

Photocatalytic Activities of Coating Films Prepared from Peroxotitanic Acid Solution-Derived Anatase Sols

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ペルオキシチタン酸溶液から誘導したアナターゼソルで作製したコーティング膜の光触媒活性

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Anatase sols were prepared from peroxotitanic acid solution by heating at 100°C for 2-20h. The sols consisted of fine anatase particles of diameters less than 20 nm and arrowhead-like particles larger than 20 nm. The sols heated for 2-6h dispersed well, whereas the sols heated for 8-20h tended to aggregate. The powders obtained by drying the sols had high specific surface areas of 180 to 245 m²·g⁻¹. On photocatalytic degradation of a commercial vegetable oil on films prepared from the sols, the weight loss was approximated by the zero-order kinetics on the oil concentration at the early stage of the degradation. The film prepared from the sol heated for 6h showed a highest rate constant of 1.68 × 10⁻⁵ g·cm⁻²·h⁻¹ under ultraviolet light irradiation at 1.4 mW·cm⁻².

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1. Introduction

Photocatalysis on anatase (TiO₂) films have attracted much attention for applications to environmental self-purifications with ultraviolet (UV) light.¹⁻³⁾ Although a number of agents for anatase coatings have been on the market, these agents have several disadvantages; strong acidity, high coating temperatures required, and so on. We have reported that peroxotitanic acid (PTA) solutions and peroxy-modified anatase (PA) sols are neutral in pH, impurity-free, and suitable for low-temperature coating of anatase films as a photocatalyst.⁴⁻⁶⁾ The adhesion and the density of the films prepared from the PTA solution were very high, while the photocatalytic decomposition of acetic acid on the films prepared from the PA sol was very fast.⁵⁾

The PA sol was synthesized by heating the PTA solution at 100°C for 6h, and it contained well-dispersed ultrafine anatase particles (9 nm) in spite of being neutral in pH. This is because of existence of the peroxy groups on their surfaces.⁴⁾ The anatase particles aggregated with heating above 120°C for 6h owing to decomposition of the peroxy groups, and it was very difficult to use them as a coating agent. The preparation conditions of the PA sols can be optimized, if conversion of the PTA solution into the PA sol and grain growth of the anatase particles can easily be controlled by only changing the heating time at 100°C.

In the present study, the anatase sols were prepared by heating the PTA solution at 100°C for various periods of time. In order to investigate the relationship between the heating time and the photocatalytic activity, the degradation of a vegetable oil under UV light was examined on the films prepared from these sols.

2. Experimental

The preparation procedure of the PTA solution was reported previously.⁴⁾ The PTA solution was heated to 100°C and kept at that temperature for 2, 4, 6, 8, 10 and 20h, and the anatase sols thus obtained were termed 2A, 4A, 6A, 8A, 10A and 20A, respectively. The morphologies of particles in the sols were observed by a transmission electron microscope (TEM; JEM-2010, JEOL). The powders obtained by drying the sols were identified by powder X-ray

diffraction (XRD) using an X-ray diffractometer (Geigerflex RAD-B, Rigaku). The crystallite size, $D_{(101)}$, was calculated using Scherrer's formula from FWHM of the (101) peak of anatase. The specific surface areas of the sols dried at 60°C were measured with a BET specific surface area meter (Auto-sorb 1, Yuasa Ionics).

The anatase sols and a commercial anatase sol (A-6, Taki Chemical Co., Ltd.; BET specific surface area: 127 m²·g⁻¹, anatase crystallite size: 17 nm) were used as coating agents. Films were prepared by dipping borosilicate glass substrates (75 × 25 × 1 mm) in the sols and were dried in air at 50°C for 10 min. This procedure was repeated several times to obtain films of about 1 μm in thickness. Finally, the films were heated in air at 60°C for 30 min. For some of the samples, heat treatment at 200°C and 400°C was performed. Since anatase particles aggregated in 8A, 10A and 20A, the films were prepared by using the sols after sonication for 30 min. The film thickness was measured by scanning electron microscope (SEM; JXA-840, JEOL) observation and conventional interference analysis⁷⁾ using a UV-visible spectrophotometer (UV-2100, Shimadzu). The photocatalytic activities of the films were evaluated by measuring the weight change of a commercial vegetable oil (Benibana Foods Co., Ltd.; oleic acid: 75 mass%, other unsaturated fatty acid: 17 mass%, saturated fatty acid: 8 mass%) on the film as a function of the irradiation time with a black fluorescent light. UV light flux was 1.4 mW·cm⁻² (320-390 nm). The initial weight of the oil was about 0.1 mg·cm⁻². The temperature was kept at 21 ± 1°C. The relative humidity was 55 ± 5%.

