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Reaction of holes in nanocrystalline TiO_2 films evaluated by highly sensitive transient absorption spectroscopy

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Abstract

Reactions of holes in nanocrystalline TiO_2 films were studied with a newly developed, highly sensitive transient absorption spectrometer. Transient absorption measurements were examined in acetonitrile, water, toluene and alcohols under low excitation intensity conditions. From these results, the reactivity of the holes could be evaluated.

Keywords: TiO_2; Transient absorption; Charge recombination; Hole transfer reaction

1. Introduction

Photocatalytic reactions of TiO_2 have been attracting much interest because they can be applied to water splitting [1], degradation of environmental pollutants [2,3], air purification [2,3], solar energy conversion [4] and so on. Much fundamental research has been carried out, and some of the discoveries have been successfully applied in industry. To improve the performance of such photocatalytic processes, the primary reaction processes have been extensively studied through various experimental techniques. The primary reaction processes are known to be photo-induced transfer of electrons and/or holes from TiO_2 to reactants at the surface. Despite much effort, the primary mechanism remains unclear. One reason for this is that photocatalytic activity is sensitive to the preparation procedure for TiO_2 photocatalysts. Thus, standard methods for evaluating this activity have been explored.

Transient absorption spectroscopy (TAS) is a powerful technique for investigating photochemical processes in detail. For photocatalytic reaction of TiO_2, transient absorption techniques have frequently been used to clarify the primary processes. The reaction of gas molecules with TiO_2 have been studied by observing infrared absorption due to electrons in TiO_2 [5]. In the solution phase, reaction between electrons and/or holes and reactants can also be studied by TAS in the visible wavelength range [6–15]. In this range, results are often confusing because spectra due to holes overlap with spectra due to electrons. We have studied photocatalytic reaction of TiO_2 over a wide wavelength range (400–2500 nm) with TAS. We identified the absorption spectra due to holes and electrons in TiO_2 [16] and investigated the temporal changes in the spectra [17]. We recently evaluated the rate constants of reactions between several alcohols and holes by using femtosecond time-resolved TAS [18].

Through these previous efforts, we elucidated three important requirements for evaluation of photocatalytic reactions of TiO_2 by TAS. The first requirement is assignment of the absorption spectra. Absorption spectra due to electrons and holes in TiO_2 are superposed upon each other, and therefore evaluating which species contribute in particular reactions is difficult. The second requirement is low excitation intensity. Laser intensity for conventional transient absorption studies is too strong, and a weak light source, such as solar light or conventional lamps, is used in practical applications. Under intense laser-pulse excitation conditions, bulk recombination between electrons and holes occurs efficiently, and therefore such active species disappear immediately. The third requirement is a long time frame. The reaction rate of active species (electrons and holes) in TiO_2 is different in each reaction system. Recently, we observed very fast reaction of holes with methanol, occurring

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within 300 ps [18]. The reaction between electrons and O_2 in methanol is known to be slow, occurring within 14 ms [15]. To evaluate these reaction systems, a long time frame is necessary.

In this study, we developed a suitable transient absorption spectrometer for evaluation of photocatalytic reactions in TiO_2. With the apparatus, it was possible to monitor the reaction of the holes with various liquids.

