

Porous anatase layer formed on titanium substrate through hydrothermal processes

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Abstract A titanium oxide layer containing crystalline anatase was formed on a titanium substrate under hydrothermal conditions. The titanium substrate was reacted in alkaline solutions, potassium hydroxide and a mixture of potassium hydroxide and calcium chloride, at over 120 °C. Potassium titanate and calcium titanate were formed on the substrate and they showed the typical texture of each titanate, the aggregate of the fibrous and the cubic particles, respectively. The layers of calcium titanate and the potassium titanate changed into a titanium oxide layer in a solution of the hydrochloric acid at 180 °C. Both the potassium and the calcium dissolved from the titanate and then the formed amorphous titanium oxide finally crystallized. The fibrous structure of the potassium titanate did not remain after the acid treatment, although the cubic microstructure of calcium titanate remained. Both samples were mainly composed of fine anatase and the grain size and the crystallite size were almost 40–50 nm and 10 nm, respectively. The photocatalytic degradation of gaseous acetaldehyde by the titanium oxide layer was observed under irradiation of UV light.

Introduction

It has been expected photocatalysts will have practical uses in the decontamination of atmosphere and water, deodorization, disinfection, antifouling, and so on. Titanium dioxide has been used as a photocatalyst because of its high photocatalytic activity and chemical stability [1]. When UV irradiated anatase, which is a type of crystalline titanium oxide, electrons were lost and electrical holes generated near its surface. The holes joined hydroxide or oxygen to the surface of the anatase, producing a hydroxide radical or oxygen radical. These radicals oxidized harmful organic matter, converting it to carbon dioxide and water. In order to use a photocatalyst, the permeability of UV radiation, the pore structure and the specific surface area must be considered, and therefore the particle size and the crystalline size of the anatase should be much smaller than the UV wavelength. When used as a photocatalyst, fine powders of anatase were usually coated on a substrate with a type of organic binder, although the binders retrograded with the irradiation of UV and the photocatalytic action.

Thin layers of titanium oxide have been formed through solution processes [2–4]. In some cases, fine titanium oxide crystals dispersed in solution, or titanium oxide sols were coated on a substrate and then dried or calcined to form film. The advantage of this method was to produce a coating at room temperature, although a higher temperature was required to crystallize titanium dioxide. Preparation of anatase film at relative low temperature was investigated as a coating on titanium and titanium alloys applied to biomaterials. Wu et al. [5] reported that anatase crystallized at 80 °C by combining different solution processes. In our previous study, a porous anatase layer was formed on a titanium substrate using inexpensive materials by two hydrothermal steps [6]. First, a calcium titanate layer was

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formed on a titanium substrate. Second, the calcium titanate coating was dissolved in hydrochloric acid solution at 180 °C, and the remaining amorphous titanium oxide crystallized to anatase. The adhesion between the anatase layer and the substrate was improved by using a thin calcium titanate coating to form the anatase layer, although it was not easy to control the thickness of the calcium titanate film because of its characteristic rough morphology, which consisted of cubic grains. We also synthesized potassium titanate film with smaller roughness in order to form a smooth thin anatase layer with good adhesion to the substrate [7].

In this study, we synthesized the titanium oxide layer on the titanium substrate by treating with alkaline solutions and acid solutions under several conditions. We also reported their photocatalytic activity, and discussed the effect of the preparation conditions on the phase, morphology and photocatalytic activity.

Experimental methods

Preparation of titanium oxide films

Titanium metal substrates (Ti 99.5 wt%: Nilaco Co. Ltd., Japan) with dimensions of $10 \times 40 \times 0.05 \text{ mm}^3$ were washed in acetone with an ultrasonic cleaner and dried in air. Reagent grade potassium hydroxide (KOH: Kanto Chemical Co. Ltd., Japan) and calcium chloride (CaCl_2 : Wako Pure Chemical Industries Ltd., Japan) were used as starting materials. They were dissolved in distilled water to prepare stock solutions. Each substrate was set in a 50 cm^3 Teflon-lined stainless steel autoclave with 20 cm^3 of solution. Two solutions were used in this study. First was a KOH solution of $1.8 \text{ mol} \cdot \text{dm}^{-3}$ concentration, and second was a mixed solution of $0.025 \text{ mol} \cdot \text{dm}^{-3}$ CaCl_2 and $1.7 \text{ mol} \cdot \text{dm}^{-3}$ KOH. The autoclaves were rotated at temperatures from 150 to 180 °C under saturated vapor pressure for 1–48 h (hereafter referred to as the alkaline treatment).

