JOURNAL OF MATERIALS SCIENCE 30 (1995) 837–841

Morphology of thin anatase coatings prepared from alkoxide solutions containing organic polymer, affecting the photocatalytic decomposition of aqueous acetic acid

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Porous anatase coatings were prepared from alkoxide solutions containing organic polymer by a dip-coating technique. The morphology of the coatings, such as pore size, pore distribution and thickness, was controlled. The effects of the morphology of the porous anatase coatings on the photocatalytic activity for the photocatalytic decomposition of aqueous acetic acid were examined.

1. Introduction

There have been many studies on TiO_2 photocatalytic reactions. Recently, the applications have been focused on purification and treatment of water and air, which are concerned in the protection of the environment, such as nature and life spaces [1]. The studies mainly treated the suspension system of TiO_2 fine powders or the reaction system containing materials on which TiO_2 fine powders were anchored, because some TiO_2 fine powders have high activity. However, there are inconsistent problems in both uses of TiO_2 fine powders and materials modified with TiO_2 fine powders. There is difficulty in recovery of TiO_2 fine powders after the reactions, and low activity due to diminution of the surface area by anchoring TiO_2 fine powders. A few papers [2–5] also described TiO_2 thin coatings showing activity as high as TiO_2 fine powders.

We have confirmed the relationships between fundamental properties and photocatalytic activities of TiO_2 for the purpose of development of a photocatalyst with high activity [6–10]. We reported that TiO_2 fine powders, which were synthesized by hydrolysis of titanium tetraisopropoxide and of which the fundamental properties were controlled, showed good activity for photocatalytic oxidation of various organic components [10]. Recently, careful examination of the effect of crystal structure of TiO_2 thin coatings, which were prepared from the alkoxide solution, on the photocatalytic property resulted in clarification that anatase phase showed high activity [11]. In this paper we report the preparation of porous anatase coatings from the alkoxide solution containing organic polymer. A few papers have discussed the preparation of not the functional porous ceramic coatings with controlled pore size, but porous SiO_2-based glass from alkoxide solutions containing organic polymer [12]. We also discuss the effects of the morphology of the TiO_2 coatings on the photocatalytic activity.

2. Experimental procedure

Precursor solutions for TiO_2 coatings were prepared by following the method reported by Takahashi and Matsuoka [13] using titanium tetraisopropoxide, ethanol, water and diethanolamine. Titanium tetraisopropoxide (14.2 g) and diethanolamine (5.3 g) were dissolved in ethanol (100 ml). After mixing vigorously at room temperature, water was added to the solution. The molar ratio of water to the alkoxide was 1. An adequate amount of polyethylene glycol ($HOCH_2(CH_2OCH_2)_nCH_2OH$, molecular weight 1800–2200) was added to the solution. The solutions containing various amounts of polyethylene glycol were transparent and light yellow. Quartz glass plates (20 mm × 20 mm × 1 mm) were used as the support substrates. TiO_2 coatings were prepared on the supports by a dip-coating method. The withdrawal speed was 100 mm min^{-1}. Gel coatings were dried at 100 °C for 30 min and then carefully heat treated in air [11]. The temperature was elevated slowly (2 °C min^{-1}) to 650 °C and kept at 650 °C for 1 h. The thickness of the TiO_2 coatings was increased by repeating the cycle from withdrawing to heating. Crystallinity of the TiO_2 coatings was identified by X-ray diffraction (XRD) employing CuK_α radiation. The accelerated voltage and the applied current were 35 kV and 20 mA, respectively. The morphology and thickness of TiO_2 coatings were observed using scanning electron

0022–2461

microscopy (SEM) with the accelerated voltage of 25 kV. Spectroscopic analysis of TiO_2 coatings was performed by using a spectrophotometer.

The photocatalytic property of TiO_2 coatings was evaluated by examining oxidation of acetic acid on the surface of TiO_2 coatings under irradiation. The quartz glass plate with TiO_2 coating was settled in the aqueous acetic acid (0.002 mol l^{-1}, 120 p.p.m.) in a quartz cell (20 mm × 30 mm × 3 mm), which had two faces (20 mm × 30 mm) as windows for spectro-measurement. One face (20 mm × 20 mm) of the quartz glass plate with TiO_2 coating was irradiated through the window along the normal direction with a high-pressure mercury lamp (100 W). During irradiation, the solution was bubbled with oxygen. The concentration of acetic acid was determined by gas chromatography every 15 min.

