

Crystal structures of TiO₂ thin coatings prepared from the alkoxide solution via the dip-coating technique affecting the photocatalytic decomposition of aqueous acetic acid

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TiO₂ coatings with different crystal structures were prepared from alkoxide solutions via the dip-coating technique. The physical properties, except the crystal structure, were adjusted to distinguish the effect of crystal structure on their photocatalytic property. The results of photocatalytic measurements using TiO₂ coatings with different crystal structures showed that the decomposition of aqueous acetic acid was enhanced by the content of anatase phase.

1. Introduction

Many studies on the photocatalysis have been carried out since the discovery in 1969 of the photo-sensitized electrolytic oxidation of water on the surface of rutile single crystal under light irradiation [1, 2]. Recently, many works have focused on applications of TiO₂ photocatalyst to purification and treatment of air and water [3–5].

Photocatalytic chemical reactions occurring on the surface of semiconductor materials depend on the process, which starts from absorption of light and results in attainment of photogenerated electrons and holes in the surface. The process is predominantly determined by fundamental physical properties of the materials. It is necessary for scientists handling photocatalysts to clarify the important factors of photocatalysts which affect the activity. A few chemists [6–8], who specialized in photocatalytic reactions, have shown interest in it.

We have discussed the relationships between physical properties of TiO₂ powders, which were prepared by hydrolysis of a titanium alkoxide, and photocatalytic properties for oxidation of organic compounds [9–12]. The crystallite size and the microstructure, rather than the specific surface area, of TiO₂ powders were found to affect the photocatalytic properties [10]. It was also noted that TiO₂ powders, which were transformed to rutile at high temperature, had large crystallite sizes, a microstructure consisting of agglomerated particles, and did not show such good photocatalytic properties. The effect of the crystal structure of TiO₂ powders on the photocatalytic property has not yet been distinguished.

Many papers have reported the preparation of functional coatings from alkoxide solutions via the dip-coating technique [13–17]. One of the advantages of the preparation of TiO₂ photocatalysts by this method is that TiO₂ is anchored easily on supports in complicated shapes. Another advantage is that the thin coatings crystallize to rutile phase at relatively low temperatures without any changes in the microstructures of the underlying layer of rutile phase. In this paper we discuss the preparation of TiO₂ coatings which have different crystal structures and also examine the primary effect of the crystal structure on the photocatalytic decomposition of acetic acid.

2. Experimental procedure

2.1. Preparation and characterization of TiO₂ coatings

Precursor solutions for TiO₂ coatings were prepared by following the method reported by Takahashi and Matsuoka [18] using titanium tetraisopropoxide, ethanol, water and diethanolamine. These reagents were used without purification or distillation. The concentration of the alkoxide in ethanol was 0.5 mol l⁻¹. The molar ratios of water and diethanolamine to the alkoxide were 1 and 2, respectively. The precursor solutions were transparent and were very stable in air. Quartz glass plates (20 mm × 20 mm × 1 mm) were used as the support substrates. TiO₂ 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 heat treated in air. Two heat cycling methods

were examined. One was heating at a fixed temperature for 1 or 24 h. The other one was a slow rise ($2^{\circ}\text{C min}^{-1}$) to an adequate temperature from 100°C and then treating at that temperature for 1 or 24 h. The thickness of the TiO_2 coatings was increased by repeating the trials from dipping to heating.

The crystallinity of TiO_2 coatings was identified by X-ray diffraction (XRD) method employing $\text{CuK}\alpha$ radiation. The accelerating voltage and applied current were 35 kV and 20 mA, respectively. The morphology and thickness of the TiO_2 coatings were observed using scanning electron microscopy (SEM) with an accelerating voltage of 25 kV. Spectroscopic analyses of TiO_2 coatings was performed using a spectrophotometer.

