

# Change in the Concentration of Dissolved Oxygen in the Suspensions of Anatase and Rutile TiO<sub>2</sub> Powders under UV Irradiation and Their Photoluminescence Properties

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We have measured the concentration of dissolved oxygen (DO) in the suspensions of anatase and rutile TiO<sub>2</sub> powders, and have observed photoluminescence (PL) of the two powders. The photoadsorption of DO occurred in the suspension of the anatase TiO<sub>2</sub> powder, but not in the suspension of the rutile TiO<sub>2</sub> powder. It was expected from this result that the anatase TiO<sub>2</sub> powder has a higher activity for the photocatalytic oxidation in the liquid phase than the rutile TiO<sub>2</sub> powder. This expectation was supported by the result of DO decrease in the suspensions with ethanol under UV irradiation. The crystal structure dependence of the DO photoadsorption corresponded to that of the PL property in the wavelength region less than 750 nm; the PL intensity of the anatase TiO<sub>2</sub> powder increased after adding ethanol, whereas that of the rutile TiO<sub>2</sub> powder remained unchanged regardless of ethanol. On the other hand, the emission band in the wavelength region 750–850 nm was observed for the rutile TiO<sub>2</sub> powder, but not for the anatase TiO<sub>2</sub> powder. This emission was quenched by ethanol. These results show that PL spectroscopy is a useful method to evaluate the photo-activity of TiO<sub>2</sub> and to study its surface conditions.

Key words: TiO<sub>2</sub>, anatase, rutile, dissolved oxygen, photoluminescence

## 1. INTRODUCTION

TiO<sub>2</sub> photocatalyst mineralizes various kinds of organic compounds because of its strong oxidizing power. It is important to know the behavior of oxygen in the photocatalytic oxidation. However, the behavior of oxygen is not fully understood. It is known that dissolved oxygen (DO) in TiO<sub>2</sub> suspension is adsorbed on the TiO<sub>2</sub> under UV irradiation (photoadsorption); nevertheless, few studies have been conducted on the DO photoadsorption in TiO<sub>2</sub> suspension [1-3].

Photoluminescence (PL) spectroscopy is a useful method for studying surface conditions of anatase and rutile TiO<sub>2</sub> samples because PL of TiO<sub>2</sub> reflects its crystal structure as well as adsorbates on its surface [4-6].

In this study, we measured the DO concentration in the suspensions of anatase and rutile TiO<sub>2</sub> powders under UV irradiation, and compared the results of the two powders. In addition, we observed PL of the two powders, and considered their surface conditions.

## 2. EXPERIMENTAL

A mainly anatase TiO<sub>2</sub> powder P25 (Nippon Aerosil) (specific surface area, 50±15 m<sup>2</sup>g<sup>-1</sup>) and a rutile TiO<sub>2</sub> powder JRC-TIO-3 (Catalysis Society of Japan) (specific surface area, 40 m<sup>2</sup>g<sup>-1</sup>) were used as received. To confirm whether the effect of organic compounds adsorbed on the TiO<sub>2</sub> powder on the O<sub>2</sub> photoadsorption is negligible, the TiO<sub>2</sub> powder was heated at 673 K for 2 h in air before the DO measurement. The water used was purified to a resistivity of > 18 MΩcm by filtration through a Milli-Q reagent water system. The TiO<sub>2</sub> suspensions used were aqueous suspensions containing 1.0 kgm<sup>-3</sup> of the TiO<sub>2</sub> powder.

The TiO<sub>2</sub> suspension (98 ml) was stirred in a flask during the DO measurement. The concentrations of DO in the TiO<sub>2</sub> suspensions were measured with a DO meter, DOL-40 (DKK), at room temperature. The neck of the flask was closed with the electrode of the DO meter and there was no gas space in the flask, so that the amount of O<sub>2</sub> in the TiO<sub>2</sub> suspension is regarded as constant

throughout the DO measurement. In the DO measurement, the TiO<sub>2</sub> suspension was irradiated with three black light tubes FL10BLB (Toshiba). The irradiation intensity was 1.9 mWcm<sup>-2</sup> at the position of the flask.

The PL of the TiO<sub>2</sub> powder was obtained using a spectrophotometer Fluorolog 3-22 (Jobin Yvon) at room temperature. The light source of the photometer was a 450 W xenon lamp. The excitation wavelength was 280 nm in the PL measurement; an optical filter (UV-33) was used to eliminate the secondary light (~560 nm).