2. Experimental

The transient absorption spectrometer that we developed is shown (Fig. 1). The third harmonic (355 nm) of a Nd^{3+}:YAG laser (HOYA Continuum, Surelite II) was employed for excitation. The repetition rate of the laser was 10 Hz, and the pulse duration was about 8 ns. The excitation light beam was incident at 20° on a sample specimen. A He–Ne laser (25 mW, 633 nm, JPS Uniphase 1145P) and a blue diode laser (20 mW, 437 nm, Neoark, TC20-4420-4.5, 20 mW) were used as probe light to detect transient absorption decay. The probe light was split into two beams by the beam splitter. One of the beams (sample beam) was incident at 90° on a sample specimen and was introduced into a Si photodiode (Hamamatsu, S-1722-02). The other beam (reference beam) was introduced directly into the same type of Si photodiode. These photodiodes were placed in a box with a small aperture to prevent stray light and sample luminescence from interfering with measurements. Photocurrent signals from both detectors were introduced into a differential amplifier (NF Electronic Instruments, 5305). Using the amplifier, the DC component of the light intensity could be cancelled out; that is, only a signal change induced by pulsed laser excitation could be detected. The amplifier could also eliminate fluctuation of the light intensity of the probe light source. To realize higher sensitivity for the transient absorption signal, the signal from both detectors must be the same. The light intensity was controlled by changing the angle of a glass plate placed in the reference beam in front of the photodiode. The signal from the amplifier was introduced into a digital oscilloscope (Tektronix, TDS5032) and transferred to a personal computer for analysis. With this system, we could measure a small absorbance change ($<10^{-5}$) after 1000 pulses, on average. The time resolution of the overall system was about 50 ns. The intensity of the laser pulse was measured with a pyroelectric energy meter (OPHIR, PE25-SH-V2). All measurements were carried out at 295 K.

TiO_2 nanoparticles were prepared by the method reported by Grätzel and co-workers [19]. The mean diameter of the primary nanoparticles was 10–15 nm. The organic paste containing the semiconductor nanoparticles was printed on a glass substrate by a screen-printing technique [20]. When the sample was calcined, the opaque film became transparent enough for spectroscopic measurements. After calcination, the mean diameter increased slightly to about 20 nm, as measured by scanning electron microscopy. The crystal phase was anatase. The TiO_2 films were 1 cm^2 (1 cm × 1 cm) in area and 2–5 μm thick.

3. Results and discussion

3.1. Effect of excitation intensity on recombination kinetics

We previously studied transient absorption in nanocrystalline TiO_2 films, which are widely used as electrodes for dye-sensitized solar cells. The sample specimens used in the present study were prepared by the procedure described in our previous publication [16]. Thus, it is possible to estimate the contribution of holes and electrons at particular wavelengths in the absorption spectrum.

At this wavelength of a blue diode laser (437 nm), absorptions due to holes are mainly expected to be observed. Thus, reactions of holes can be evaluated quantitatively. Actually, contribution of electrons in the signal is less than 10% [16]. At the wavelength of a He–Ne laser (633 nm), absorptions due to both electrons and holes are expected to be observed with a ratio of 1:2. Under the condition, reactions of both species can be evaluated. Thus, the reaction of electrons can be evaluated after subtraction of the signal due to holes obtained from the blue-laser experiments.

Fig. 2 shows transient absorption decay recorded using He–Ne laser (633 nm) at various excitation light intensities I_{ex} (dotted line, 0.14; solid line, 0.28; and solid line, 3.4 mJ cm^{-2}) normalized at time = 0. The decay rate seems to increase with increasing excitation intensity, suggesting that bulk recombination between holes and electrons

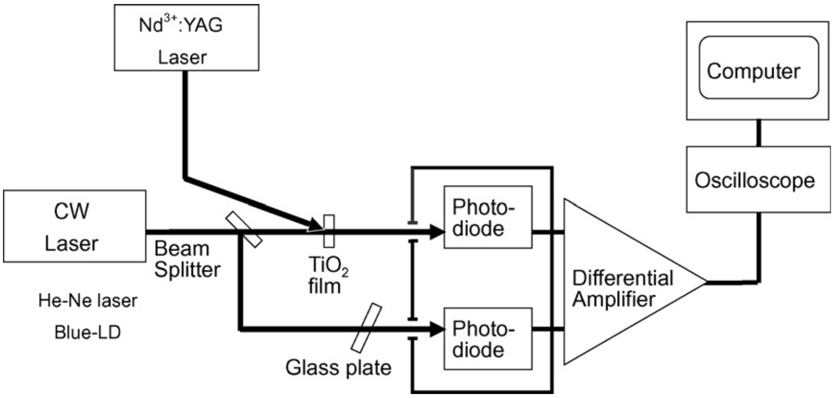

Fig. 1. Transient absorption spectrometer developed.

