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Effect of Excitation Wavelength on Ultrafast Electron–Hole Recombination in Titanium(IV) Oxide Powders Irradiated by Femtosecond Laser Pulses

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Femtosecond time-resolved diffuse reflectance measurement was carried out for anatase and rutile TiO_2 powder systems in air. Anomalous rapid decay in the first few picoseconds after a rise in absorption was observed in both anatase and rutile TiO_2 powders when TiO_2 powder was excited by light pulses of near-band-gap energy, while it was not observed in the case of over-band-gap irradiation. These results suggest that the recombination dynamics does not depend on the crystal structure, if the wavelength dependence is normalized using energy relative to their absorption edges.

Photoirradiation of TiO_2 photocatalysts with light, the energy of which is greater than their band gap, creates pairs of electrons in the conduction band and positive holes in the valence band. They then react with species adsorbed on the surface or in solution to induce redox reactions or, otherwise, undergo mutual recombination without substantial chemical reactions.

Recently, femtosecond time-resolved diffuse reflectance (fs-TRDR) spectroscopic measurements have been performed to monitor charge-carrier trapping and recombination kinetics in TiO_2 nanoclusters.[1–5] Furube et al.[2] investigated the recombination dynamics of photogenerated charge carriers in several TiO_2 photocatalytic powders (standard photocatalytic powder JRC-TIO-1, -2, -3, -4, and -5 supplied by the Catalysis Society of Japan) generated by 390-nm light by means of fs-TRDR spectroscopy. They showed that electron–hole recombination kinetics depended strongly on crystal structure of TiO_2 powders and that charge carriers in anatase TiO_2 recombine faster than do those in rutile TiO_2. We, however, found no such rapid decay of photoexcited carriers in JRC-TIO-2, which is composed of anatase, as investigated by a femtosecond TRDR technique with 310-nm excitation. This discrepancy might be caused by the difference in wavelengths of the pump pulse. While Furube et al. used a 390-nm pump pulse, which corresponds roughly to the band gap of anatase TiO_2 (3.2 eV), we employed 310-nm light, the energy of which is much higher than the energy gap of anatase.

In the present study, we investigated the excitation wavelength-dependent carrier dynamics in anatase and rutile TiO_2 by fs-TRDR. In this paper, the effect of excitation wavelength on the ultrafast charge-carrier recombination dynamics is described and discussed in relation to the optical and photocatalytic properties of semiconductor powders.

Two kinds of TiO_2 powders, JRC-TIO-2 and JRC-TIO-5 were mainly examined in the present work. As a pretreatment for TRDR measurements, these powders were ground thoroughly in an agate mortar. No further treatments were carried out. The average particle diameters of JRC-TIO-2 and JRC-TIO-5 were 400 and 640 nm, respectively.

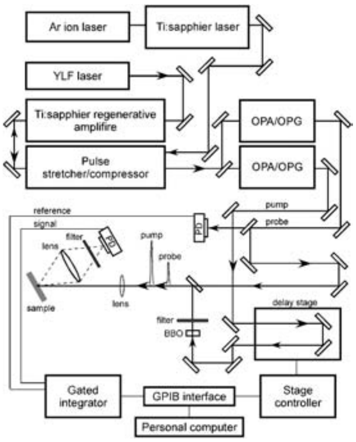

Figure 1. Schematic diagram of the femtosecond laser system and the time-resolved diffuse reflectance spectrometer.

A schematic diagram of the experimental arrangement for fs-TRDR measurement is shown in Figure 1. A femtosecond pulse train generated by a Ti:sapphire regenerative amplifier system (Quantronix, 4812RGA/4823S/C) was used to pump two (optical parametric generation/optical parametric amplification (OPG/OPA) systems (Light Conversion, TOPAS). The 620-nm output pulses from one OPG/OPA were mainly used as a probe beam (ca. 1.5 μJ/pulse) so that trapped carriers in TiO_2 could be monitored.[1] A 620–820-nm output beam from the other OPG/OPA was frequency-doubled in a BBO crystal and used as a pump beam (ca. 0.1 μJ/pulse). The probe beam was split into two, one for reference and the other for the sample. Both signals were detected by photodiodes (Hamamatsu Photonics Co. Ltd., S2387-66R). The pump and probe beams were collinearly focused and overlapped at the sample. Diffuse reflectance data were accumulated and recorded using a personal computer as follows:

$$\%absorption = 100 \times (1 - R/R_0), \qquad (1)$$

where R and R_0 represent the intensities of diffused light from the sample with and without a pump beam, respectively. Both R and R_0 were corrected by the reference beam intensity of each probe pulse.