2.2. Measurement of the activity of TiO_2 coatings for photocatalytic decomposition of aqueous acetic acid

TiO_2 coating was settled in aqueous acetic acid with a concentration of 0.002 mol l^{-1} (120 p.p.m.) in a quartz cell ($20 \text{ mm} \times 30 \text{ mm} \times 3 \text{ mm}$). A high-pressure mercury lamp (100 W) was used as a light source. One face ($20 \text{ mm} \times 20 \text{ mm}$) of the TiO_2 coating was irradiated along the normal direction. 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

The crystal structures of the TiO_2 coatings depended on the heating cycle. TiO_2 coatings crystallized to mixed phases of anatase and rutile by heat treatment at 650°C . Single phase of rutile was prepared by heat treatment at a fixed temperature (750°C) for 24 h. TiO_2 coatings which were slowly heated to 1000°C and then kept at that temperature for 24 h were still single-phase anatase. It is thought that the coatings which were slowly heated crystallized under the influence of the substrate rather than the coating which was heated at a fixed temperature.

Transformation from anatase to rutile seemed to be suppressed due to a gradual expansion of the substrate owing to the slowly increasing temperature. Thick coatings were prepared by combining the heating cycles to control the crystal structure. Figs 1–3 show the XRD profiles of TiO_2 coatings, which were prepared by repeating various cycles three and ten times. Thick anatase coating was prepared by repeating the cycle from dipping to heating, which consisted of slowly increasing the temperature to 650°C and then treating for 1 h. Rutile coating was prepared by repeating the cycle from dipping to heating at a fixed temperature of 650°C for 1 h on an underlayer of rutile, which was first prepared on the substrate surface. The coating prepared by three cycles was single-phase rutile (Fig. 3a); however, the coating prepared by ten cycles contained a small amount of anatase (Fig. 3b). The heating temperature was determined as 650°C on the basis of the data for alkoxy-derived TiO_2 powder [9, 10]. It has been reported that the

TiO_2 powders heat treated at 600 or 700°C had a crystallite size in the range $20\text{--}30 \text{ nm}$ and a microstructure consisting of aggregates of individual fine particles without necking, and showed good photocatalytic properties. It should be noted that the surface regions of the coatings, where the thickness increased by this method, seemed to have similar values of

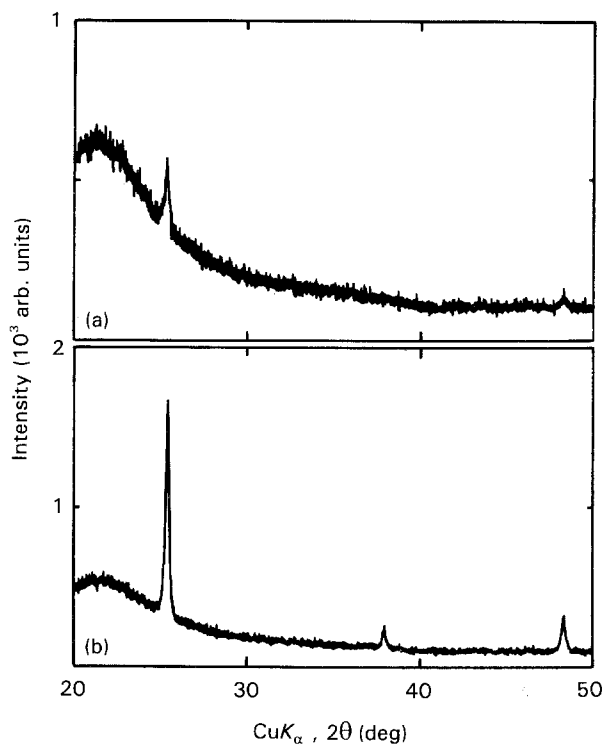


Figure 1 XRD profiles of TiO_2 coatings prepared by repeated cycles of dipping and heat treatment by increasing the temperature to 650°C and treating for 1 h, (a) three cycles, and (b) ten cycles.

