

# Photocatalytic Activity of TiO<sub>2</sub> Thin Films Prepared by the Sol-Gel Method : Primary Particle Size as a Predominant Factor

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Photocatalytic activity decreases when TiO<sub>2</sub> is coated on a glass substrate containing alkali ions such as Na<sup>+</sup>. As a reason for the decrease in the activity, many reports have proposed that the Na<sup>+</sup> ions become recombination centers of electrons and holes. However, evidence for this proposition is insufficient. In order to study the influence of Na<sup>+</sup> on TiO<sub>2</sub> photocatalytic activity, TiO<sub>2</sub> thin films were prepared on various glass substrates by using the sol-gel method. Properties such as crystal phases, primary particle sizes and elements of the TiO<sub>2</sub> thin films were measured. The photocatalytic activities of the thin films were determined by degradation of gas phase trichloroethylene (TCE). It was found that the photocatalytic activities of the TiO<sub>2</sub> thin films increased with decrease of not Na<sup>+</sup> concentration but primary particle size. Sodium ions were found to increase the particle size of the TiO<sub>2</sub> at the initial step of anatase formation. Therefore, the change of the particle size by Na<sup>+</sup> was a dominant cause of various photocatalytic activities. The effect of Na<sup>+</sup> as the recombination center may not become a dominant factor. The present results suggest that higher photocatalytic activity of the TiO<sub>2</sub> thin film can be obtained by preparing small size of anatase crystal.

Keywords: Photocatalytic activity; Primary particle size; Glass substrate; Na<sup>+</sup> ions; TCE

## 1. INTRODUCTION

TiO<sub>2</sub> photocatalyst is effective in the degradation of organic compounds such as acetone, ethanol, trichloroethylene (TCE), chloroform, and so on<sup>1,2</sup>. TCE was known as a pollutant of soil and/or underground water, and purification works using gas-phase photocatalytic reactions have already been tried in Japan and other countries<sup>3-7</sup>.

In general, TiO<sub>2</sub> was coated on solid substrates is needed to. Glass is suitable for the substrate, because, glass has been used in our surrounding, and it has high cohesion with TiO<sub>2</sub> thin film. Moreover, the TiO<sub>2</sub> thin film coated on glass substrate shows high efficiency to supplied photo energy because glass is transparent for the light<sup>8</sup>.

However, coating of TiO<sub>2</sub> on the glass substrates has some problems. The most serious problem is decrease of photocatalytic activity. When the glass, containing alkali ions such as Na<sup>+</sup> and is used widely for inexpensive, was used by the substrate of the TiO<sub>2</sub> thin films, the photocatalytic activity of TiO<sub>2</sub> decrease<sup>9-11</sup>. It was reported due to diffusion of Na<sup>+</sup> from the glass substrate to the TiO<sub>2</sub> film, and many reports proposed the role of the Na<sup>+</sup> ions as recombination centers of electrons and holes<sup>9-11</sup>. In those reports, however, evidence for this proposition has been insufficient. Thus, we study the photocatalytic activities of TiO<sub>2</sub> thin films that were prepared on various glass substrates. We report the influences of Na<sup>+</sup> on the photocatalytic activities and on the properties of the TiO<sub>2</sub> thin films.

## 2. EXPERIMENTAL

### 2.1 Preparation of the TiO<sub>2</sub> thin films

The TiO<sub>2</sub> thin films were prepared on three kinds of

glass. The size of all glass substrates was 6.1 × 2.6 cm<sup>2</sup> in square and 0.1 cm in thickness. Glass substrates are fused silica glass, crown glass, crown glass coated with a SiO<sub>2</sub> layer (Crown/SiO<sub>2</sub>). The fused silica glass does not contain Na<sup>+</sup>, and Crown glass contains 11 wt% of Na<sub>2</sub>O as its components. For the Crown/SiO<sub>2</sub> substrate, a SiO<sub>2</sub> layer is known to hinder the Na<sup>+</sup> diffusion to the TiO<sub>2</sub> thin film. In our study, the SiO<sub>2</sub> layer was prepared by a sol-gel method. A mixture containing 23 ml of tetraethyl silicate (TES), 200 ml of dehydrated ethanol, and 2.7 ml of HCl was stirred for 30 min, and the crown glass substrates were dipped into and pulled up from the sol at 4.6 cm/min, and then dried in air. The dip-coating process was repeated three times, and the samples were heated at 500°C for 30 min. On these glass substrates, the TiO<sub>2</sub> thin films were also prepared by the sol-gel method. A mixture containing 29 ml of Ti(IV)isopropoxide, 200 ml of dehydrated ethanol, and 2.7 ml of HCl was stirred for 2.5 h. The glass substrates were dipped into this sol and pulled up eight times. And then, they were heated at temperatures ranged from 200 - 500°C with a 50°C interval for 3.5 h.

