Femtosecond Diffuse Reflectance Spectroscopy of Aqueous Titanium(IV) Oxide Suspension: Correlation of Electron-Hole Recombination Kinetics with Photocatalytic Activity

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Pump-probe diffuse reflectance measurements were carried out on particulate titanium(IV) oxide photocatalysts in the form of aqueous suspension and dry powder. A linear relation between second-order rate constants of electron-hole recombination for the suspension and powder systems was seen by analyses of decay profile of charge carriers. Presence of air gave negligible effect on the recombination kinetics, but loading of platinum (Pt) significantly reduced the rate constant.

Semiconductor photocatalytic reaction, which occurs at photoirradiated interface between a semiconductor surface and a solution, is of great importance for both fundamental studies and practical applications.[1] Among the semiconductors, titanium(IV) oxide (TiO_2) is one of the most efficient and promising material for photocatalytic reactions. It is known that we can see so much difference in the photocatalytic activity, depending on the nature of TiO_2. Many authors claimed the factors controlling the activity, e.g., crystal structure, surface area, or surface hydroxyls. Recombination of electron-hole might be also one of the most significant factors giving influence on the activity and depend strongly on the nature of TiO_2 particles.[2] For TiO_2 powders and colloids, it has been proved by the femtosecond diffuse reflection spectroscopy that decay kinetics of photoexcited electrons trapped in surface sites reflects the recombination of electron and positive hole.[3,4] The aim of the present study is to evaluate the recombination rate for several kind of TiO_2 powders and to correlate the kinetic parameters with their photocatalytic activity[5]. Effects of reaction conditions, i.e., air and Pt loading, on the kinetics in picosecond time regime are also studied.

A colliding pulse mode-locked laser pumped by an argon ion laser was used throughout the study. The train of ca. 50 fs pulses is amplified at 30 Hz by a Q-switched Nd:YAG laser. The 620 nm light beam was split into pump and probe beams, the former of which was frequency doubled by a KDP crystal (maximum 1.7 μJ pulse). These two collinear beams were irradiated onto a quartz vertical-flow cell. Diffuse-reflected probe light from the suspension was focused and introduced to a photomultiplier tube through a monochromator. Absorption was recorded, as a function of probe delay, as $(1 - R/R_0)$ in which R and R_0 represent the intensity at a given delay and in the absence of pump pulse, respectively. TiO_2 suspensions (10 mg cm^{-3}) were prepared with Milli-Q water, sonicated for at least 10 min, and circulated through the quartz cell. Diffuse reflection from TiO_2 powders was measured in air.

Figure 1 shows representative time profiles of aqueous TiO_2 suspensions. It was commonly observed that a pump beam of wavelength at 310 nm induced very rapid (< ca. 250 fs) rise of absorption at 620 nm and its gradual decay, as has been reported previously.[4] The maximum absorption was 4-5 % irrespective of TiO_2 samples. The present profiles could be fitted to a second-order kinetics with an equation of,

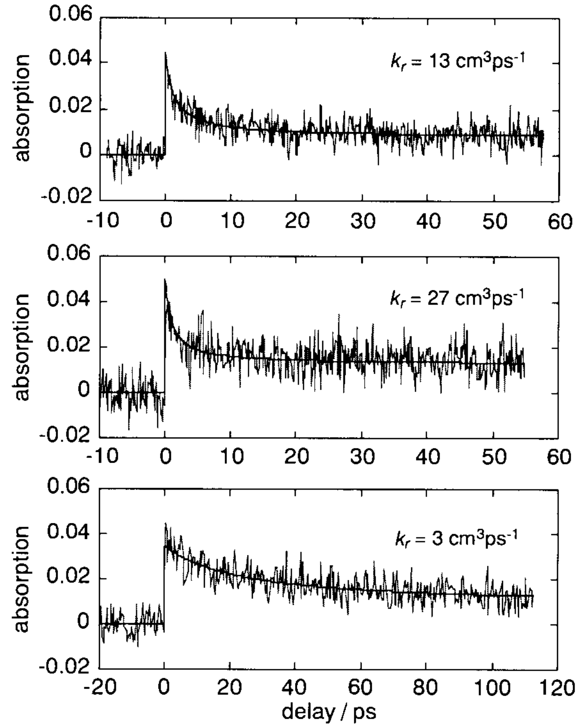

Figure 1. Representative decay profiles of TiO_2 suspension induced by ultrafast pump (ca. 50 fs). Results of P-25 (upper), Idemitsu UF (amorphous; middle), and JRC-TIO-2 (lower) were shown. Solid lines indicate the fitting with equation 1.

$$(\text{absorption}) = \alpha \{[e_0] / (1 + k_r [e_0] t) + BL\}, \qquad (1)$$

where $[e_0]$, BL, k_r, and t refer to initial concentration of trapped electron just after the pump pulse, base line corresponding to relatively long lived trapped electron, second-order rate constant for electron-hole recombination, and delay time.[6] This is based on the assumption that the trapped electron gives visible-light absorption and disappears by recombination with positive hole in the ps time scale. A parameter α (cm^3) includes photoabsorption cross section and penetration depth. The decay profile depended strongly on the pump beam intensity; the intenser the pump beam, the higher the maximum and the steeper the decay, but the decay curves were reproduced with almost same k_r value (Table 1) when α is assumed to be unity for a series of measurements.

