

# NEAR-INFRARED LUMINESCENCE STUDY OF SINGLET OXYGEN FORMATION ON TiO<sub>2</sub> PHOTOCATALYSTS

Toshihiro Daimon; Yoshinori Murakami; Yoshio, Nosaka  
Nagaoka University of Technology,  
Nagaoka, 940-2188, Japan  
e-mail [e013528@chem.nagaokaut.ac.jp](mailto:e013528@chem.nagaokaut.ac.jp)

## 1. Introduction

Titanium oxide photocatalyst is expected to be utilized as one of the most powerful technologies for environmental purification. However, the photocatalytic reaction may produce by-products more detrimental than the original substance. Therefore, the investigation in the reaction mechanism for individual substance is very important. Photocatalytic reaction with titanium oxide is induced by electrons and positive holes produced inside the titanium oxide solid with an ultraviolet radiation. They diffuse near the surface and initiate the reaction. Hydroxyl radical ( $\cdot\text{OH}$ ) and super oxide radical ( $\cdot\text{O}_2^-$ ) produced by the photoinduced hole and electron, respectively have been studied widely as a key species. However, when the photoproduced  $\cdot\text{O}_2^-$  reacts with holes, it is possible to become singlet oxygen ( $^1\Delta_g, ^1\Sigma_g^+$ ) which is one of the active oxygen species. But the formations of singlet oxygen have not been established clearly yet. Thus, in this research, the phosphorescence of the singlet oxygen generated on titanium oxide photocatalysts was measured by a gated photon counting method and the behavior of singlet oxygen was studied.

## 2. Experimental

In the present experiment various kinds of titanium oxide powder were used as powder in air and aqueous suspension in various media (water, heavy water, ethanol, etc.) placed in a  $1 \times 1$  cm quartz cell. Measurements in aqueous suspension were performed under agitation by a magnetic stirrer. Excitation light was THG (355 nm) beam of a pulsed Nd:YAG laser. The beam was passed HOYA-U350 filter and the dielectric multilayer film plane mirrors to eliminate the stray light. The photon of luminescence was counted with a SR445-SR400 counter after concentrated the light with a lens, passed by HOYA-IR-80, separated by monochromator and put into the photomultiplier (cooled at 200 K by liquid nitrogen). The gated-photon-counting method changing wavelength and delay time enabled us to evaluate luminescence intensity and life time for each sample. To measure the spectrum, the detection between  $0.5 \mu\text{s}$  and  $1.5 \mu\text{s}$  (Delay time  $1.5 \mu\text{s}$ , Gate width  $5.0 \mu\text{s}$ ) after the laser pulse was accumulated for 300 times by changing wavelength. To measure the life time, the light intensity at the wavelength of 1270nm, was accumulated by 5000 times for the detection between  $0.5 \mu\text{s}$  and  $4.0 \mu\text{s}$  (Delay time  $0.5 \sim 4.0 \mu\text{s}$ , Gate width  $0.5 \mu\text{s}$ ) after the laser pulse.

Photocatalytic TiO<sub>2</sub> powders used were the reference photocatalysts of the Catalysis Society of Japan TIO-4, 6, 7, 8, 9, 10, 11, 12 and 13, brookite type titanium oxide NTB-01 (Showa titanium, Inc.), and Degussa P25 (Japan Aerosil, Inc.), MT500B (Tayca, Inc.) rutile.

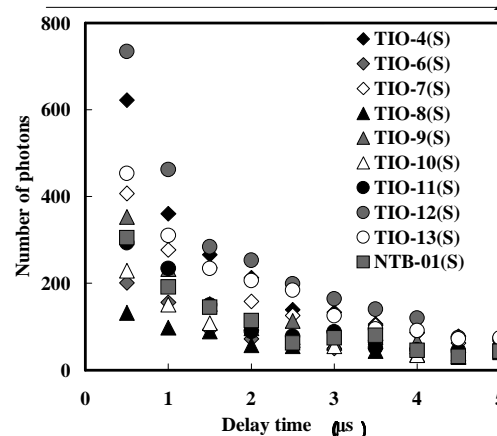
## 3. Results and discussion

As a result of experiments for side irradiation the spectrum with a peak at 1270 nm was obtained. The spectrum was identical to that obtained for the rose bengal sensitizer. From this observation, it is ascertained that singlet oxygen was formed in these aqueous suspension reaction systems of titanium oxide photocatalysts. For both samples of P25 and MT500B, the luminescence spectrums of the singlet oxygen were observed though

they were broader with a peak at 1270nm. When the luminescence intensities of these samples were compared, the spectrum intensity of P25 was about twice of that of MT500B. Thus, a larger amounts of singlet oxygen is generated by anatase than rutile. Moreover, when the water-ethanol mixed solution was used for suspension medium of TiO<sub>2</sub>, the peak for luminescence intensity had the largest of water, and it decreased with increasing the ethanol content. That is, the amount of luminescence decreases in the presence of ethanol. This phenomenon can be explained as that the generation reaction was suppressed since the active hole which oxidizes  $\cdot\text{O}_2^-$  was consumed for the oxidization of alcohol, and oxygen was consumed to oxidize alcohol, etc. Experiment by front irradiation in which the measurement of powder samples was attained, more sensitive than the side one. The spectrum of the singlet oxygen having the peak near 1270nm was observed in suspension and in air. The decrease in the amount of luminescence by adding alcohol was also seen, corresponding to the above results of side irradiation. The light intensity of luminescence observed in air was higher than that in the suspension with pure water. Table 1 shows the luminescence intensity and the life time calculated from the experiment in heavy water, water, and ethanol. On the amount of luminescence, highest intensity was observed for the suspension of heavy water, and water, air, and ethanol follow in this order. Moreover, the life time of the singlet oxygen in air was longer than that in each solution. The life time of singlet oxygen emission in water was the shortest in these solutions. These results showed the same tendency seen in literature. Furthermore, as for the titanium oxide after heat treatment, the life time was prolonged slightly. Because the hydroxy group at the surface of titanium oxide could be removed by heat treatment, the luminescence life time became long. Fig. 1 shows the luminescence intensity and the life time for the reference TiO<sub>2</sub> photocatalysts of the Catalysis Society of Japan and brookite type titanium oxide NTB-01. When these samples were compared in their luminescence life time, the sample of large anatase content showed the longer life time. Moreover, the brookite type titania is not inferior to anatase in the luminescence intensity and the life time.

**Table 1 The luminescence intensity and the life time, TiO<sub>2</sub> (P25) aqueous suspension in various media**

media	I <sub>0</sub>	τ /μ s
Air	705	
Air(heat treatment)	611	1.59
H <sub>2</sub> O	833	1.75
D <sub>2</sub> O	849	1.32
EtOH	485	1.83
		2.07



**Fig. 1 The luminescence of the reference photocatalysts of Catalysis Society of Japan and NTB-01.**