3. Results and discussion

Fig. 1 show scanning electron micrographs of the surfaces of TiO_2 coatings prepared from the precursor solutions (a) without and (b–d) with polyethylene glycol (0.5, 1.0 and 2.0 g, respectively). It was observed that TiO_2 coatings prepared from the precursor solution without polyethylene glycol had fine granular microstructure and flat texture. Different microstructures developed in TiO_2 coatings prepared from the precursor solutions with polyethylene glycol. There are fine pores in the coatings. The size and number of the pores were related to the amount of polyethylene glycol. The diameters of the pores in the coatings prepared from the precursor solutions containing 0.5, 1.0 and 2.0 g polyethylene glycol were several tens of nanometres, 100–150 nm and 200–350 nm, respectively. The pores were distributed homogeneously over the surface of TiO_2 coatings. Fig. 2 shows scanning electron micrographs of the edge profiles of TiO_2 coatings which were prepared using the precursor solutions (a) without and (b–d) with polyethylene glycol (0.5, 1.0 and 2.0 g, respectively) and repeating the cycle from withdrawing to heating ten times. The thickness of the coatings was in the range 300–500 nm. It was observed that the thickness of the coatings increased with the pore size, which was determined by the amount of polyethylene glycol. The coatings prepared from the precursor solution containing 2.0 g polyethylene glycol was porous not only in the surface region but also in the interior region, as shown in Figs 1d and 2d.