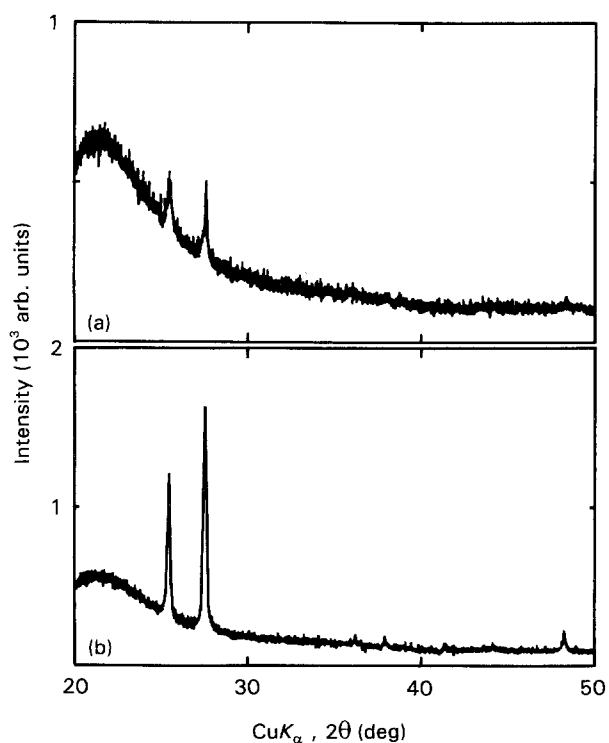


Figure 2 XRD profiles of TiO_2 coatings prepared by repeated cycles of dipping and heat treatment at a fixed temperature of 650°C for 1 h, (a) three cycles and (b) ten cycles.

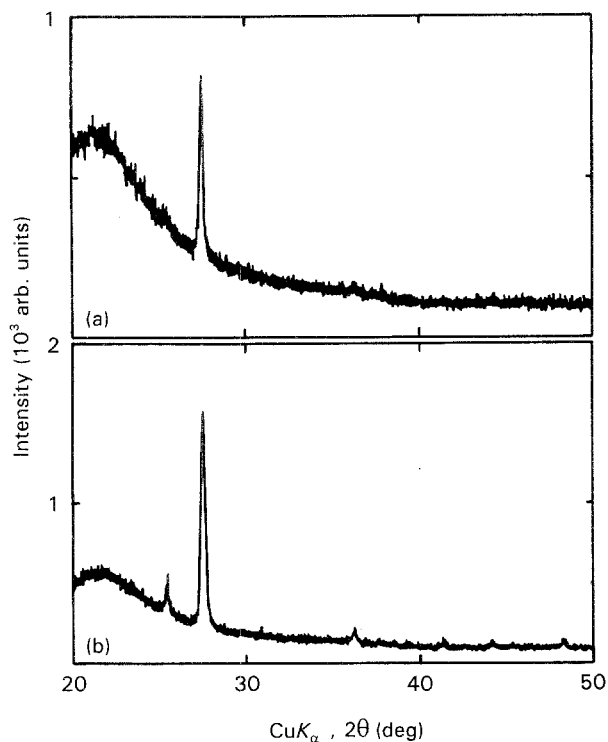


Figure 3 XRD profiles of TiO_2 coatings prepared by repeated cycles of dipping and heat treatment of heating at a fixed temperature of 650°C for 1 h, (a) two cycles and (b) nine cycles on an underlayer of rutile phase.

crystallite size to the TiO_2 powders and unnecked structures.

Fig. 4a and b are scanning electron micrographs of the surfaces of the coatings prepared by repeating different cycles ten times. There were no differences in the microstructures beyond the existence of cracks between these coatings. More cracks were generated in the coating which underwent a heat cycle at fixed temperatures higher than 650°C for 1 h, ten times. Both coatings had a granular texture. Careful observations indicated that the coatings consisted of very fine particles, the diameter of which was too small to measure exactly in the micrographs (about several tens of nanometres). The thickness was determined from scanning electron micrographs of edge profiles of coatings. The thickness of the coating prepared by repeating the cycle ten times was about 300 nm. Therefore, the thickness of the coating prepared by one cycle was found to be about 30 nm, and agreed with the crystallite size. The crystal structures of thick coatings are considered to depend upon the crystallization states of thin regions which are prepared by one cycle. A homogeneous texture rather than a layer structure was observed along the depth direction of the coatings.

