Preparation of Transparent TiO_2 Thin Film Photocatalyst and Its Photocatalytic Activity

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Transparent TiO_2 thin films with high photocatalytic activity were prepared on glass substrates via the sol-gel method from tetraisopropyl titanium ethanol solution containing polyethylene glycol and diethylene glycol. Transparency of these TiO_2 thin films was 80% in the visible region. Photocatalytic activity of the TiO_2 thin films was studied using the decomposition of gaseous acetaldehyde. We found that the quantum yield with those films was similar to that with one of the most photoactive commercial TiO_2 powders, Degussa P-25.

Environmental purification using TiO_2 photocatalysts has attracted a great deal of attention with the increasing number of recent environmental problems in society.[1-6] We have been studying the application of TiO_2 thin film photocatalysts in the field of new functionalized building materials. However, prior to the present work, highly transparent TiO_2 films with high photocatalytic activities have not been available.

The present paper deals with the preparation of transparent and efficient TiO_2 thin film photocatalysts via the sol-gel method. Organic/polymer additives such as polyethylene glycol (PEG) and diethylene glycol (DEG) were introduced during the dip-coating process.[7] The former was chosen to increase the surface area of the film. On the other hand, the latter is expected to play an important role to stabilize the dipping solution.[8] Control of the surface microstructure of the TiO_2 thin films can be achieved through the calcination. It was expected that high photocatalytic activity could be obtained by controlling the microstructure.

The starting solution for the sol-gel reaction was prepared by mixing 10 g of $Ti(OCH(CH_3)_2)_4$ (Wako Chemical Co.), 80 mL of C_2H_5OH (Wako Chemical Co.), and 10 g of the organic/polymer additives, PEG with molecular weight of 600 (Wako Chemical Co.), and DEG monoethylether (Wako Chemical Co.). The weight percentage of PEG (based on the total weight of PEG plus DEG) was controlled to be 0, 25, 50, 75, and 100%, designated as DEG4-TiO_2, PEG1DEG3-TiO_2, PEGDEG-TiO_2, PEG3DEG1-TiO_2, and PEG4-TiO_2, respectively. We also prepared TiO_2 thin film photocatalysts without additives, but they were unstable. TiO_2 thin films were obtained by dipping SiO_2-coated glass slides into the starting solution.[9] The pull-up speed was 1.5 mm/s. The dipping was carried out 10-40 times in a glove box under a 10 % relative humidity atmosphere in air. The resulting samples were calcined at 450℃ for 1 hour after every ten dippings. The thickness of a 40x-dipped film was estimated to be about 0.6 mm via the SEM observation of the cross-sections. The apparent area of the TiO_2 thin films was 12.7 cm^2.

The photocatalytic activity of the TiO_2 thin films was evaluated by measuring the concentration changes of acetaldehyde as a reactant and of product CO_2 as a function of irradiation time under UV light illumination with six 10-W fluorescent black-light bulbs (BL). The UV light intensity over the range of 300 to 380 nm on the TiO_2 thin film was 1.2 mW/cm^2. Air saturated with acetaldehyde, 1 mL, was injected into a l-liter Pyrex glass vessel, so that the concentration of acetaldehyde vapor was 1000 ppm. Irradiation was conducted at room temperature after equilibrium between gaseous and adsorbed acetaldehyde on the TiO_2 thin film was achieved. For comparison, a similar photodecomposition experiment was also carried out using one of the most photoactive commercial TiO_2 powders (Nippon Aerosil Co. P-25) by spreading 0.0116 g of P-25 powder uniformly onto a slide glass of the same size as that of the TiO_2 thin films described above.

Solutions with no added DEG were unstable. TiO_2 microparticles were formed spontaneously after the solution was mixed for several minutes. The XRD patterns for all of the samples showed typical diffraction features due to the anatase structure (d=3.52, 1.89, and 2.38 ±).[10] The TiO_2 thin film photocatalyst surface was very flat, without any structure in SEM images at 10,000x magnification. The organic components of the unfired coatings were decomposed during the heat treatment. Although the TiO_2 films became thicker by increasing the number of dippings, the transmittance in the visible region (> 400 nm) remained about 70 to 80 %, almost independent of the number of dippings, as shown in Fig. 1. The photocatalytic activity of the film was proportionally increased by increasing the dipping number.

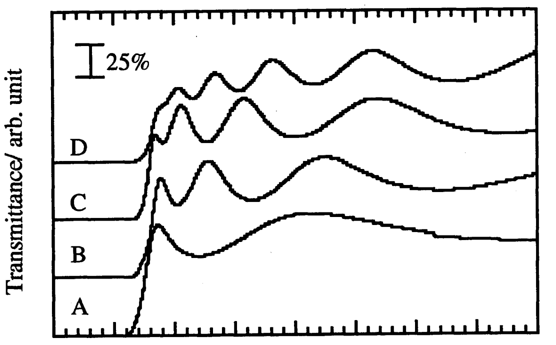

Figure 1. Transmittance spectra for TiO_2 thin films with increasing number of dippings . (a) 10x, (b) 20x, (c) 30x, and (d) 40x.