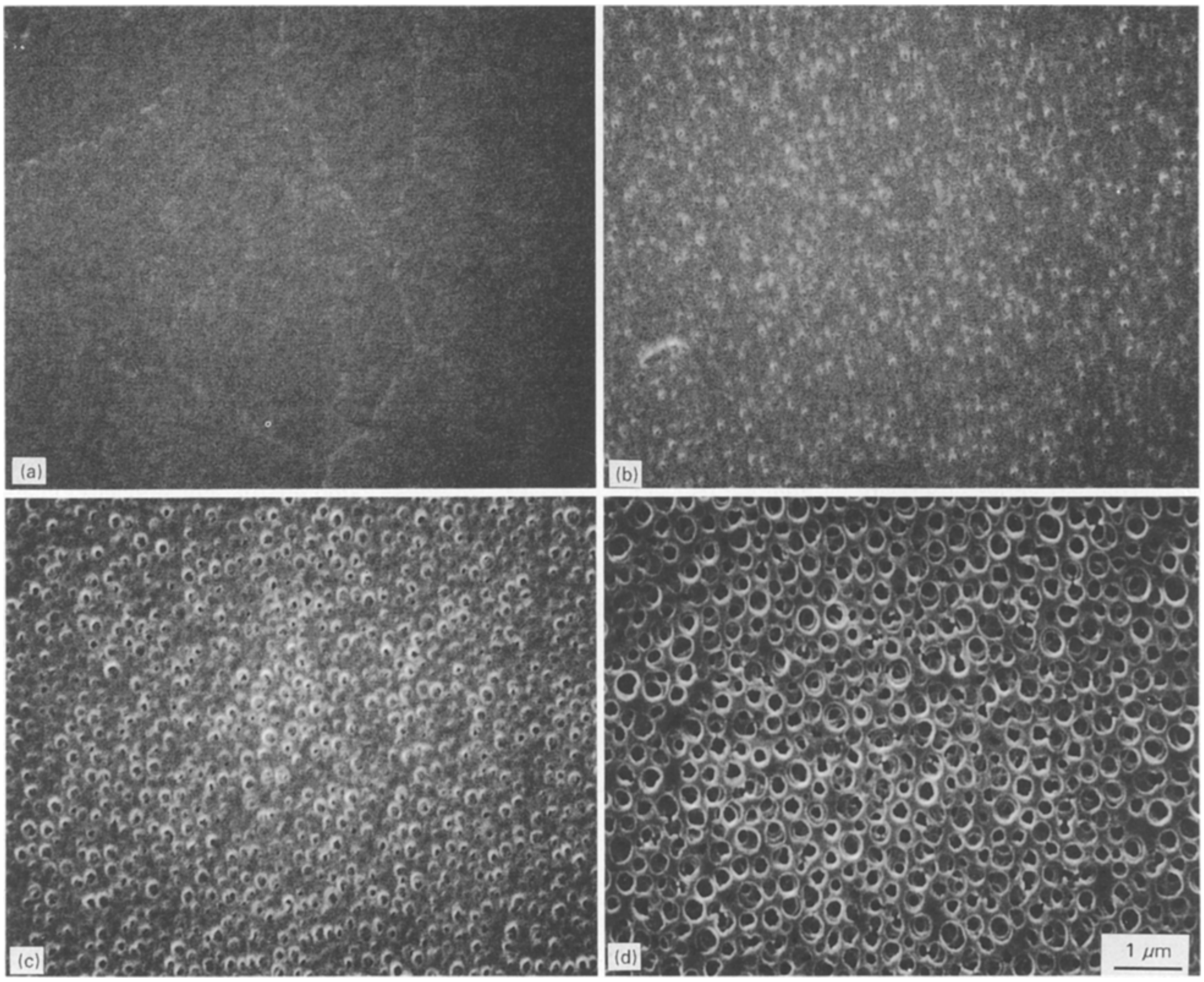

Figure 1 Scanning electron micrographs of the surfaces of TiO_2 coatings which were prepared from the precursor solutions: (a) without additives, and containing (b) 0.5 g, (c) 1.0 g, and (d) 2.0 g polyethylene glycol.