Fig. 5a and b show typical visible spectra of TiO_2 coatings with different thicknesses in the wavelength range 600–250 nm. The absorption edge of the TiO_2 coating which was prepared by three cycles of dipping and heating to 650°C and treating for 1 h (as shown in Fig. 5a), was observed at a shorter wavelength range than that of the TiO_2 coating which was prepared by ten cycles (as shown in Fig. 5b). The shift is considered to occur due to the difference in development of

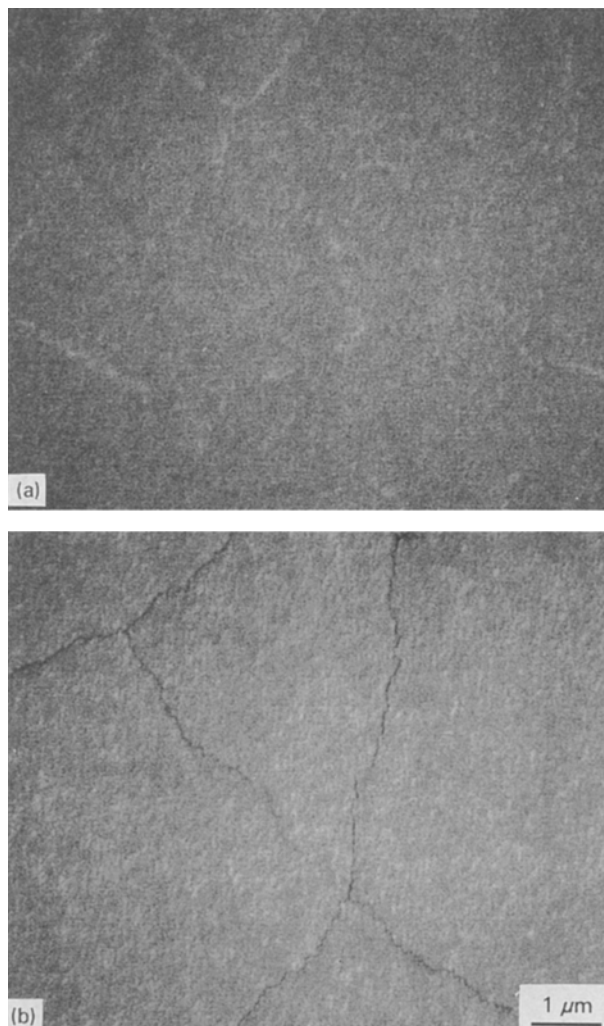


Figure 4 Scanning electron micrographs of the surface of TiO_2 coatings, (a) prepared by ten cycles of dipping and heat treatment on raising the temperature to 650°C and treating for 1 h, and (b) prepared by nine cycles of dipping and heat treatment at a fixed temperature of 650°C on an underlayer of rutile phase.

crystallites within the coating by repeating the cycles containing the heating process. The thin coating which underwent a short-term heat treatment, consisted of relatively small crystallites and showed pseudo-“blue shift” like fine particles [19, 20]. The bands due to the interference colour of the coating appeared in the wavelength range 600–370 nm. It was also observed that the absorption edge shifted to longer wavelength ranges with the transformation from anatase to rutile (Fig. 6a–c).