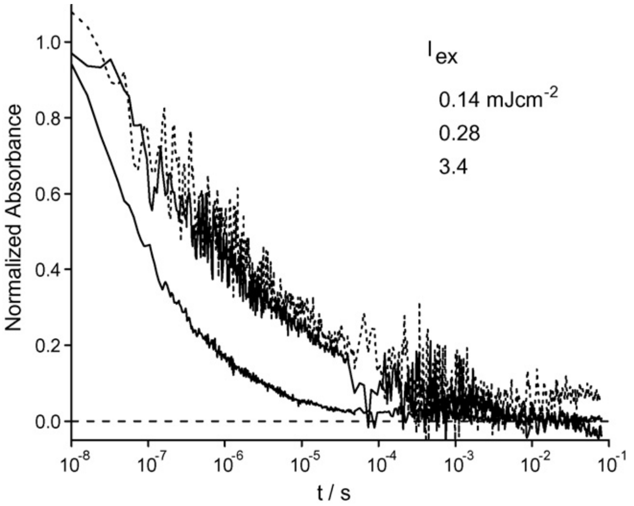

Fig. 2. Transient absorption decay of nanocrystalline TiO_2 films dried in air observed at various excitation intensities (dotted line, 0.14; solid line, 0.28; and solid line, 3.4 mJ cm^{-2}) normalized at time = 0 ns.

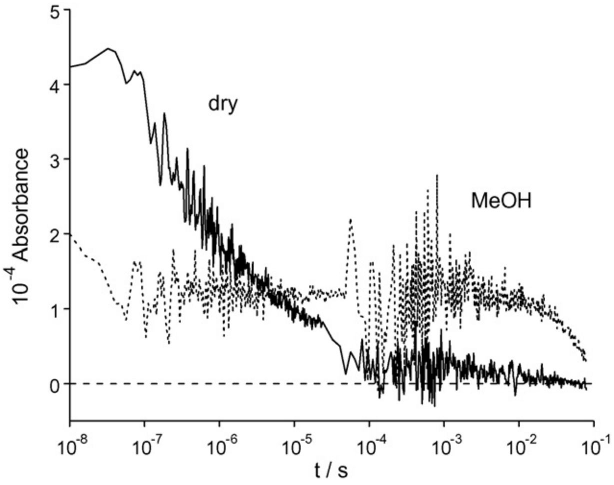

Fig. 3. Transient absorption decay of nanocrystalline TiO_2 films dried in air (solid line) and immersed in methanol (broken line).

dominated. At weak excitation intensities, by contrast, the decay profiles were similar to each other, which indicates that geminate recombination occurred. It was found that the geminate recombination proceeds within 1 μs [16]. This dependence on light intensity can be explained with the model proposed by Durrant et al. for understanding similar phenomena in dye-sensitized TiO_2 films [15]; namely, interparticle transfer of holes and electrons is slow, and only geminate recombination occurs in the particles under low-density conditions. In fact, we found that one electron–hole pair is produced in the particles at 0.28 mJ cm^{-2}. Thus, the same kinetics can be expected under conditions of extremely weak light irradiation, such as sunlight.

The transient absorption signal can be detected up to 80 ms (Fig. 2). Although the decay profile of ultrafast reactions, such as the reaction between holes and methanol molecules [18], cannot be measured directly, the time resolution of the present spectrometer is sufficiently better than the time for the recombination event, which occurs within a 1-μs time range. Thus, fast reactions can be followed indirectly with any substantial decrease of the initial absorbance, and slower reactions can be detected directly with any change in decay. As we mentioned, at least three requirements for TAS study of photocatalytic reactions of TiO_2 must be fulfilled. The spectrometer developed in our laboratory can be used for this purpose.