### 2.2 Measurements of property and photocatalytic activity of the TiO<sub>2</sub> thin films

Thickness of the SiO<sub>2</sub> layer in Crown/SiO<sub>2</sub> glass was measured with an Ellipsometry (JASCO M-220), and it was ca. 80 nm. The thicknesses of the TiO<sub>2</sub> thin films were calculated based on absorption spectra measured with a spectrophotometer (Hitachi 220). All the prepared TiO<sub>2</sub> thin films had ca. 400 nm of thickness. Crystal phases were determined by using an X-ray diffractometer (XRD: Rigaku 2000). And, primary particle sizes of the TiO<sub>2</sub> thin films were calculated using the Scherrer's formula from the XRD peak. Element analyses were carried out with a microprobe

X-ray photoelectron spectrometer (Shimazu-Kratos Analytical XSM 800), which gave the atomic concentration of Na in 2 nm of the surface layer in the TiO<sub>2</sub> films. The photocatalytic activities of the TiO<sub>2</sub> thin films were determined by degradation of gas phase trichloroethylene (TCE) in a batch-type reactor (volume = 106 ml) made of Pyrex glass. The initial concentration of TCE was ca. 940 ppmv. The degradation reaction of TCE was carried out using eight 20 W black light fluorescent lamps (peak wavelength = 352 nm, intensity = 1.2 mW/cm<sup>2</sup>) and was monitored with a Fourier transform infrared spectrometer (Nicolet 800).

### 3. RESULTS AND DISCUSSION

Table I shows the crystal phase of the TiO<sub>2</sub> films determined by XRD. For the TiO<sub>2</sub> thin films on fused silica and Crown/SiO<sub>2</sub>, the anatase phases were observed at 300°C. In contrast, it was over 400°C in the cases of the films on crown glass. In our previously study, we reported that anatase formation temperature was higher for TiO<sub>2</sub> thin films coated on the glass containing alkali ions than that containing non-alkali ions, and suggested that Na<sup>+</sup> ions increased anatase formation temperature<sup>12</sup>. The results in Table I were consistent with the previous results. In particular, the result of the TiO<sub>2</sub> thin film on Crown/SiO<sub>2</sub> glass suggests that the SiO<sub>2</sub> layer interrupted diffusion of Na<sup>+</sup> ions and that Na<sup>+</sup> increased the anatase formation temperature. Table II shows atomic concentration of Na in each thin film. Na<sup>+</sup> ions were not contained in the TiO<sub>2</sub> thin film coated on fused silica glass substrates. The TiO<sub>2</sub> thin films coated on crown and Crown/SiO<sub>2</sub> glass heated at 500°C showed higher atomic concentrations of Na than that at 300°C. Lim et al. reported that many Na<sup>+</sup> ions diffused from alkali-silicate glass with increasing heating

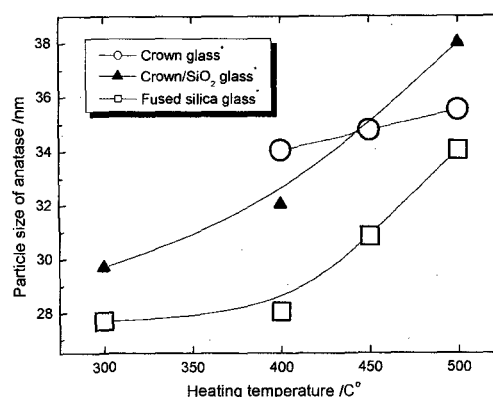
**Table I** Crystal phase of the TiO<sub>2</sub> thin films on each glass substrate.

Heating temp. / °C	Glass substrate						
	200	250	300	350	400	450	500
Crown	x	x	x	x	A	A	A
Crown/SiO <sub>2</sub>	x	x	A	*	A	*	A
Fused silica	x	x	A	*	A	A	A

A: Anatase. X: Amorphous. \*: Not analyzed.

**Table II** Atomic concentration of Na (%) for the TiO<sub>2</sub> thin films coated on different glass substrates heated at 300 and 500°C.