3. Results and discussion

During heating of the PTA solution to prepare the anatase sols, a yellow color owing to the peroxy groups lightened with the heating time, and disappeared after heating for 10h. 2A and 4A were transparent, 6A was translucent, and aggregation of anatase particles occurred in 8A, 10A and 20A. It was reported previously that the peroxy groups were detected in 6A by FT-IR analysis and these groups promoted the dispersion of the ultrafine anatase particles generated in the sols.⁴⁾ However, the

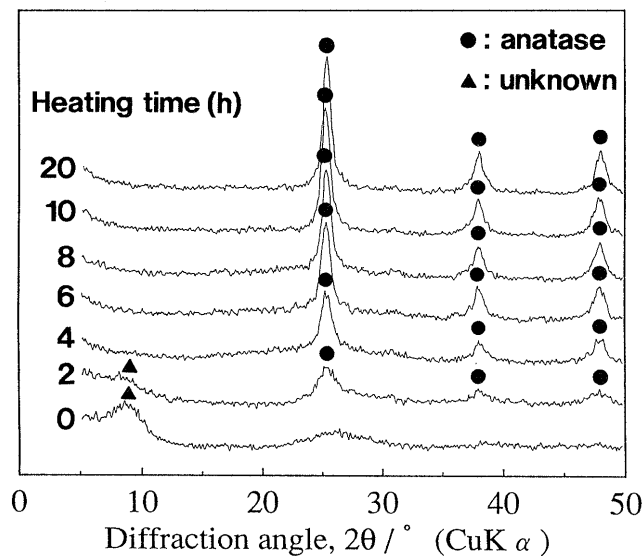


Fig. 1. XRD patterns for the powders obtained by drying the sols prepared by heating the PTA solution at 100°C for various periods of time.