3.2. Reaction of holes with methanol

Transient absorption decay of a nanocrystalline TiO_2 films in air and in methanol under weak excitation conditions (I_{ex} = 0.25 mJ cm^{-2}) observed at 633 nm is shown (Fig. 3). The surface of TiO_2 is reported to be covered with water molecules [21], and to examine the effect of adsorbed water molecules, we measured the transient absorption signal in a vessel filled with N_2 gas just after baking the films at 800 K for 2 h. Baking the vessel had no effect, which suggests that adsorbed water molecules are not important for the photocatalytic reactions of the films studied herein. Hence, a film dried in air can be used as a reference sample for the evaluation of photocatalytic reactions.

The initial absorbance observed at 633 nm of the films immersed in methanol is about one-third that of films dried in air (Fig. 3). We have already reported that the reaction between holes and methanol molecules is very efficient from the results of transient absorption signal observed at 415 nm [18]. Thus, the remaining signal in methanol can be assigned to absorption due to electrons, and the signal decays very slowly through reaction with oxygen molecules in methanol. The concentration of oxygen is estimated to be 2 mM in air-saturated methanol [22]. The decay of electrons can be roughly fitted by a single-exponential function, and the time constant is estimated to be 70 ms, which is slightly longer than the rate constant reported by Durrant and co-workers [15]. Almost all active species disappear within the repetition period of the excitation laser (10 Hz). Thus, photocatalytic reactions of TiO_2 can be evaluated by using the spectrometer developed in our laboratory.

3.3. Reactivity of holes with acetonitrile, water and toluene

The transient absorption decay of nanocrystalline TiO_2 films recorded at 633 nm in various solvents (acetonitrile, water and toluene) (solid lines) together with that in air (broken lines) is shown (Fig. 4). The transient absorption signals change very little in the solvents; the change is so slight that it suggests no chemical reactions have occurred.

Photocatalytic reactions of TiO_2 with acetonitrile, water and toluene have been studied, and these solvent molecules are decomposed by photocatalytic reactions. The degradation of acetonitrile has been studied in aqueous solution and in the gas phase [23,24]. Photocatalytic reactions of water and TiO_2 have been widely explored because of their potential application for hydrogen production by solar light irradiation [1,25,26].

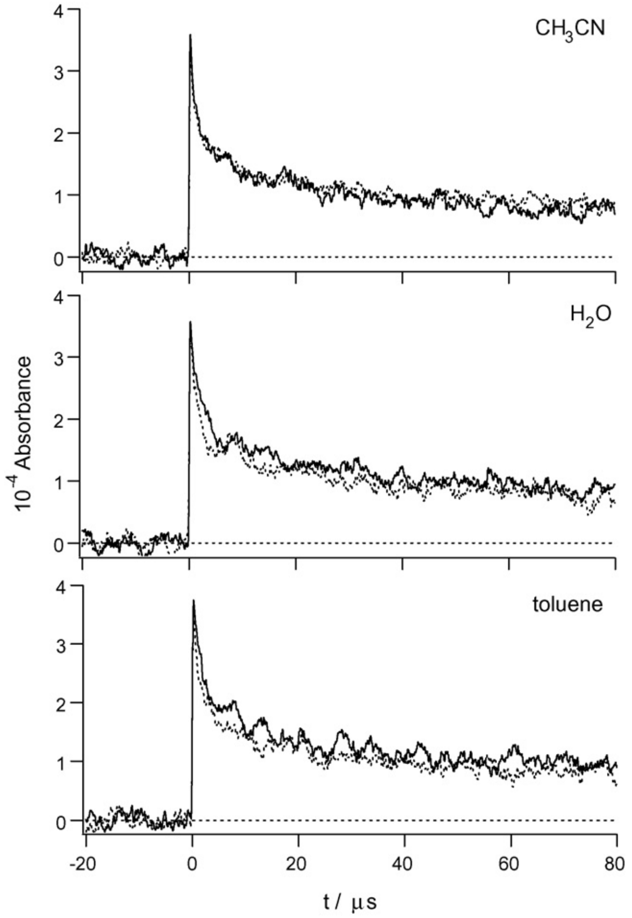

Fig. 4. Transient absorption decay of nanocrystalline TiO_2 films dried in air (broken lines) and immersed in acetonitrile, water or toluene (solid lines).