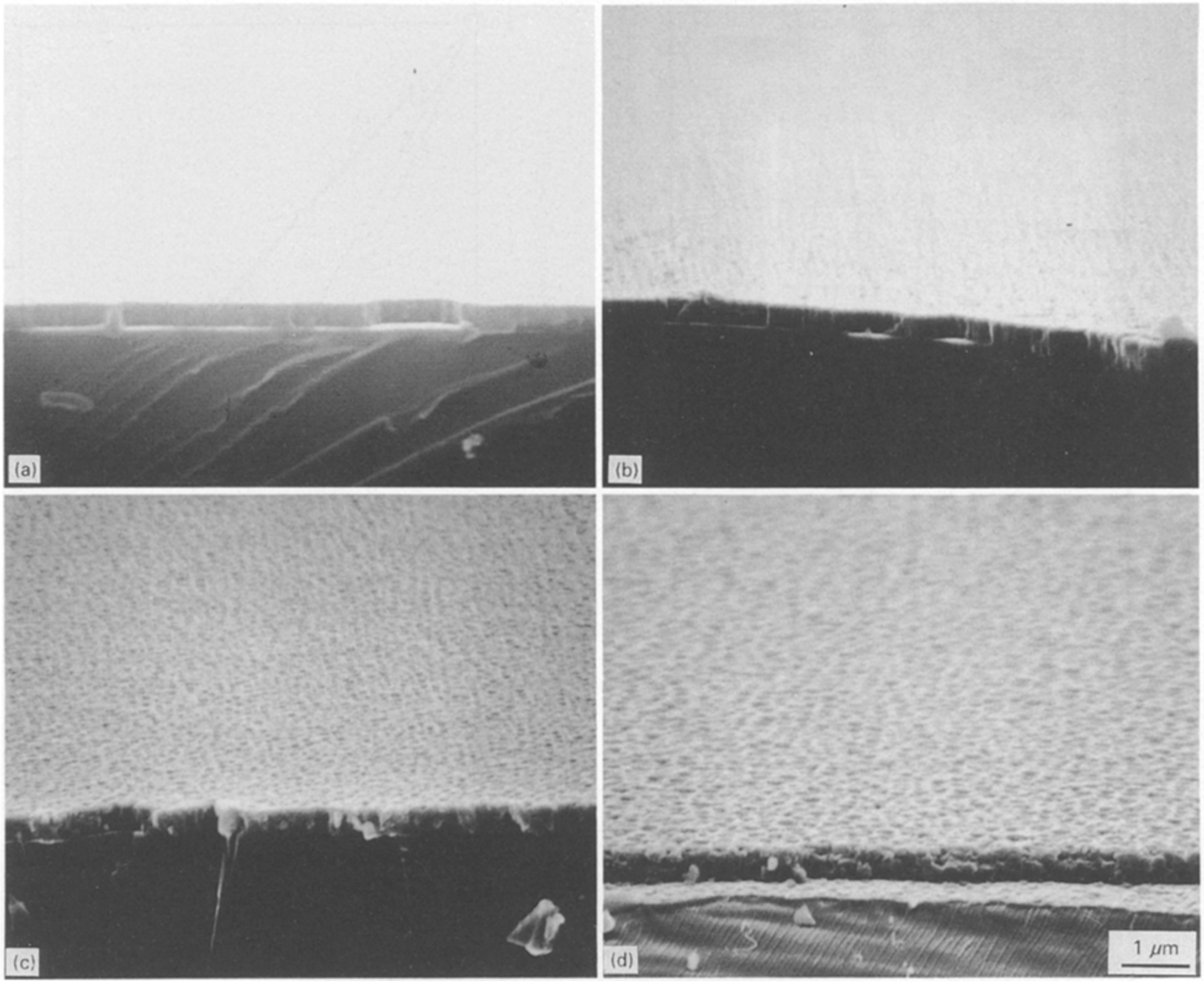

Figure 2 Scanning electron micrographs of edge profiles of TiO_2 coatings which were prepared from the precursor solutions: (a) without additives, and (b) 0.5 g, (c) 1.0 g, and (d) 2.0 g polyethylene glycol.

Fig. 3 shows visible spectra of TiO_2 coatings, which were prepared by using the various precursor solutions and repeating the cycle ten times, in the wavelength range 600–250 nm. The absorption edges of each coating were about 340 nm. The transmittance of TiO_2 coatings prepared from the precursor solution containing 2.0 g polyethylene glycol was very low, due to scattering of light by homogeneously distributed pores with diameters in the range 200–350 nm. Bands of interference colour were observed for the coatings prepared from the precursor solutions containing less than 2.0 g polyethylene glycol.

TiO_2 coatings, which were heated at 650 °C, as mentioned above, were single-phase anatase. The crystallite size of TiO_2 coatings heated at 650 °C was considered to be adjusted to a value adequate to show high photocatalytic activity on the basis of the data on TiO_2 powders [7]. The weight of the TiO_2 coating prepared by one cycle from withdrawing to heating was 0.0001 g, independently of the amount of polyethylene glycol. The weight of the TiO_2 coatings increased in proportion to the number of cycles.

Fig. 4 shows the results of photocatalytic measurements for TiO_2 coatings which were prepared by using the precursor solutions without and with polyethylene glycol and repeating the cycle ten times. It was found that acetic acid decomposed linearly with irradiation time on the surface of all TiO_2 coatings. Acetic acid decomposed effectively on TiO_2 coatings which were prepared from the precursor solutions containing 1.0 or 2.0 g polyethylene glycol. The morphology of TiO_2 coatings, i.e. many pores with diameters larger than 100 nm, resulted in enhancement of photocatalytic activity. It seems that the activity of photocatalytic decomposition of acetic acid is independent of the pore size in the range more than 100 nm in diameter.

Figs 5 and 6 show the results of the photocatalytic measurements for the porous TiO_2 coatings, which were prepared from the precursor solutions containing 1.0 and 2.0 g, respectively, of polyethylene glycol, with different thickness. For the porous TiO_2 coatings prepared from the precursor solution containing 1.0 g polyethylene glycol, the thickness which was obtained by repeating the cycle ten times was enough to enhance the photocatalytic activity for photo-excited decomposition of acetic acid. The photocatalytic activity of the relatively thick TiO_2 coatings prepared from the precursor solution containing 1.0 g polyethylene glycol was higher than that prepared from the precursor solution containing 2.0 g polyethylene