After rinsing in distilled water using an ultrasonic cleaner and drying at 70 °C for 24 h, the samples were set in the autoclave with 20 cm^3 of the aqueous solutions of hydrochloric acid (HCl; Wako Pure Chemical Industries Ltd., Japan) at temperatures from 150 to 180 °C for 3–48 h. The pH of the treated solution was adjusted (at 20 °C) from 1.0 to 2.0 (acid treatment).

Characterization

The substrates were weighed before and after each treatment. Synthesized layers were analyzed by thin film X-ray diffraction (TF-XRD: X'Pert-MPD-PW3050, Philips, Netherlands) using Cu radiation to identify the crystalline

phases. The morphology of the film was observed by a scanning electron microscope (SEM: JSM-5310, JEOL, Japan) and a field emission scanning electron microscope (S-800, HITACHI, Japan).

The photocatalytic degradation of acetaldehyde by the titanium oxide layer was analyzed at 20 °C. The titanium oxide layer was prepared on titanium substrates with dimensions of $20 \times 50 \times 0.05 \text{ mm}^3$ for the measurement. Five substrates prepared under the same conditions were placed in the Pyrex glass reactor with a capacity of $1,000 \text{ cm}^3$ in a dry booth. Gaseous acetaldehyde of 40 ppm was introduced into the reactor. After the reactor was left in the dark for 30 min, the concentration of the acetaldehyde was measured as a function of the irradiation time under UV light using a black light. The intensity of the irradiation was $1.2 \text{ mW} \cdot \text{cm}^{-2}$.

Results and discussion

Formation of titanium oxide layer

Figure 1 shows the TF-XRD patterns of the substrate after the alkaline treatment and the acid treatment. Titanates were formed on the substrate after the alkaline treatment. Layers of potassium titanate and calcium titanate formed at 150 °C for 24 h in the solutions of $1.8 \text{ mol} \cdot \text{dm}^{-3}$ KOH and the mixed solution of $1.7 \text{ mol} \cdot \text{dm}^{-3}$ KOH and $0.025 \text{ mol} \cdot \text{dm}^{-3}$ CaCl_2 , respectively. After the acid treatment with HCl solution (pH 2.0 at 20 °C) at 180 °C for 24 h, both titanates decomposed and a crystalline titanium oxide layer formed on the titanium substrate. From the TF-XRD patterns after the acid treatment, the major

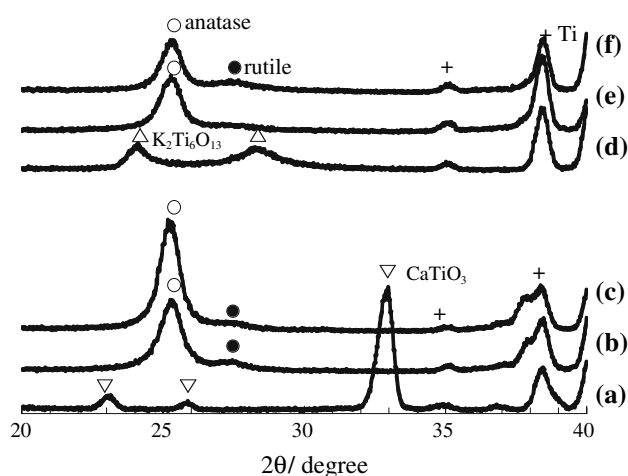


Fig. 1 TF-XRD patterns of the substrate after the alkaline treatment using; (a) mixed solution of CaCl_2 and KOH, (d) KOH at 150 °C for 24 h, and after the acid treatment at 180 °C of (a) for (b) 24 h, (c) 48 h, and of (d) for (e) 24 h, (f) 48 h

phase was anatase, and the crystallite size seemed to be very small or the crystallinity seemed to be low. The crystallite sizes were estimated to be about 10 nm from the full width at half maximum of the XRD patterns. In some samples, rutile also formed and the TF-XRD patterns were broader than for anatase. In our previous study, the formation of rutile had begun by 24 h and increased with the duration of the acid treatment [7].

The SEM photographs of the alkaline-treated layers before and after the acid treatment are shown in Fig. 2. The calcium titanate layer was composed of euhedral cubic grains and a stepped surface (Fig. 2a), whereas the potassium titanate layer looked like a porous aggregate composed of fibrous particles. After the acid treatment, the cubic frames of the calcium titanate grains remained although the fibrous structure of the potassium titanate layer was not observed. The titanium oxide layer was an aggregate of round grains and their sizes were about 40–50 nm, in spite of the kind of precursor titanate.