### 3. RESULTS AND DISCUSSION

The DO concentration in the suspension of the mainly anatase TiO<sub>2</sub> powder decreased under UV irradiation, whereas that in the suspension of the rutile TiO<sub>2</sub> powder remained unchanged regardless of the UV irradiation (Fig.1). The DO concentration in the suspension of another anatase TiO<sub>2</sub> powder, AMT600 (Tayca) (specific surface area, 45–65 m<sup>2</sup>g<sup>-1</sup>), decreased similarly to that of the mainly anatase TiO<sub>2</sub> powder under UV irradiation. These results mean that the photoadsorption of DO occurs in the suspension of anatase TiO<sub>2</sub> powder [1,3], but not in the suspension of rutile TiO<sub>2</sub> powder [2]. This difference between the anatase and rutile TiO<sub>2</sub> powders in the liquid phase agrees with that in the gas phase; anatase TiO<sub>2</sub> has a much higher activity of O<sub>2</sub> photoadsorption in the gas phase than rutile TiO<sub>2</sub> [7]. The more oxygen adsorption capacity TiO<sub>2</sub> has, the higher activity for the photocatalytic oxidation it has [7,8], and hence the mainly anatase TiO<sub>2</sub> powder is expected to have a much higher activity of the photocatalytic oxidation than the rutile powder.

To compare the photocatalytic activities of the mainly anatase TiO<sub>2</sub> powder and the rutile TiO<sub>2</sub> powder for the oxidation in the liquid phase, the DO concentrations in the suspensions of the two powders with ethanol (1.0 vol.%) were measured under UV irradiation. In this DO measurement, the decrease in DO indicates the consumption of the DO for the photocatalytic oxidation of ethanol. The decrease in DO in the suspension of the mainly anatase TiO<sub>2</sub> powder was much larger than that in the suspension of the rutile TiO<sub>2</sub> powder (Fig.2). This

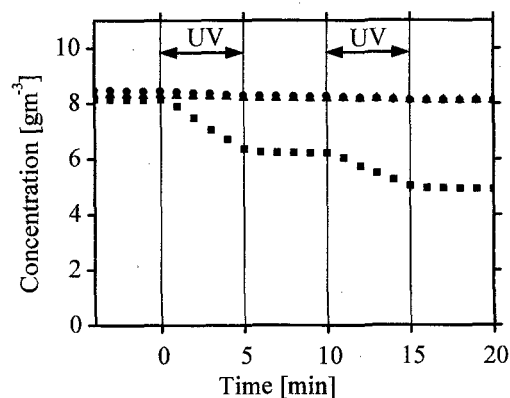


Fig.1. The change in the concentration of dissolved oxygen by the UV irradiation in pure water (circle) and in the suspensions of the rutile TiO<sub>2</sub> powder (triangle) and the mainly anatase TiO<sub>2</sub> powder (square).

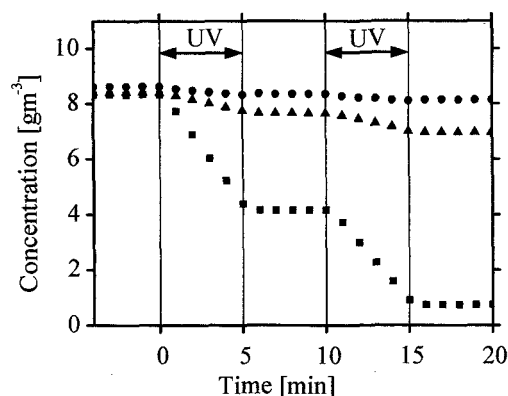


Fig.2. The change in the concentration of dissolved oxygen by the UV irradiation in 1.0 vol.% ethanol solution (circle) and in the suspensions of the rutile TiO<sub>2</sub> powder (triangle) and the mainly anatase TiO<sub>2</sub> powder (square).

result suggests that, as we expected in the previous paragraph, the mainly anatase TiO<sub>2</sub> powder have a much higher activity of the photocatalytic oxidation than the rutile TiO<sub>2</sub> powder. Thus, one could evaluate the activity of TiO<sub>2</sub> for the photocatalytic oxidation in the liquid phase from the activity for the photoadsorption of DO in the TiO<sub>2</sub> suspension. The rutile TiO<sub>2</sub> powder had a low photocatalytic activity, although the DO photoadsorption did not occur in the suspension of the rutile TiO<sub>2</sub> powder under UV irradiation (Fig.1).

To understand the difference between the surface conditions of the TiO<sub>2</sub> powders, their PL spectra were measured. Fig.3 shows the PL spectra of the mainly anatase TiO<sub>2</sub> powder in air and in air with ethanol vapor.