For transient absorption study, Rabani et al. could not observe this reaction at the microsecond time range [9], which is similar to the present results. However, Yamakata et al. could observe the reaction over a slower time range [5]. Photocatalytic degradation of toluene by TiO_2 in air has been studied in the gas phase and in the liquid phase, and a model including hole transfer to toluene molecules has been proposed as the primary process [27,28].

In the present study, we observed no chemical reactions in acetonitrile, water or toluene, whereas degradation of these solvent molecules was observed. This discrepancy may be due to the differences between photocatalysts. Our nanocrystalline TiO_2 sample films have been widely used for electrodes in dye-sensitized solar cells [4,19,20], but photocatalytic activity of the films did not evaluate in detail. We tentatively conclude that our sample is not suitable for these reactions. Thus, it is interesting to investigate the differences in activities among different catalysts.

3.4. Reaction of holes with large-sized alcohols

Reaction of holes in TiO_2 with methanol is known to be very efficient. We have already studied the reaction rate of the reactions of holes with methanol, ethanol and 2-propanol [18]. These reactions are very efficient, with efficiencies estimated to be almost unity. The reaction rate tends to decrease with increasing molecule size. At present, the reason is not clear, but the difference in oxidation potential among alcohols may affect the reaction rate.

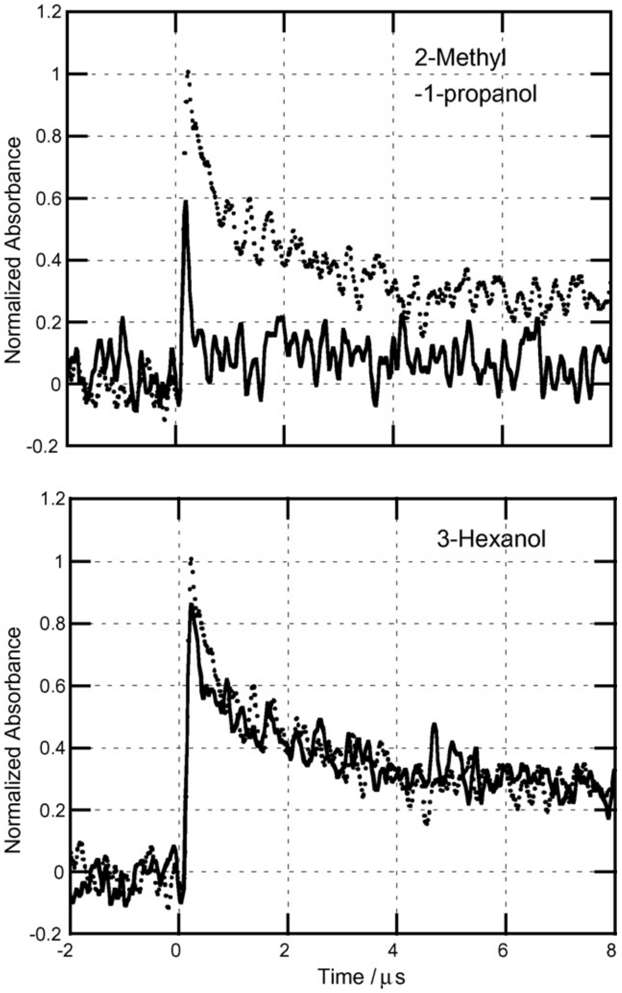

Fig. 5. Transient absorption decay of nanocrystalline TiO_2 films dried in acetonitrile (broken lines) and immersed in 2-methyl-1-propanol and 3-hexanol (solid lines) recorded by using a blue-laser diode (437 nm).