Effect of the treating conditions

During the alkaline treatment, the surface of the titanium substrate was attacked by the alkaline solution at elevated temperature and part of the substrate dissolved. In a second process, the dissolved titanium reacted with the potassium ions or the calcium ions to form the potassium titanate layer or the calcium titanate layer on the substrate.

Figure 3 shows the change in the weight of the substrate during the alkaline treatment in KOH solution at various temperatures. The weight of the substrate decreased with the duration of treatment until 1 h. The weight of the substrate increased rapidly with the duration by the deposition of the titanate on the substrate at 180 °C between 1 and 6 h, and then the increase in deposition was more gradual after 6 h. On the other hand, at 80 and 150 °C after

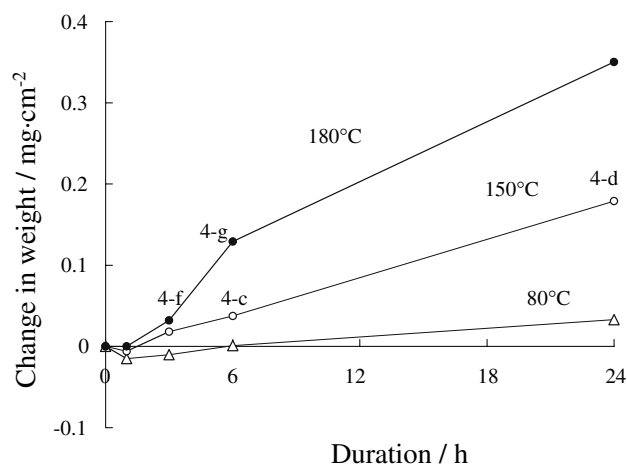


Fig. 3 Change in weight of the substrate during the alkaline treatment in $1.8 \text{ mol} \cdot \text{dm}^{-3}$ KOH solution at various temperatures

1 h, the amount of titanate increased gradually as the deposition rates were almost constant. The weight loss of the substrate, to its minimum weight at 1 hr, reduced with increasing reacting temperature. Potassium titanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$) was detected by XRD analysis after the reaction in KOH solution at 180 °C for 1 h, although no crystalline phase was detected by XRD on the surface of the titanium substrate treated at 80 and 150 °C for the same duration. The formation of the titanate layer and the dissolution of the titanium substrate were also accelerated by the higher temperature.

Figure 4 shows the SEM photographs of the samples after the alkaline treatment for various reacting durations. The left and the right photographs were the surface of the samples obtained at 150 °C and at 180 °C, respectively. Fibrous particles of the potassium titanate were not recognized at 150 °C for 1 h as shown in Fig. 4a. Porous aggregation of the fibrous particles formed on the substrate

Fig. 2 SEM photographs of the synthesized layers. (a); calcium titanate (synthesized at 150 °C for 24 h), (b) and (c); after the acid treatment of calcium titanate layer (HCl, at 180 °C for 24 h), (d); potassium titanate (synthesized at 150 °C for 24 h), (e) and (f); after the acid treatment of potassium titanate layer (HCl, at 180 °C for 24 h)