The PL intensity in air with ethanol vapor was significantly larger than that in air. This result agrees with that reported previously [5,6]. In the present study, the same result as shown in Fig.3 was obtained even for the suspension of the mainly anatase  $\text{TiO}_2$  powder. The influence of ethanol on the PL is explained as follows [4-6]: ethanol is adsorbed on  $\text{TiO}_2$  surface as a positively charged adsorbate, and decreases the efficiency of charge separation in the  $\text{TiO}_2$  near the surface, and thereby increases the recombination of the photoinduced electron and the hole in the  $\text{TiO}_2$ . This means the increase in PL intensity of the  $\text{TiO}_2$ .

On the other hand, the PL spectrum of the rutile  $\text{TiO}_2$  powder in air was identical with that in air with ethanol vapor in the wavelength region shorter than 750 nm (Fig.4); the influence of ethanol on the PL, as shown for the mainly anatase  $\text{TiO}_2$  powder in the previous paragraph, was not observed for the rutile  $\text{TiO}_2$  powder. We found that the crystal structure dependence of the PL property corresponds to that of the DO photoadsorption (Fig.1). In the wavelength region 750–850 nm, however, the PL intensity in air was much larger than that in air with ethanol vapor (Fig.4). This emission band is attributed to oxygen vacancy in  $\text{TiO}_2$  [9], and hence the influence of ethanol on the PL can be explained as follows: ethanol is adsorbed on the  $\text{TiO}_2$  surface near the oxygen vacancy at which the photoinduced hole is trapped, and quenches the emission corresponding to the electron transition from the excited state to the trapped state or the trapped state to the grand state.

#### 4. CONCLUSION

The photoadsorption of DO occurred in the suspension of the mainly anatase  $\text{TiO}_2$  powder, but not in the suspension of the rutile  $\text{TiO}_2$  powder. It was expected from this result that the mainly anatase  $\text{TiO}_2$  powder has a higher activity for the photocatalytic oxidation in the liquid phase than the rutile  $\text{TiO}_2$  powder. This expectation was supported by the result of DO decrease in the suspensions with ethanol under UV irradiation. The crystal structure dependence of the DO photoadsorption corresponded to that of the PL property in the wavelength region less than 750 nm. On the other

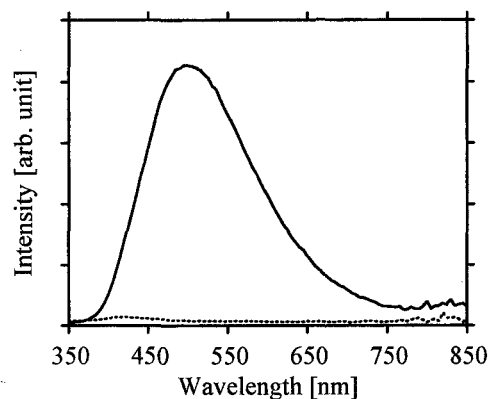


Fig.3. PL spectra of the mainly anatase  $\text{TiO}_2$  powder in air (dotted curve) and in air with ethanol vapor (solid curve). The excitation wavelength was 280 nm.

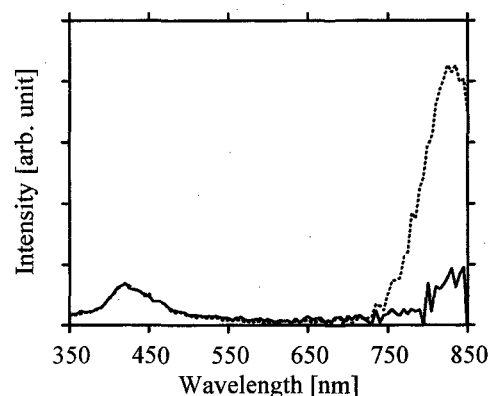


Fig.4. PL spectra of the rutile  $\text{TiO}_2$  powder in air (dotted curve) and in air with ethanol vapor (solid curve). The excitation wavelength was 280 nm.

hand, the emission band in the wavelength region 750–850 nm was observed for the rutile  $\text{TiO}_2$  powder, but not for the mainly anatase  $\text{TiO}_2$  powder. This emission, which was attributed to oxygen vacancy in the  $\text{TiO}_2$ , was quenched by ethanol. This result indicates that ethanol is adsorbed on the  $\text{TiO}_2$  surface near the oxygen vacancy. These results show that PL spectroscopy is a useful method to evaluate the photo-activity of  $\text{TiO}_2$  and to study its surface conditions.

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