Figure 2 shows the time dependence of the photodegradation of acetaldehyde (Fig. 2A) and the CO_2 production (Fig. 2B) in

Table 1. Quantum yields (%) for photo-decomposition of acetaldehyde and CO_2 production with various TiO_2 thin films and P25 powder under BL irradiation

Samples	PEG4	PEG3DEG1	PEGDEG	PEG1DEG3	DEG4	P-25
CH_3COOH	19.2	19.3	13.6	17.8	6.7	23.4
CO_2	40.3	33.9	38.1	39.8	2.2	16.0
Total	59.5	53.2	51.7	57.6	8.9	33.4

Acetaldehyde conc.: 1000 ppm; catalyst area: 12.7 cm^2; light intensity: 1.2 mW/cm^2.

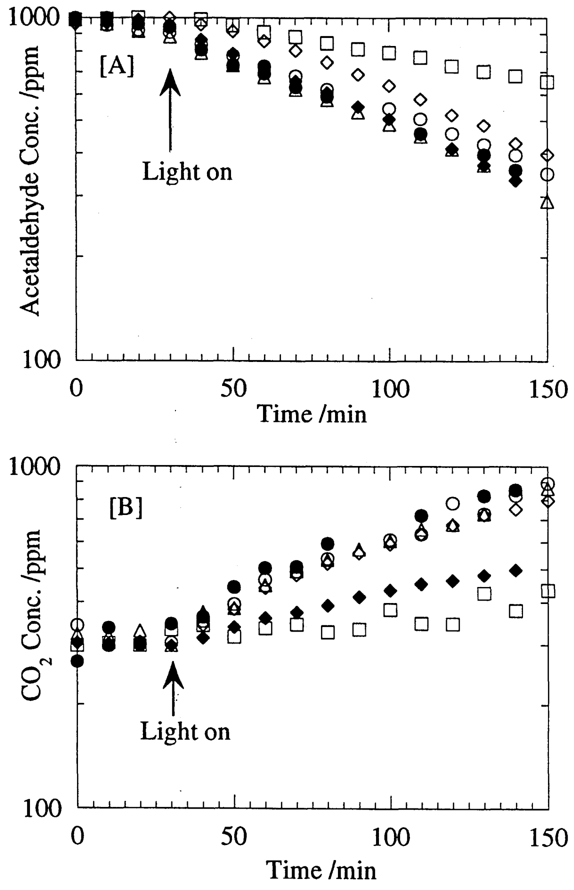

Figure 2. Plots of concentration vs. irradiation time on the photocatalytic decomposition of acetaldehyde (A) and CO_2 production (B) under BL irradiation on various TiO_2 thin films. (□) DEG4-TiO_2, (○)PEG1DEG3-TiO_2, (◇) PEGDEG-TiO_2, (△) PEG3DEG1-TiO_2, (●) PEG4-TiO_2, and (◆) P-25. Initial acetaldehyde conc.: 1000 ppm; catalyst area: 12.7 cm^2; light intensity: 1.2 mW/cm^2.

the presence of various TiO_2 thin films and P-25 powder. Photocatalytic activities for all of the TiO_2 thin films except for DEG4-TiO_2 were excellent. They were comparable to that of the P-25 powder.

Table 1 presents the quantum yields for the generation of the reaction intermediate, acetic acid, via the photodecomposition of acetaldehyde, and the CO_2 production. The apparent quantum yields were evaluated from the initial rates of acetaldehyde decomposition and CO_2 production.[11] As shown in Table 1, generation rates for the intermediate were almost the same for the TiO_2 thin film photocatalysts and P-25, while CO_2 generation rates were significantly higher for the TiO_2 thin film photocatalysts than for P-25.

These data suggest that the acetic acid is adsorbed stronger on the TiO_2 thin films than on P-25. The adsorbed acetaldehyde is photodecomposed to acetic acid, and this intermediate may desorb easier from the P-25 surface than from the TiO_2 film surface. The resulting acetic acid adsorbed on the photocatalyst surface can be further decomposed to CO_2. The development of a more detailed mechanism to explain the high quantum yields for CO_2 production on the TiO_2 thin film photocatalysts will be an objective of future work.

In summary, we have successfully prepared transparent and highly efficient TiO_2 thin film photocatalysts via the sol-gel method with PEG and DEG as additives. The key factor in the preparation of such TiO_2 thin films with controlled surface microstructure was the introduction of the organic/polymer components into the starting solution under low humidity conditions. These thin film photocatalysts may provide a great opportunity for the development of passive systems for air purification in enclosed living and work spaces .

References and Notes

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