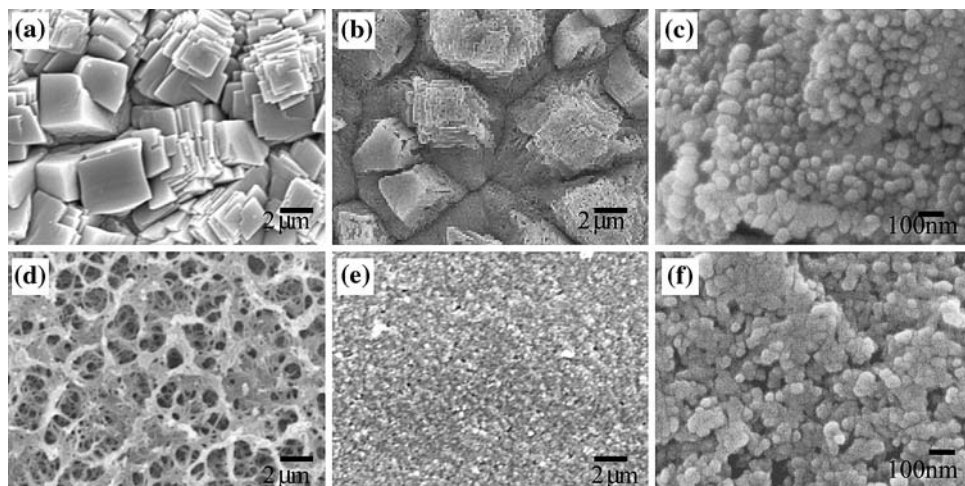
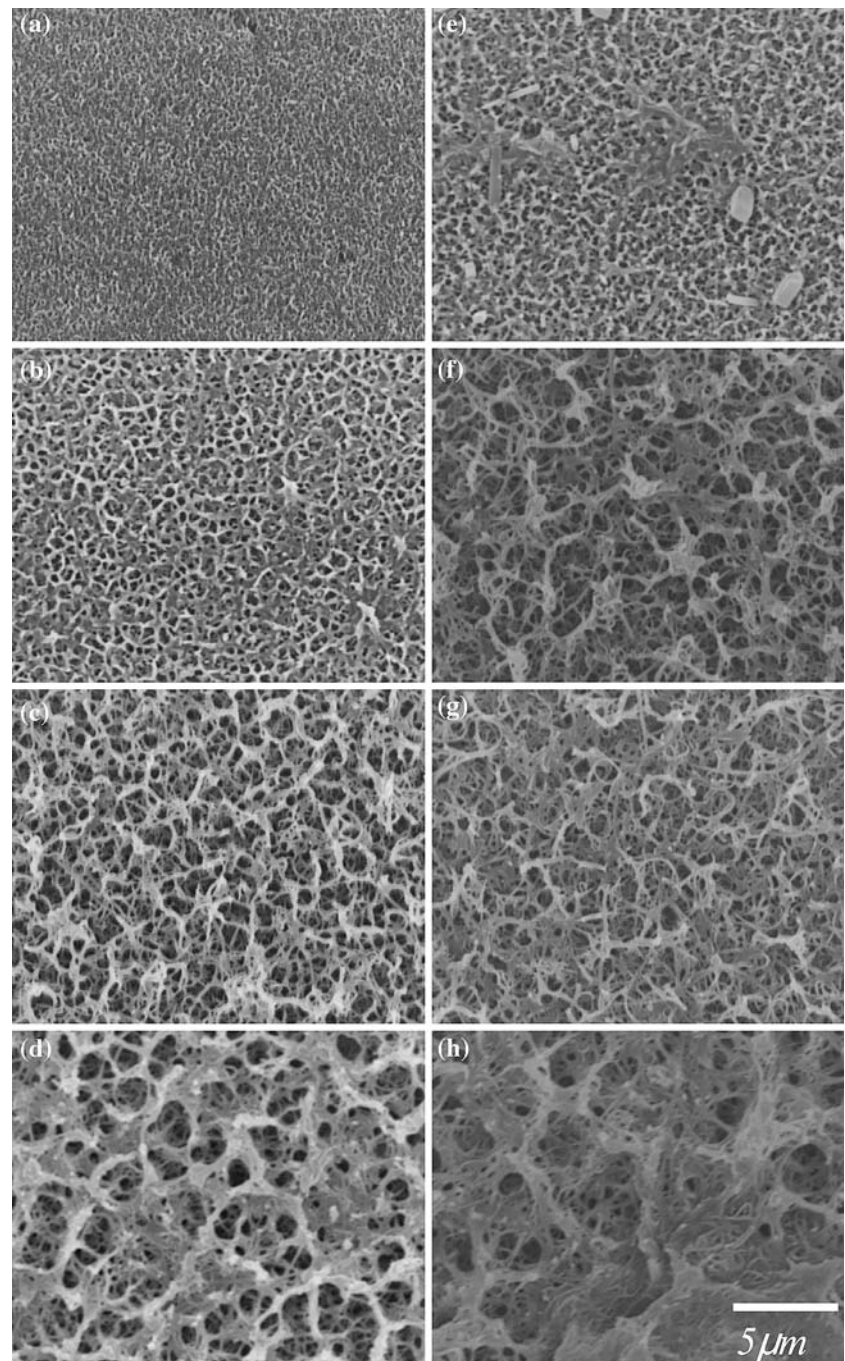


Fig. 4 SEM photographs of the potassium titanate layers synthesized for various durations at 150 °C for (a) 1 h, (b) 3 h, (c) 6 h and (d) 24 h, and at 180 °C for (e) 1 h, (f) 3 h, (g) 6 h and (h) 24 h



and the size of the pores developed with the duration of the reaction at 150 °C (Fig. 4b–d). On the other hand, fibrous particles were recognized on the substrate having reacted for 1 h at 180 °C as shown in Fig. 4e. The porous structure also developed with reaction duration at 180 °C. The surface of the titanate layers became rougher with reaction duration and temperature, with the growth of fibrous particles and the development of porous structure to form larger pores.

