to acetaldehyde. Therefore, we can expect that the TiO_2-containing paper reported herein will show good deodorizing activity under room light illumination.

Because the UV light intensity from a white fluorescent bulb is rather weak, the strength of the paper remained good. However, it is easily imagined that such a highly photoactive TiO_2 powder adsorbed on the pulp could decompose the pulp itself, resulting in a decrease of the paper strength under strong UV light irradiation. Moreover, the strength of the TiO_2-containing paper decreased by increasing the amount of TiO_2 contained in the paper even without UV irradiation because TiO_2 inhibited interfiber bonding in the TiO_2-containing paper. Therefore, for practical use, we may need to develop a method to retain the paper strength without compromissing the high photocatalytic activity.

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