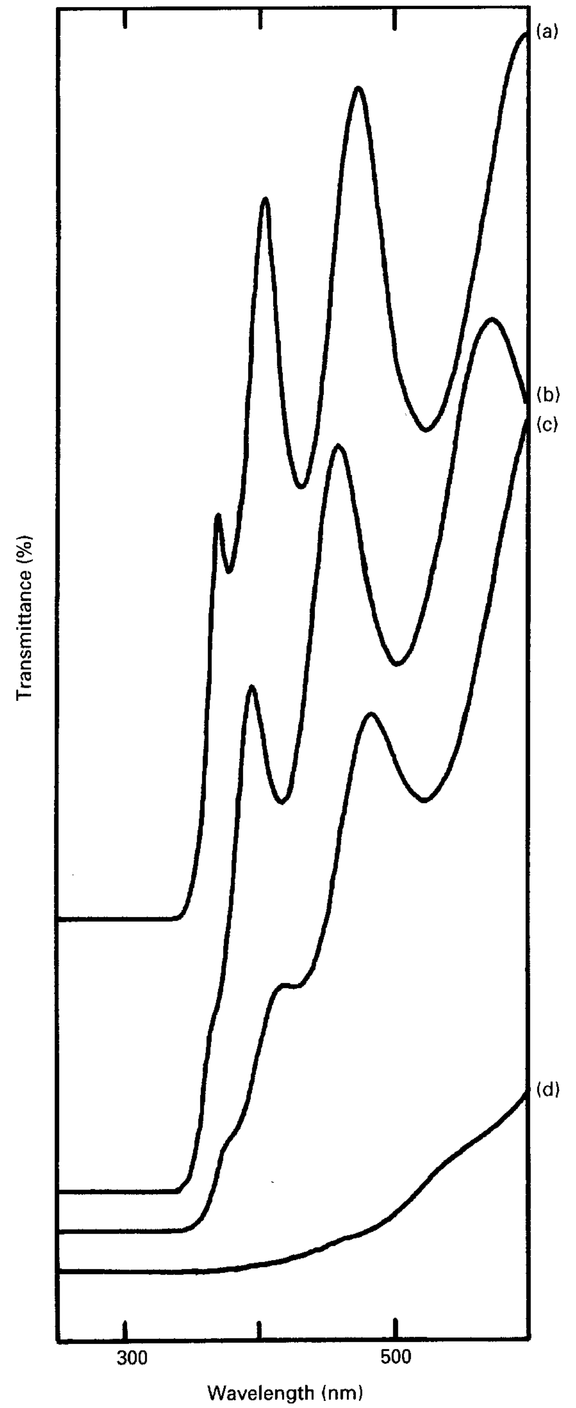

Figure 3 Visible spectra of TiO_2 coatings which were prepared by repeating the cycle ten times and using the precursor solutions: (a) without additives, and containing (b) 0.5 g, (c) 1.0 g, and (d) 2.0 g polyethylene glycol.

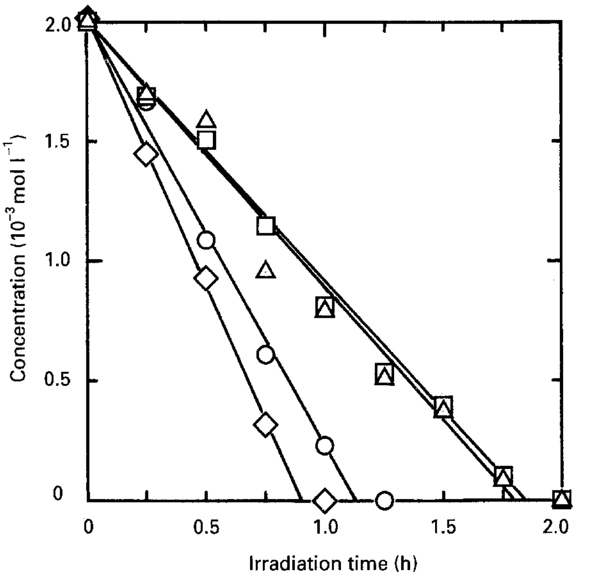

Figure 4 The relationships between the content of acetic acid and irradiation time for TiO_2 coatings which were prepared from the precursor solutions: (□) without additives, and containing (△) 0.5 g, (◇) 1.0 g, and (○) 2.0 g polyethylene glycol.

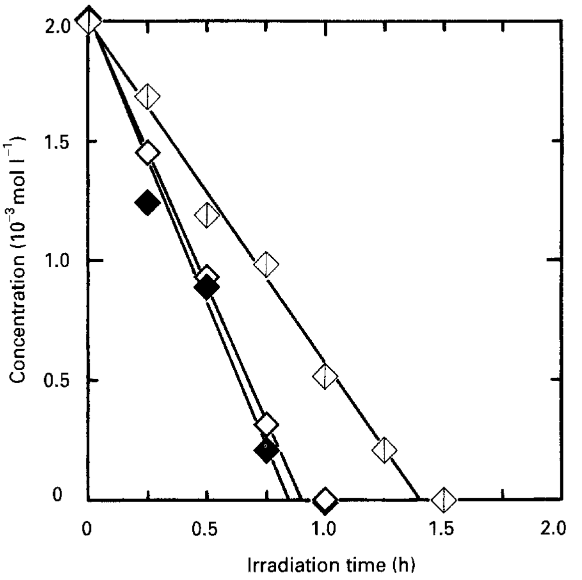

Figure 5 The relationships between the content of acetic acid and irradiation time for TiO_2 coatings with various thicknesses, which were prepared by using the precursor solution containing 1.0 g of polyethylene glycol and repeating the cycle (⟐) 5, (◇) 10, and (◆) 15 times.

glycol. These results indicate that the photocatalytic activity depends on both the distances to which light can sink in order to excite electron–hole pairs in TiO_2 coatings, and to which the reactant can reach to capture the electrons or the holes generated in TiO_2 coatings. The TiO_2 coating prepared from the precursor solution containing 2.0 g polyethylene glycol had relatively large pores and porous microstructure in the interior region. Therefore, the distance which the reactant reached was relatively great. It should be noted, however, that light did not sink as far due to scattering by the homogeneously distributed pores. Contrarily, for the porous TiO_2 coatings prepared from the precursor solution containing 1.0 g polyethylene glycol, light sank into the relatively continuous and transparent matrix. The electron–hole pairs generated, separated and then were effectively captured by the reactant.