The morphology of the potassium titanate changed with an increase in the amount of the titanate layer, regardless of the condition of the alkaline treatment. The samples shown in Fig. 4c and f were similar in morphology and their amounts of potassium titanate layer were almost equal (noted in Fig. 3 as 4-c and 4-f, respectively), although the preparation conditions of the samples were different. A similar case was found in the samples shown in Fig. 4d and g. The morphology and the amount of potassium titanate layer were not

able to be controlled independently, with the KOH concentration constant in the alkaline treatment. In the above case, only either the amount or the morphology of the potassium titanate layer was able to be controlled by changing the treating temperature and the duration.

The effects of the duration and the temperature of the alkaline treatment on the formation of anatase after the acid treatment were investigated. The preparation conditions are shown in Table 1. The titanium substrates were treated in $1.8 \text{ mol} \cdot \text{dm}^{-3}$ KOH solution at 150 and 180 °C for 1–6 h as the alkaline treatment, and then treated in pH 2.0 HCl solution at 180 °C for 3 h as the acid treatment. The TF-XRD patterns after the acid treatment are shown in Figs. 5 and 6, with the temperature of the alkaline treatments 150 and 180 °C, respectively. Anatase formed in all samples. In sample 6-d, rutile also formed as shown in Fig. 6d. The intensity of the anatase peak increased with the duration of the alkaline treatment as shown in Figs. 5a–c and 6a–c. The amount of anatase increased with that of the potassium titanate before the acid treatment because the amount of potassium titanate increased with the duration of the alkaline treatment. Anatase also formed in sample 5-a, although potassium titanate was not detected by the TF-XRD before the acid treatment. Samples with almost equal amounts of potassium titanate were 4-c and 4-f (noted in Fig. 3), and their sample names were changed to 5-c and 6-b after the acid treatment, respectively, as shown in Table 1. The TF-XRD patterns of samples 5-c and 6-b are shown in Fig. 5c and Fig. 6b, and the intensity of their anatase peaks seem to be at comparable levels. Two other samples with almost equal amounts of potassium titanate were 4-d and 4-g (noted in Fig. 3), and their sample names were changed after acid treatment to 5-d and 6-c, respectively. However, samples 5-d and 6-c were treated in acid for 24 and 3 h, respectively. The TF-XRD patterns of

samples 5-d and 6-c are shown in Fig. 5d and Fig. 6c, and the intensity of the anatase peak of 5-d was stronger than that of 6-c, and the rutile peak was observed in 5-d. From the above results, it was found that the amount of the anatase after the same acid treatment increased with the amount of the potassium titanate before the acid treatment. It was also found that the formation of the anatase increased with the duration of the acid treatment, although the formation of rutile also increased with the excess acid treatment.

Figure 7 shows the TF-XRD patterns of the potassium titanate layer treated in various concentrations of HCl solution at 180 °C for 6 h. The preparation conditions of the samples are shown in Table 1. The crystalline titanium

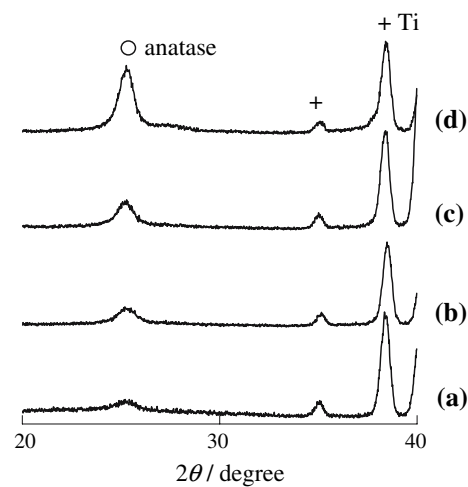


Fig. 5 TF-XRD patterns of the samples after the acid treatment in pH 2.0 HCl solution at 180 °C for 3 h (a–c) and 24 h (d), and the alkaline treatment was $1.8 \text{ mol} \cdot \text{dm}^{-3}$ KOH solution at 150 °C for (a) 1 h, (b) 3 h, (c) 6 h and (d) 24 h

Table 1 Preparation condition of the samples shown in Figs. 5–7

	Alkaline treatment*			Acid treatment**		
	Temp/°C	Duration/h	SEM #	Concentration	Temp/°C	Duration/h
5-a	150	1	4-a	pH 2.0	180	3
5-b	150	3	4-b	pH 2.0	180	3
5-c	150	6	4-c	pH 2.0	180	3
5-d	150	24	4-d	pH 2.0	180	24
6-a	180	1	4-e	pH 2.0	180	3
6-b	180	3	4-f	pH 2.0	180	3
6-c	180	6	4-g	pH 2.0	180	3
6-d	180	24	4-h	pH 2.0	180	24
7-a	150	24	4-d	$1.0 \text{ mol} \cdot \text{dm}^{-3}$	180	6
7-b	150	24	4-d	pH 1.0	180	6
7-c	150	24	4-d	pH 1.4	180	6
7-d	150	24	4-d	pH 2.0	180	6