Glass substrate	Heating temp.	
	300°C	500°C
Crown glass	1.86	11.09
Crown/SiO <sub>2</sub> glass	0.74	3.53
Fused silica glass	0.00	0.00

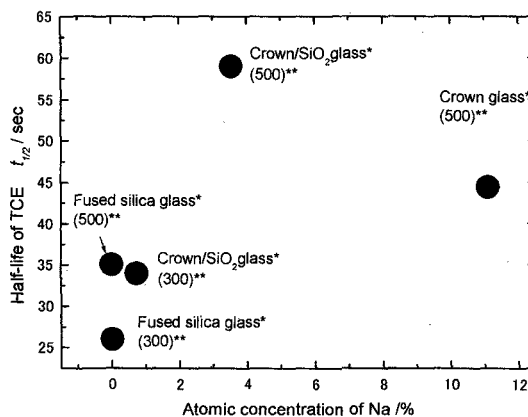


**Figure 1** Primary particle sizes of TiO<sub>2</sub> thin films coated on Crown glass, Crown/SiO<sub>2</sub> glass and Fused silica glass, heated at different temperatures. (\*: Glass substrates)

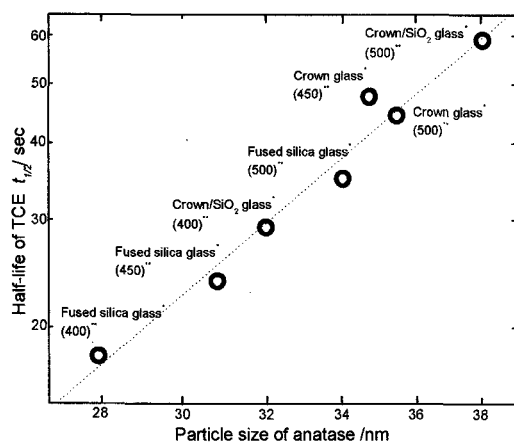
temperature<sup>13</sup>. Na concentration was highest for the thin film coated on the crown glass substrate, heated at 500°C. These results show that SiO<sub>2</sub> layer interrupted Na<sup>+</sup> diffusion not perfectly but effectively.

Figure 1 shows the particle size of anatase as a function of heating temperature. The anatase particle size increased with the temperature for all the substrates, though the particle size for fused silica was smaller than that for the other substrates. This result suggests that Na<sup>+</sup> ion increases particle size of anatase even though its amounts are very small. In order to compare photocatalytic activity for these thin films, TCE was degraded by photocatalysis.

Figure 2 shows half-lives of TCE and atomic concentrations of Na. The photocatalytic activity of the TiO<sub>2</sub> thin films on crown glass contained the highest Na atomic concentration, was similar to that on Crown/SiO<sub>2</sub> glass at 500°C. According to the suggestion that Na<sup>+</sup> decreases photocatalytic activity owing to its behavior as a recombination center of electrons and holes<sup>9-11</sup>, the photocatalytic activity should decrease with increasing



**Figure 2** The relationship between the half-lives of TCE and the Na<sup>+</sup> concentrations in the surface layers (about 2 nm) of the TiO<sub>2</sub> thin films (\*: Glass substrate, \*\*: Heating temperature); The result of TiO<sub>2</sub> thin film on crown glass heated at 300°C was not shown because anatase was not formed in this thin film.



**Figure 3** The relationship between the half-lives of TCE and the particle sizes of TiO<sub>2</sub> thin films. (\*: Glass substrate, \*\*: Heating temperature)

Na atomic concentration in TiO<sub>2</sub> thin films. However, our results suggest that Na<sup>+</sup> ions may not work as recombination centers. Thus, we searched other factors affecting the photocatalytic activity.

Harada et al. reported that photocatalytic activity for powdered rutile TiO<sub>2</sub> were affected by particle size<sup>14</sup>. Figure 3 shows the relationship between the half-lives and the particle sizes in the TiO<sub>2</sub> thin films coated on all glass substrates. The results for the TiO<sub>2</sub> thin films coated on crown glass heated at 400°C and those coated on fused silica and Crown/SiO<sub>2</sub> glass heated 300°C were not included. Because, it was considered that these were initial steps of anatase formation, and had not sufficient anatase for photocatalysis. The line is approximate. The smaller the particle sizes were, the shorter the half-lives of TCE were, hence the photocatalytic activities of TiO<sub>2</sub> thin films increased with a decrease of particle size. Therefore, when TCE was decomposed with the TiO<sub>2</sub> thin films on various types of glass substrates, the photocatalytic activity depended on the sizes of the anatase crystals. Further, Na<sup>+</sup> influenced the particle size of the TiO<sub>2</sub> thin films.

Therefore, we have concluded that Na<sup>+</sup> should be affect on the photocatalytic activity of the TiO<sub>2</sub> not by working as the recombination centers but by changing the particle size.

We appreciate Mr. M. Kondo of the Instrumental Analysis Center of Yokohama National University for his help with the XPS measurement.

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(Received October 10, 2003; Accepted June 30, 2004)