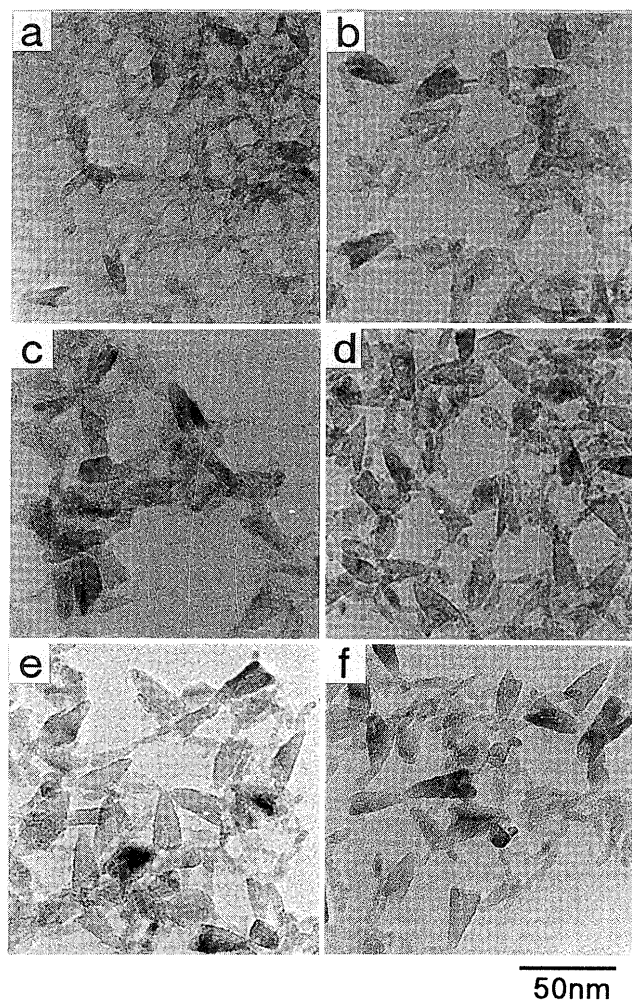


Fig. 2. TEM photographs of anatase particles in the sols obtained by heating the PTA solution at 100°C for (a) 2, (b) 4, (c) 6, (d) 8, (e) 10 and (f) 20h.

peroxy groups could not be detected in the sols heated for 8–20h. It was, therefore, presumable that the aggregations in 8A, 10A and 20A were due to decomposition of the peroxy groups by heating.

The XRD patterns for the powders obtained by drying the sols are shown in Fig. 1. PTA and 2A showed a broad hump around 8 degrees of 2θ . Anatase was precipitated by heating the solutions for 2–20h. For the heating times longer than 4h, only the anatase phase was detected. The TEM images of the sols are shown in Fig. 2. The sols consisted of fine anatase crystals of diameters less than 20 nm and arrowhead-like crystals larger than 20 nm. The arrowhead-like particles increased in size with increasing heating time. The anatase crystallite sizes, $D_{(101)}$, and the specific surface areas of the dried powders are shown in Fig. 3. $D_{(101)}$ increased with the heating time; from 5.3 nm (2h) to 12.5 nm (20h). The specific surface areas of the powders decreased from 245 down to 180 $\text{m}^2 \cdot \text{g}^{-1}$, but they were still larger than that of a commercial anatase sol A-6 (127 $\text{m}^2 \cdot \text{g}^{-1}$).

Photocatalytic degradation of the vegetable oil on the films prepared from the sols and finally heated at 60°C are shown in Fig. 4 as a function of UV light irradiation time.

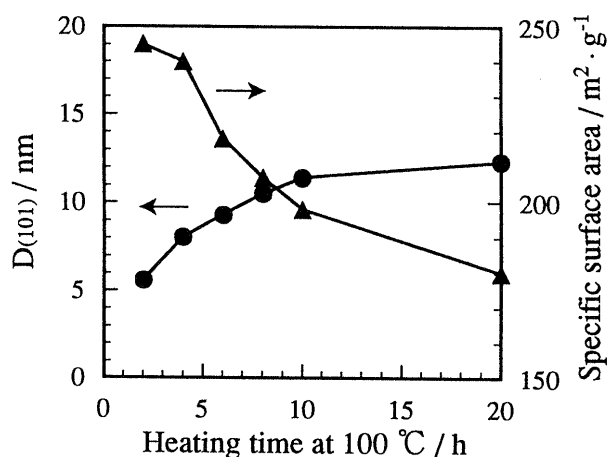


Fig. 3. Anatase crystallite sizes, $D_{(101)}$, and the specific surface areas of the dried powders as a function of the heating time of the PTA solution.

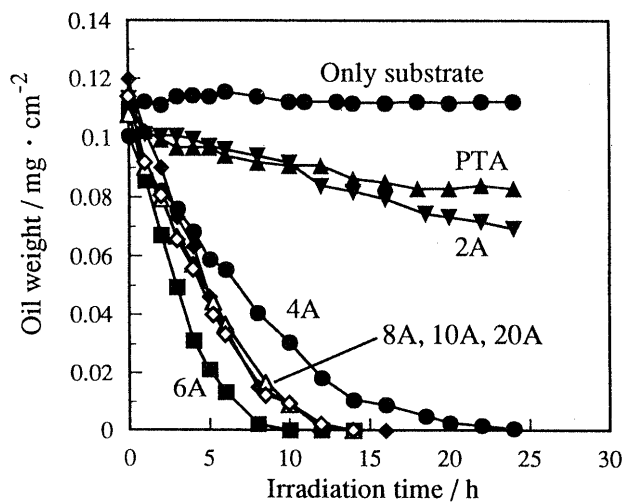


Fig. 4. Photocatalytic degradation of a vegetable oil on the anatase films dried at 60°C as a function of the UV light irradiation time. UV light flux: $1.4 \text{ mW} \cdot \text{cm}^{-2}$.