* $1.8 \text{ mol} \cdot \text{dm}^{-3}$ KOH solution

** HCl solution

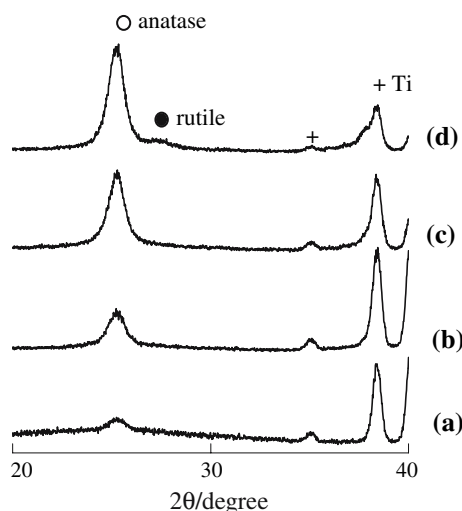


Fig. 6 TF-XRD patterns of the samples after the acid treatment in pH 2.0 HCl solution at 180 °C for 3 h (a–c) and 24 h (d), and the alkaline treatment was 1.8 mol · dm⁻³ KOH solution at 180 °C for (a) 1 h, (b) 3 h, (c) 6 h and (d) 24 h

oxide phase of sample 7-d was only anatase (Fig. 7d), and rutile coexisted in samples 7-b and 7-c (Fig. 7b, c). The anatase peak was not detected and only rutile was recognized in sample 7-a as shown in Fig. 7a. The intensity of the anatase peak decreased with an increase in concentration of HCl (or a decrease in pH), while the peak of rutile increased. During the acid treatment, amorphous titanium oxide or low crystalline titanium oxide formed on the substrate by dissolving potassium from the potassium titanate. The amorphous titanium oxide seemed to rearrange to form anatase in the HCl solution under the

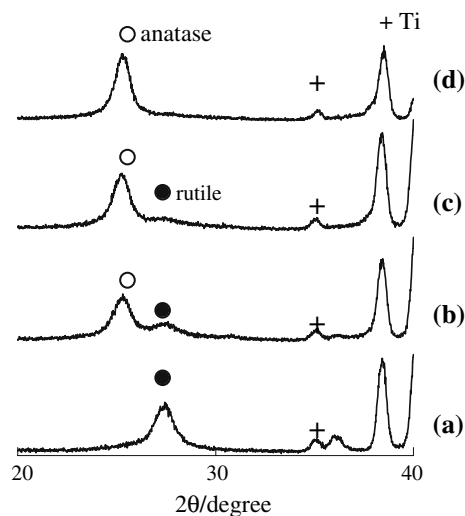


Fig. 7 TF-XRD patterns of the potassium titanate layer treated in various concentrations of HCl solution at 180 °C for 6 h and the potassium titanate layer was prepared at 150 °C for 24 h. (a) 1.0 mol · dm⁻³, (b) pH 1.0, (c) pH 1.4 and (d) pH 2.0

hydrothermal condition, when acid concentration was not too high. The higher acid concentration increased the solubility of the titanium oxide, and then the amorphous titanium oxide was thought to be dissolved and to precipitate as rutile, a thermodynamically stable crystalline phase [8].

As for the above results, it was found that the type of crystalline titanium oxide phase was mainly controlled by acid concentration, and that the amount of anatase depended on the amount of titanate layer formed by the alkaline treatment. The potassium titanate layer appeared to act as the precursor resource of anatase. A thick potassium titanate layer was required to form a thick anatase layer. It was necessary to adjust the pH of the HCl solution to be greater than 1.0 to form anatase. The amount of anatase increased during the acid treatment and a long duration led to the formation of rutile.