Under dark conditions without irradiation, the content of acetic acid did not change for each measurement using various TiO_2 coatings.

4. Conclusion

The porous anatase coatings could be prepared from alkoxide solutions containing polyethylene glycol by

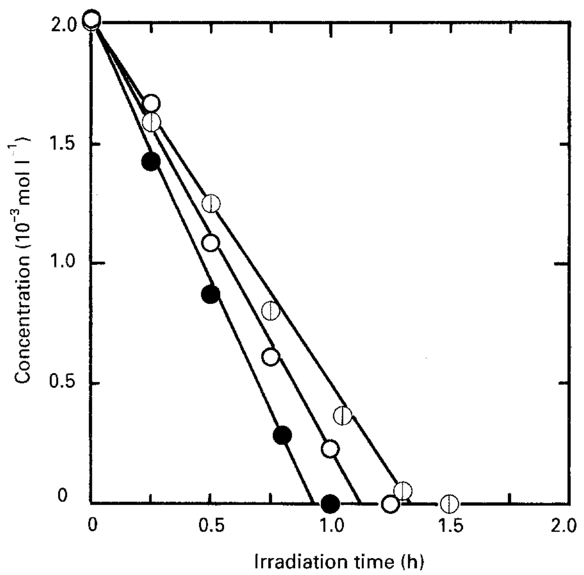

Figure 6 The relationships between the content of acetic acid and irradiation time for TiO_2 coatings with various thicknesses, which were prepared by using the precursor solution containing, 2.0 g polyethylene glycol and repeating the cycle (⦶) 5, (○) 10, and (●) 15 times.

the dip-coating technique. The number and size of pores was related to the amount of polyethylene glycol. It was found that the morphology of the porous anatase coatings, such as pore size, pore distribution and thickness, affected the photocatalytic activity. The thin anatase coatings, having homogeneously distributed pores with diameters in the range 100–150 nm, showed good photocatalytic activity for decomposition of aqueous acetic acid. The porous anatase coatings are expected to be applied to deodorization or purification of air and water.

References

1. D. F. OLLIS and H. AL-EKABI (eds), "Proceedings of the First International Conference on TiO_2 Photocatalytic Purification and Treatment of Water and Air", London, November 1992 (Elsevier Science, Amsterdam, 1993).
2. R. W. MATTEWS, *J. Phys. Chem.* **91** (1987) 3328.
3. M. TAKAHASHI, K. MITA, H. TOYUKI and M. KUME, *J. Mater. Sci.* **24** (1989) 243.
4. C. M.-RANDOLPH, A. J. MCEVOY and M. GRATZEL, *ibid.* **26** (1991) 3305.
5. T. YOKO, A. YUASA, K. KAMIYA and S. SAKKA, *J. Electrochem. Soc.* **138** (1991) 2279.
6. K. KATO, *Ceram. Trans.* **22** (1991) 63.
7. *Idem, Bull. Chem. Soc. Jpn* **65** (1992) 34.
8. *Idem, J. Ceram. Soc. Jpn* **101** (1993) 245.
9. T. KATO, Y. BUTSGAN, K. KATO, B. H. LOO and A. FUJISHIMA, *Denki Kagaku* **61** (1993) 877.
10. K. KATO, in "Proceedings of the First International Conference on TiO_2 Photocatalytic Purification and Treatment of Water and Air". London, November 1992, edited by D. F. Ollis and H. Al-Ekabi (Elsevier Science, Amsterdam, 1993) p. 809.
11. K. KATO, A. TSUZUKI, H. TAODA, Y. TORII, T. KATO and Y. BUTSUGAN, *J. Mater. Sci.*, in press.
12. T. YAZAWA, A. MIYAKE and H. TANAKA, *J. Ceram. Soc. Jpn* **99** (1991) 1094.
13. Y. TAKAHASHI and Y. MATSUOKA, *J. Mater. Sci.* **23** (1988) 2259.

Received 22 October 1993
and accepted 27 July 1994