The 6A film completely removed the oil with the UV light irradiation for 10h, and turned out to have the highest photocatalytic activity. At the early stage of the photocatalytic degradation of the oil, the weight change showed a linear decay. This means that the rate of the weight loss is independent of the oil concentration on the film since the concentration of the oil was too high as compared to the incident photon flux.⁸⁾ The weight loss can, therefore, be approximated by the zero-order kinetics, and hence the rate equation is described as follows:

$$C = -kt + C_0 \quad (1)$$

where C is the oil weight per unit area, k is the zero-order rate constant of the weight loss, t is the time and C_0 is the initial oil weight per unit area. At the later stage of the photocatalytic degradation of the oil, the weight change did not show a linear decay. This is probably because the weight loss at the early stage of the photocatalytic degradation would be due to volatilization of the oil partially decomposed.

On the other hand, although the PTA film should not have the photocatalytic activity, the weight of the PTA film decreased with UV light irradiation. Figure 5 shows the weight changes of the films themselves prepared from PTA, 2A, 4A and 6A and finally heated at 60°C as a function of the UV light irradiation time. The weight of the films prepared from PTA, 2A, 4A and 6A decreased by UV light irradiation. A light-yellow color of the PTA films disappeared after the irradiation for 10h. This was probably because the peroxy groups in the films were decomposed by UV light irradiation, releasing water or oxygen gas. Therefore, the weight changes for PTA, 2A, 4A and 6A films in Fig. 4 partially include the weight loss of the films themselves. On the other hand, the weight of the films prepared from 8A, 10A, 20A and a commercial anatase sol (A-6) did not change.

The zero-order rate constants for the weight losses via the photocatalytic degradation of the oil on the films are shown in Fig. 6. The weight changes of the oil on the PTA, 2A and 4A films were corrected with the weight changes of the films themselves. It was found that the 6A film showed a highest rate constant ($1.68 \times 10^{-5} \text{ g} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$). This is probably because the specific surface area of 6A is higher than those of 8A, 10A and 20A. The low photocatalytic activities of 2A and 4A films were probably due to the insufficient conversion of 2A and 4A from PTA to the anatase phase.

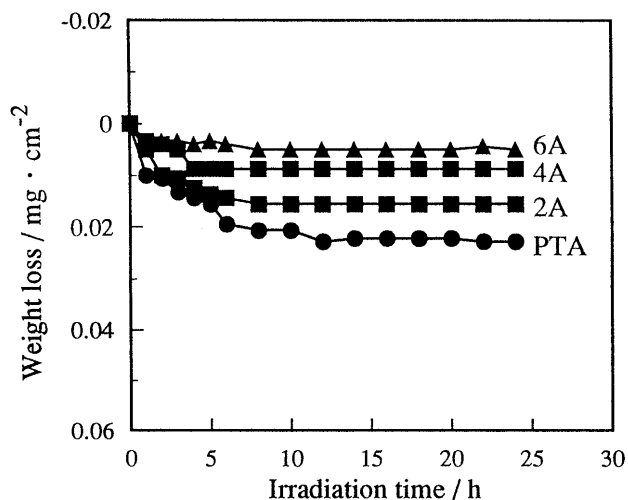


Fig. 5. Weight loss of the films prepared from the PTA solution, 2A, 4A and 6A at 60°C as a function of the UV light irradiation time. UV light flux: $1.4 \text{ mW} \cdot \text{cm}^{-2}$.