Decomposition of acetaldehyde under UV

The photocatalytic activity of the titanium oxide layer was examined for the decomposition of gaseous acetaldehyde under the irradiation of UV light. Table 2 shows the preparation conditions of the sample with different crystalline phases of titanium oxide. Samples other than 8-e were derived from a potassium titanate layer, while sample 8-e was derived from a calcium titanate layer. Figure 8 shows the change in the concentration of acetaldehyde during the UV irradiation by the titanium oxide layers listed in Table 2. The acetaldehyde in the glass reactors decomposed completely with 10 min irradiation for samples 8-c and 8-d. On the other hand, more than 30 min were required to decompose acetaldehyde in the reactor for the sample 8-a, in which anatase did not form. The sample derived from a calcium titanate layer also showed rapid decomposition of acetaldehyde (8-e). The differences among the decomposition rates of the acetaldehyde by the samples with anatase were little in our measurements, although the decomposition rate increased with the amount of anatase. The photocatalytic reaction occurred at the surface of the titanium oxide layer. The anatase, which contributed to the decomposition of acetaldehyde as the photocatalyst, should exist on or near the surface. A difference in photocatalytic degradation was also caused by the surface morphology of the layer, when there was sufficient anatase to cover the surface of the substrate. The decomposition rate of the acetaldehyde with sample 8-d was larger than that with 8-e, although the amount of anatase of sample 8-e seemed to be more than that of 8-d, from the TF-XRD patterns shown in Fig. 1c and f. Sample 8-e was not a lustrous white, whereas samples 8-c (same sample as 7-d) and 8-d were. Samples 8-c and 8-d showed slightly better activity at 10 min irradiation. The roughness

Table 2 Preparation conditions and the crystalline phases of samples for UV irradiation in Fig. 8

Sample #	Alkaline treatment (KOH, CaCl ₂ solution)				Phase of layer*	Acid treatment (HCl solution)			
	KOH/mol · dm ⁻³	CaCl ₂ /mol · dm ⁻³	Temp/°C	Duration/h		HCl concentration	Temp/°C	Duration/h	Phases of layer*
8-a	1.8	0	150	24	K ₂ Ti ₆ O ₁₃	1.0 mol · dm ⁻³	180	3	rutile
8-b	1.8	0	150	24	K ₂ Ti ₆ O ₁₃	pH 1.4	180	24	anatase, rutile
8-c (7-d)	1.8	0	150	24	K ₂ Ti ₆ O ₁₃	pH 2.0	180	6	anatase
8-d (1-f)	1.8	0	150	24	K ₂ Ti ₆ O ₁₃	pH 2.0	180	48	anatase, rutile**
8-e (1-c)	1.7	0.025	150	24	CaTiO ₃	pH 2.0	180	48	anatase, rutile**

* Neither K₂Ti₆O₁₃ nor CaTiO₃ remained after the acid treatment

** Weak peak of XRD pattern

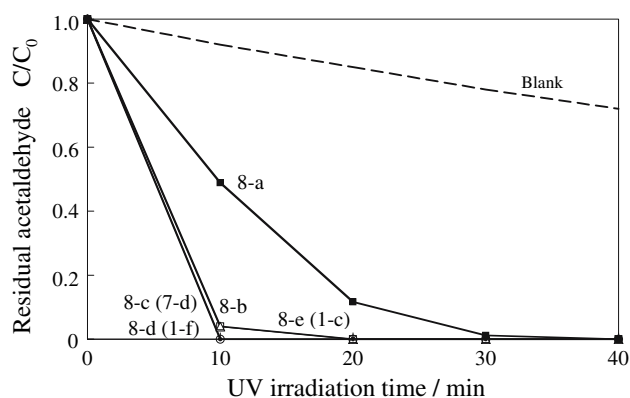


Fig. 8 Change in the concentration of acetaldehyde during the UV irradiation by the titanium oxide layers prepared in various HCl concentrations and duration of the acid treatment at 180 °C. Alkaline treatment: 150 °C for 24 h. Preparation conditions are listed in Table 2

of the surface seemed to influence the photocatalytic degradation.

In order to decrease the reaction duration without decreasing the initial photocatalytic activity, preparation conditions were selected as in Table 3. The pH of the HCl solution was fixed to 2.0, because rutile did not form as easily under this condition. Figure 9 shows the TF-XRD patterns of the samples referred to in Table 3. The crystalline phase of the samples was anatase, and rutile had not formed. Figure 10 shows the change in the concentration of acetaldehyde during the UV irradiation by the titanium oxide layers prepared with the conditions in Table 3. As shown in Fig. 10, the acetaldehyde was decomposed completely in the glass reactors at 10 min irradiation for sample 7-d. For sample 9-d, 20 min was required to decompose acetaldehyde in the reactor. Acetaldehyde still remained in the reactor at 40 min for samples 5-b and 5-c. From the results of TF-XRD shown in Fig. 9, the decomposition rate of acetaldehyde increased with the diffraction