Fig. 7 shows the changes in the concentration of acetic acid contained in the solutions surrounding the TiO_2 coatings in different crystal phases with irradiation time. Decomposition of acetic acid proceeded in the surface of the TiO_2 coatings. In particular, the coating in single-phase anatase showed high activity. Acetic acid was decomposed completely in 2 h by the coating. Fig. 8 shows the results of blank tests. The change in the concentration of the solution surrounding the quartz glass substrates without coatings with irradiation agreed with that of the solution surrounding the TiO_2 coating without irradiation. These facts indicate that the decomposition of acetic acid proceeds via the photoexcited TiO_2 coatings. The increase in the concentration was caused by evaporation

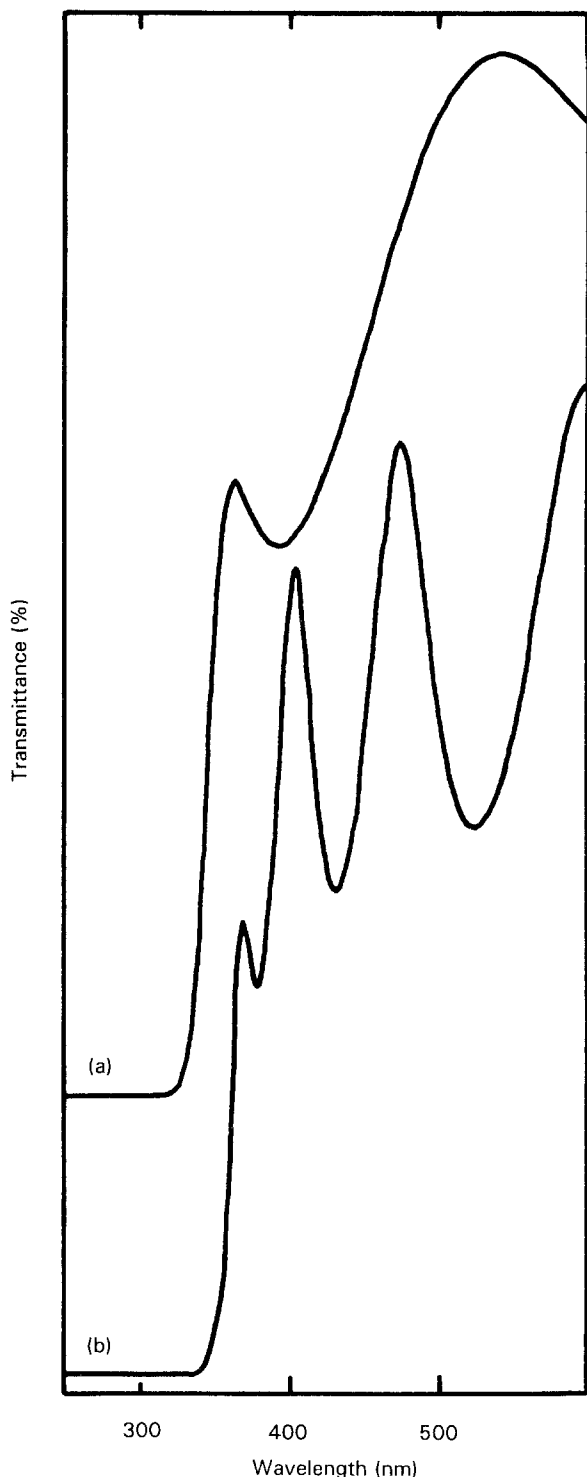


Figure 5 Visible spectra of TiO₂ coatings prepared by (a) three and (b) ten cycles of dipping and heat treatment on raising the temperature to 650 °C and treating for 1 h.

of water during the measurement. Fig. 9 shows the relationship between the fraction of anatase phase in the mixed phase and the percentage of decomposition of acetic acid after 1.5 h. The fraction ($I_a/(I_a + I_r)$) was determined from the intensities of the highest peaks (I_a = anatase, $2\theta = 25.3^\circ$, I_r = rutile, $2\theta = 27.5^\circ$) in the XRD profiles. The percentage decomposition of acetic acid increased with the fraction of anatase phase.