Figure 2 shows the time profiles of transient absorption of 620 nm for the anatase TiO_2 powder (JRC-TIO-2) excited by various excitation wavelengths of light. In the case of 350- or 360-nm excitation, a rapid (<ca. 1 ps) rise and subsequent gradual decay were observed. This behavior is very similar to the results in the case of a 310-nm pump, as described in the previous paper.[4] When the excitation wavelength was set to 370 to 410 nm, however, a very rapid decay over a few picoseconds was observed after the rapid rise in absorption. After this rapid decay, a very slow decay corresponding to relatively long-lived

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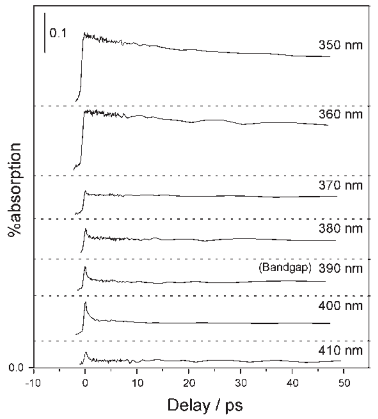

Figure 2. Excitation wavelength dependence of transient absorption decay profiles observed for JRC-TIO-2 (anatase).

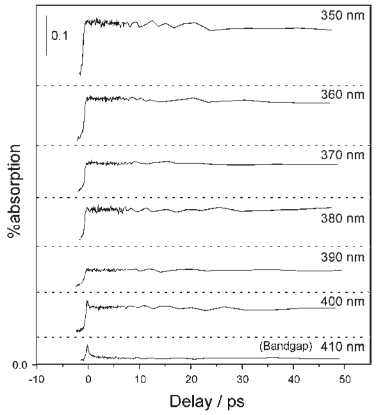

Figure 3. Excitation wavelength dependence of transient absorption decay profiles observed for JRC-TIO-5 (rutile).

trapped carriers was observed.[5] It should be noted here that the decay profile reported by Furube et al.[2] for JRC-TIO-2 by a 390-nm pump, mentioned above, was almost the same as that observed at the same pump wavelength in the present study. Since the band-gap energy of anatase TiO_2 is 3.2 eV (ca. 390 nm), no absorption was expected when JRC-TIO-2 was irradiated by a pump pulse with a wavelength longer than 390 nm. However, appreciable absorption was seen at >390 nm pumping. One of the possible reasons for this absorption is that a two-photon absorption process occurs in TiO_2 by intense femtosecond laser pulses.

Figure 3 shows the time profiles of transient absorption in rutile TiO_2 powder (JRC-TIO-5) observed with various pump wavelengths. In the case of rutile TiO_2 powder, a rapid (<ca. 1 ps) rise and a subsequent gradual decay were observed at 350- to 390-nm excitation. The behavior was quite similar to that observed in the case of anatase TiO_2 powder when the pump wavelength was set to 350 or 360 nm. With pumping at longer wavelengths, i.e., 370–410 nm, almost constant absorption following very rapid decay was observed, and the constant absorption became smaller with increase in the pump wavelength. Thus, in the case of rutile TiO_2, a very rapid decay in the early stage was observed in the case of 400- or 410-nm pumping.

While the effects of pump wavelength on electron–hole recombination dynamics were very similar in the two TiO_2 powders, a difference between pump wavelengths causing very rapid decay was observed in the case of anatase and rutile crystallites: >370 nm for anatase and >400 nm for rutile. It should be noted that this ca. 30-nm difference in pump wavelength coincides quite well with the difference in absorption edge between anatase (3.2 eV = 388 nm) and rutile (3.0 eV = 413 nm). These results suggest that there is, basically, no difference between electron–hole recombination dynamics of anatase and rutile TiO_2, i.e., the recombination dynamics does not depend on the crystal structure, if the wavelength dependence is normalized using energy relative to their absorption edges. Since only limited information is available at present to discuss the origin of the rapid decay, further detail investigation may be required

In conclusion, the results shown in this article suggested that the electron–hole recombination in the early stage of a particulate photocatalytic reaction strongly depends on the excitation pump wavelength; irradiation at a near-band-gap wavelength led to a very fast recombination, which was not observed in the case of over-band-gap irradiation. Surprisingly, the very fast recombination was seen at an excitation wavelength of ca. 20 nm shorter than the band gap (390 and 410 nm for anatase and rutile crystallites, respectively). Since the light intensity (photon flux) in the present pump-probe measurement system was much higher than that in ordinary photocatalytic systems, it is difficult to directly compare the results with those of conventional photocatalytic reactions. However, it should be noted that appreciable wavelength dependence exists and that this should be taken into account when discussing the kinetics and photocatalytic activity by comparing the experimental results obtained by different light sources or those for TiO_2 powders of different crystal compositions.

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