Table 3 Preparation conditions of samples for UV irradiation in Fig. 9

Sample #	Alkaline treatment 1.8 mol · dm ⁻³ KOH solution		Acid treatment pH 2.0 HCl solution	
	Temp/°C	Duration/h	Temp/°C	Duration/h
5-b	150	3	180	3
5-c	150	6	180	3
7-d	150	24	180	6
9-d	180	3	180	6

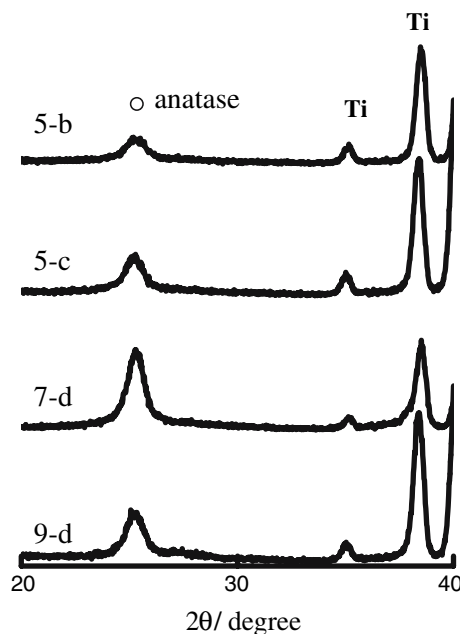


Fig. 9 TF-XRD patterns of the samples after the acid treatment at 180 °C. The sample preparation conditions are summarized in Table 3

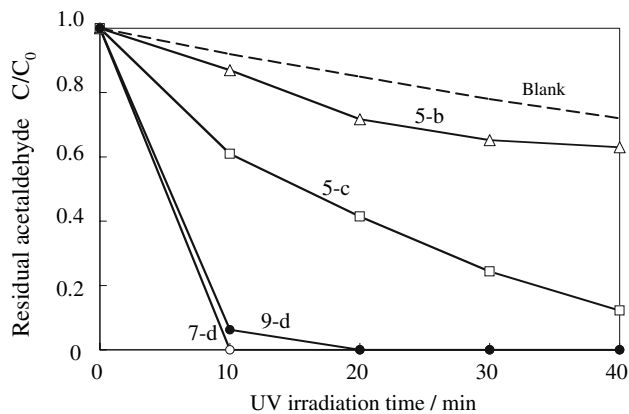


Fig. 10 Change in the concentration of acetaldehyde during the UV irradiation by the titanium oxide layers prepared in various durations and temperature of the alkaline treatment. The acid treatment: pH 2.0, at 180 °C; Preparation conditions are listed in Table 3

intensity of anatase, and also with the amount of anatase, when the amount of anatase was not sufficient to cover the substrate.

The weight of the alkaline-treated substrate decreased with increasing duration of acid treatment. The temperature and the concentration of the acid also promoted the dissolution of the alkaline titanate layer. The fracture of the layer might be caused by excessive reaction because of the excess decomposition of the alkaline titanate layer. The potassium titanate layer was required to supply enough titanium oxide to easily crystallize anatase. The optimum preparation condition of the alkaline treatment was 4-d (at 150 °C for 24 h) for the photocatalyst of this study. The condition of the alkaline treatment of 4-g (at 180 °C for 6 h) was thought to be almost equal to that of 4-d. From the above results, both the alkaline and the acid treatments could be shortened to 6 h at 180 °C.

Conclusions

Crystalline titanium oxide layers with anatase were fabricated on a titanium substrate by two steps of hydrothermal

treatments, the alkaline treatment and the acid treatment. A layer of potassium titanate or other titanate formed on the substrate during the alkaline treatment. The potassium ion or other soluble element dissolved from the titanate layer and the remaining titanium oxide was crystallized to anatase in HCl solution during the acid treatment. For a photocatalyst, a sufficient amount of fine anatase crystals and a comparatively smooth surface were optimum. The amount of anatase increased with the increase in the titanate before the acid treatment and the potassium titanate layer grew with temperature and duration of reaction. The concentration of HCl solution should be decreased to avoid the formation of rutile and the fracturing of the layer caused by excess decomposition of the titanate layer. A lustrous anatase layer, which was composed of fine anatase with grain size and crystallite size almost 40–50 nm and 10 nm, respectively, on the titanium substrate was prepared using $1.8 \text{ mmol} \cdot \text{dm}^{-3}$ KOH solution and HCl solution (pH 2.0). The alkaline and the acid treatments could be shortened to 6 h at 180 °C. The rapid photocatalytic degradation of gaseous acetaldehyde by this layer was observed under irradiation of UV light.

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