4. Conclusion

TiO₂ coatings with appropriate physical properties,

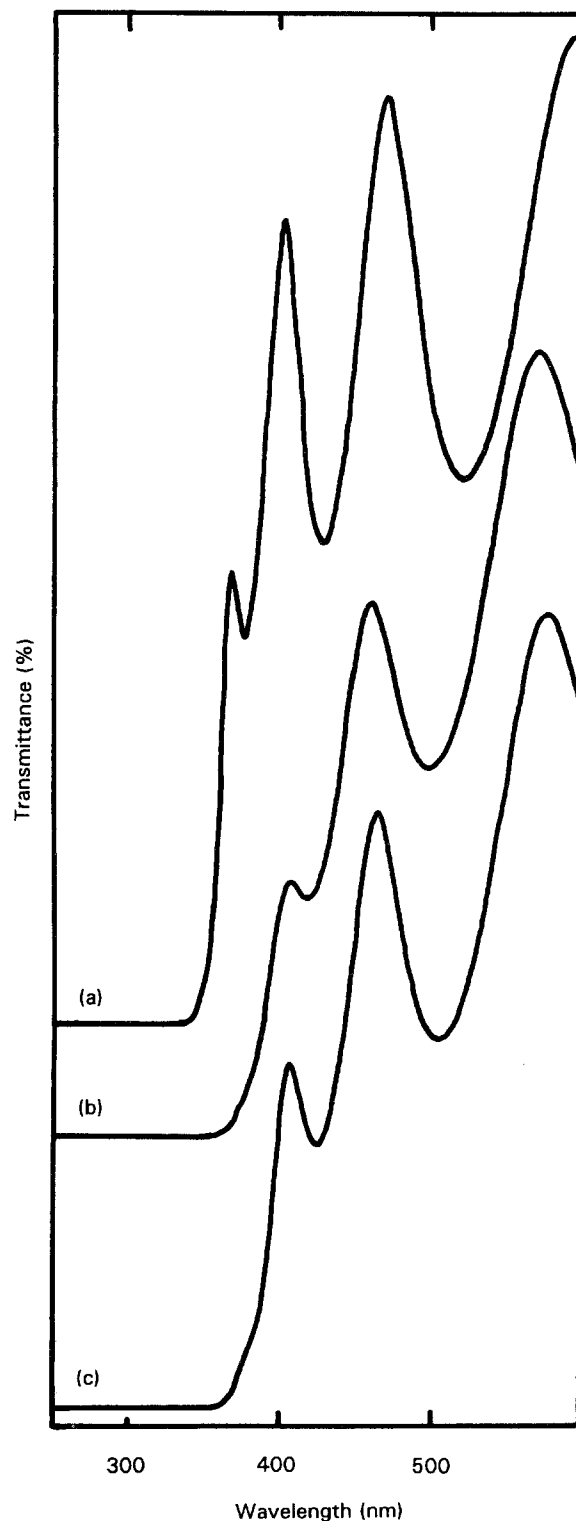


Figure 6 Visible spectra of various TiO₂ coatings. (a) TiO₂ coating prepared by ten cycles of dipping and heat treatment by raising the temperature to 650 °C and treating for 1 h, (b) TiO₂ coating prepared by ten cycles of dipping and heat treatment at a fixed temperature of 650 °C for 1 h, (c) TiO₂ coating prepared by nine cycles of dipping and heat treatment at a fixed temperature of 650 °C for 1 h, on an underlayer of rutile phase.

except the crystal structure, were prepared from alkoxide solutions via the dip-coating technique. The crystal structure of the TiO₂ coating was found to depend upon the crystallization of a thin layer, which was prepared by one cycle, and of which the thickness agreed with the crystallite size. The photocatalytic decomposition of acetic acid proceeded on the TiO₂