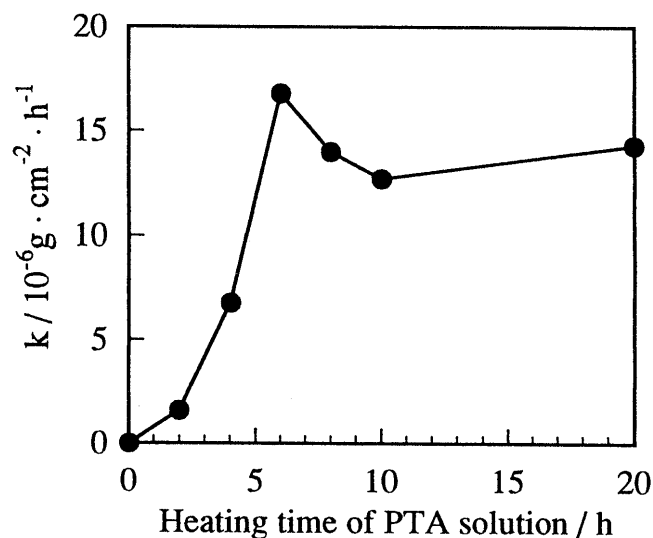


Fig. 6. The zero-order rate constants (k) for the weight loss via photocatalytic degradation of the vegetable oil on the anatase films prepared at 60°C as a function of the heating time of the PTA solution. UV light flux: $1.4 \text{ mW} \cdot \text{cm}^{-2}$.

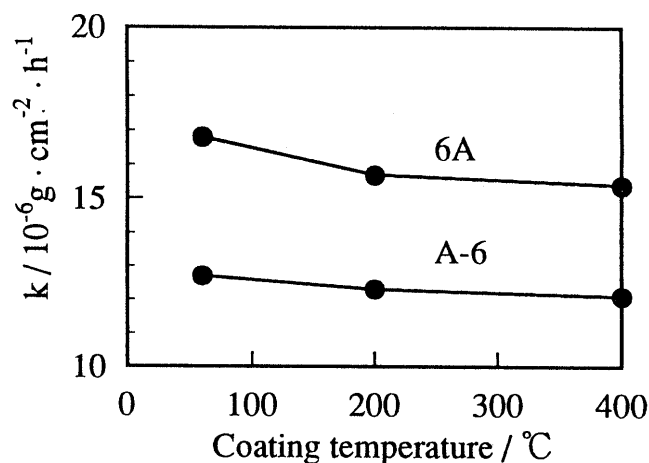


Fig. 7. The zero-order rate constants (k) for the weight loss via photocatalytic degradation of the vegetable oil on the films coated from 6A and commercial anatase sol (A-6) as a function of the coating temperature. UV light flux: $1.4 \text{ mW} \cdot \text{cm}^{-2}$.

The zero-order rate constants for the weight losses of the oil on the films prepared from 6A and a commercial anatase sol (A-6) and finally heated at 60–400°C are shown in Fig. 7. The rate constants for 6A was higher than that for A-6. This is probably because the specific surface area of 6A ($218 \text{ m}^2 \cdot \text{g}^{-1}$) is higher than that of A-6 ($127 \text{ m}^2 \cdot \text{g}^{-1}$). The high reaction rate for the 6A film was kept within the final heat treatment temperature range of 60 to 400°C. In the previous paper,⁵⁾ the 6A film showed strong adhesion even when heated at temperatures lower than 300°C. Therefore, 6A is expected to be a very useful coating agent for the photocatalytic applications to metals, glass, plastics and so on.

4. Summary

We studied the properties of the anatase sols obtained by heating the PTA solution at 100°C for 2 to 20h and the photocatalytic activities of the films prepared from the sols for the vegetable oil degradation, obtaining the following results:

(1) Well-dispersed anatase sols were obtained by heating the PTA solution at 100°C for 2–6h.

(2) The sols consisted of fine particles smaller than 20 nm and arrowhead-like particles larger than 20 nm, and had high specific surface areas (180–245 m²·g⁻¹).

(3) The photocatalytic weight losses of the vegetable oil on the films prepared from the sols obeyed the zero-order kinetics.

(4) The film prepared from 6A showed the highest photocatalytic reaction rate, which was slightly lowered by increasing final heat treatment temperature up to 400°C.

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