Compared with results of powder reflection measurement, the profile for suspensions showed lower absorption (ca. 0.04 for all the suspensions and ca. 0.2 for powders) and poor signal-to-noise ratio, leading to fluctuation of k_r values. However, in the two different measurements, similar tendency of k_r

Table 1. Kinetic parameters[a] obtained from time profiles of several TiO_2 samples measured in air

TiO_2[b]	$k_r(s)$/cm^3ps^{-1}	%$BL(s)$	$k_r(p)$/cm^3ps^{-1}	%$BL(p)$
P-25	12-13	18-21	2.2	20
P-25/Pt	3	7	1.3	0
home made[c]	4-10	27-45	1.4	33
HyCOM(0)[d]	15-20	24	3.0	21
HyCOM(973)[e]	4-9	27-36	1.3	16
HyCOM(973)/Pt	3-6	19	0.51	0
Idemitsu UF	27	25	——[f]	——[f]
JRC-TIO-2	3	14	——[f]	——[f]

[a] Characters *s* and *p* in parentheses refer to suspension and powder, respectively. [b] Used without pre-treatment. [c] Anatase. [d] As prepared. [e] HyCOM(0) was calcined in air at 973 K. [f] Not measured.

dependence on the kind of TiO_2 samples was seen (Figure 2) when calculated temporally by assuming that α is 1 in both systems. An almost linear correlation suggests that we observe the same photoreaction process in both systems. A slope of ca. 5.7 resembles the reciprocal ratio of maximum absorption (ca. 5) and this may be related to difference in the parameter α.

As clearly seen in Table 1 and Figure 2, kinetic parameters of photoirradiated TiO_2 suspension depended strongly on the nature of TiO_2. As a general trend, the higher the photocatalytic activity, the smaller k_r has been seen (by the calculation using α as 1). Amorphous TiO_2 (Idemitsu UF) giving no X-ray diffraction peaks and negligible photocatalytic activity[2] showed the largest k_r, i.e., the fastest recombination. Although this TiO_2 has relatively large surface area, ca. 115 $m^2\ g^{-1}$ (BET method) to adsorb much amount of substrates, the faster recombination should make the overall activity to be negligible. HyCOM (Hydrothermal Crystallization in Organic Media)[7] TiO_2 without post calcination gave moderate k_r, in spite of larger surface area of 140 $m^2\ g^{-1}$, as expected from its high activity. Calcination at 973 K (HyCOM(973)) reduced k_r drastically, corresponding to the fact that the calcination enhanced the photocatalytic activity while it reduced surface area. The calcination would reduce number of crystal defects, acting as recombination center. Preliminary results showed that recombination rate for HyCOM (973) was ca. 2.5 times slower than that for P-25.[8] The ratio obtained in this study, ca. 2, supports this. An interesting fact is that k_r for JRC-TIO-2 (supplied from Catalysis Society of Japan as a "reference catalyst") was significantly smaller than that of P-25, the properties and activity of which closely resemble JRC-TIO-4, though Furube and coworkers reported the faster decay for TIO-2 than TIO-4.[5] One of the possible reasons for the discrepancy is the difference in the wavelength of pump beam; in the previous report 390 nm light, which is almost same as the band gap of anatase TiO_2, was employed, while in our system 310 nm pump beam can undoubtedly excite electron beyond the gap.

By using the P-25 suspension, two separate measurements were performed under air and Ar bubbling, but no appreciable difference was observed. Three possible reasons could account for the negligible oxygen (O_2) effect. (i) Reaction of electron with O_2, observed in continuous irradiation, can not be seen in ps time range. (ii) Strong adsorption of oxygen on the surface make O_2 left even after Ar bubbling. (iii) Number of photons absorbed by one TiO_2 particle is too large to be influenced by the adsorbed O_2. Although the reason is ambiguous, it is clear that practically we need not to deaerate the suspension before and during measurements.

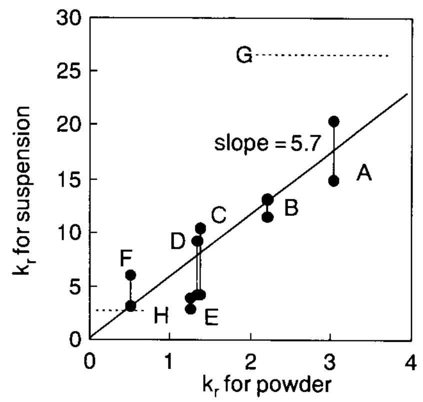

Figure 2. Relation between k_r values (cm^3ps^{-1}) obtained in the powder and suspension systems. A: HyCOM (0), B: P-25, C: home-made, D: HyCOM(700), E: P-25/Pt, F: HyCOM(700)/Pt, G: Idemitsu UF, and H: JRC-TIO-2. Dotted lines shows k_r for suspension of sample without powder measurements.

It is well known that Pt loading enhances the activity. Table 1 shows the effect of the Pt loading[9] on the parameters of P-25 and HyCOM(700). It is clear for both TiO_2's that the loading reduces k_r, i.e., life-time of trapped electron is increased, though faster decay of trapped electrons, i.e., larger k_r, by their transfer to the Pt site would be expected. Also found is that %*BL*, percentage of *BL* component in the overall absorption, $[e_0]$ + *BL*, decreased significantly, especially in the case of P-25. On the assumption that what we see is trapping of electrons at the sites followed by their recombination with holes, the above-mentioned results suggest that the trapped electron of longer life time, giving BL, moves to Pt during ps time region, thus leading to improvement of overall efficiency of utilizing photoexcited electrons.

In conclusion, through the femtosecond time-resolved study, it is shown that the nature of TiO_2 gives differences especially in rate constant for electron-hole recombination and observed value could be a relative measure for photocatalytic activity.

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References and Note

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