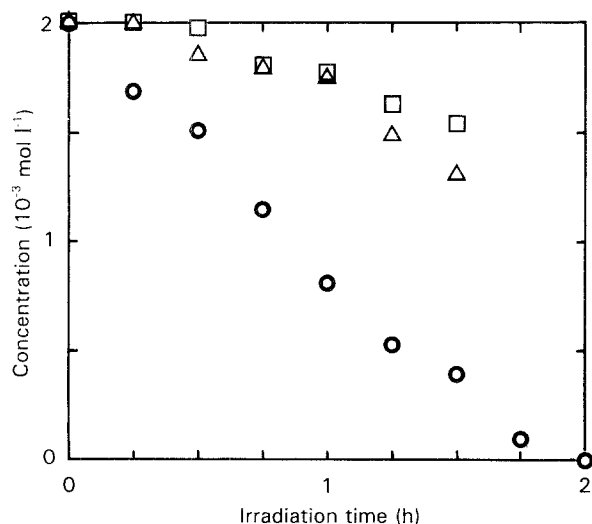


Figure 7 Changes in the concentration of acetic acid in the solutions surrounding various TiO₂ coatings with irradiation time. (○) TiO₂ coating prepared from ten cycles of dipping and heat treatment by raising the temperature to 650°C and treating for 1 h, (△) TiO₂ coating prepared from ten cycles of dipping and heat treatment at a fixed temperature of 650°C for 1 h, (□) TiO₂ coating prepared from nine cycles of dipping and heat treatment at a fixed temperature of 650°C for 1 h, on an underlayer of rutile phase.

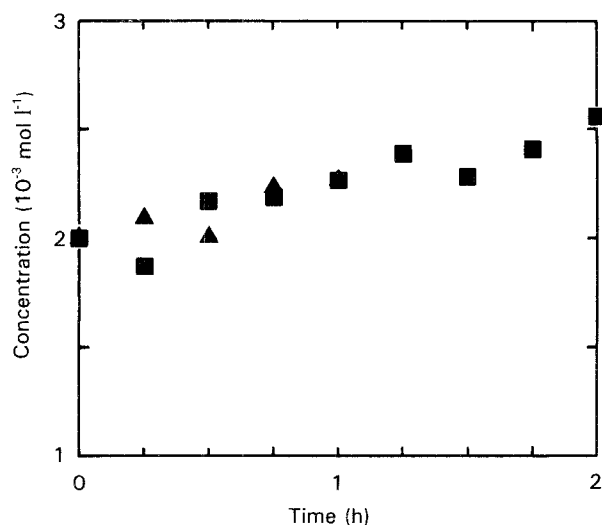


Figure 8 Changes in the concentration of acetic acid in the solutions surrounding (■) quartz glass substrates with irradiation, and (▲) the TiO₂ coating without irradiation, during bubbling with oxygen.

coatings. The effectiveness of the decomposition reaction increased with the content of anatase phase. Aqueous acetic acid in the concentration of 0.002 mol l⁻¹ (120 p.p.m.) decomposed completely in 2 h on the surface of the photoexcited TiO₂ coating in the anatase phase with a thickness of 300 nm. The TiO₂ coating in single-phase anatase was found to be an excellent photocatalyst for the decomposition of aqueous acetic acid.

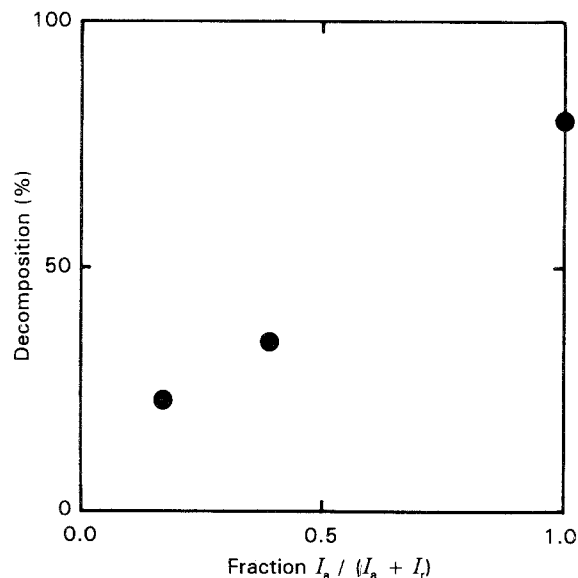


Figure 9 Relationship between the percentage decomposition of acetic acid after irradiation for 1.5 h and the fraction of anatase phase.

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