Fig. 5 shows the transient absorption signals of films in 2-methyl-1-propanol and 3-hexanol (solid lines) recorded at 437 nm together with the signal of films in acetonitrile (broken lines). The signal in 2-methyl-1-propanol is steeply decays at early time range and remaining absorbance is about 10% of the initial absorbance in acetonitrile. The steep decay reflects the fast reaction between holes and 2-methyl-1-propanol molecules. From the results, we estimate the efficiency of the reaction evaluated to be more than 0.9. For 3-hexanol, on the contrary, slight decrease of the transient absorption signal can be seen. From this, we estimate the efficiency of the reaction to be about 0.15.

Fig. 6 shows the transient absorption signals of films in 2-methyl-1-propanol and 3-hexanol (solid lines) recorded at 633 nm together with the signal of films in air (broken lines). The initial absorbance with 2-methyl-1-propanol is one third that observed in air, and the decay rate slows down compared to

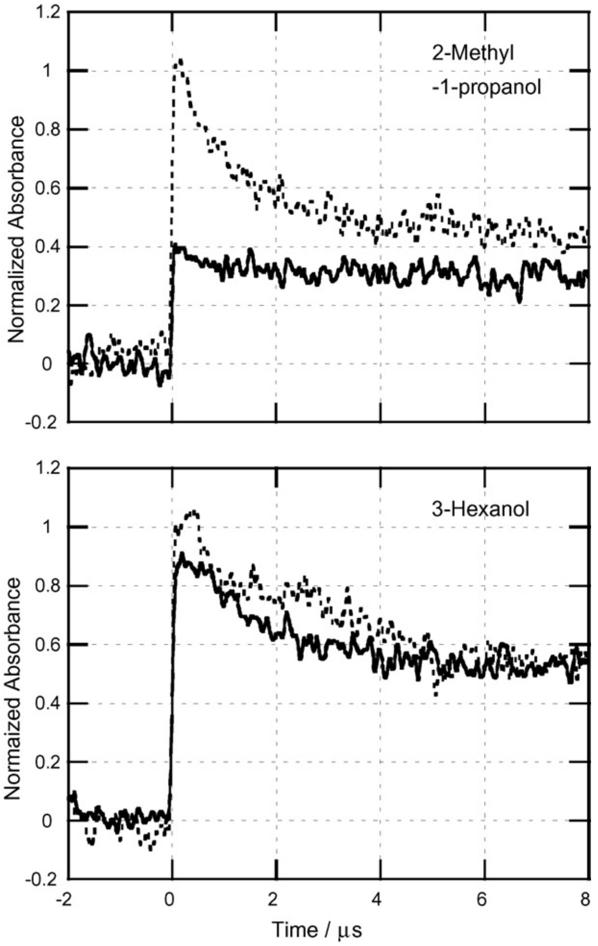

Fig. 6. Transient absorption decay of nanocrystalline TiO_2 films dried in air (broken lines) and immersed in 2-methyl-1-propanol and 3-hexanol (solid lines) recorded by using a He–Ne laser (633 nm).

the rate for the sample dried in air, becoming similar to the rate observed in methanol. This clearly shows that the reaction between holes and 2-methyl-1-propanol molecules is very efficient, which is consistent with the fact obtained from the results at 437-nm observation (Fig. 5). For 3-hexanol, slight decrease of the transient absorption signal can be seen, which is similar to that observed at 437 nm. The small reaction efficiency (0.15) can be also obtained from the results.

The primary process of the reaction can be considered to be hole transfer from TiO_2 to adsorbed alcohol molecules. Thus, the ionization potential of a donor molecule is an important parameter for evaluating reactivity. The ionization potentials (I_p) of the alcohols studied are reported to be 10.02 eV for 2-methyl-1-propanol and 9.63 eV for 3-hexanol [29]. Although ionization potentials are not much different, reactivity of these molecules with holes in TiO_2 is different as shown in Figs. 5 and 6. Namely, there seems to be no correlation between I_p values and reactivity. This implies that the reactivity difference observed in the present study is not due to hole transfer.

The adsorption efficiency of alcohol molecules on the TiO_2 surface may affect the apparent reactivity of holes. As shown for 3-hexanol, 15% of the holes react immediately, and the remaining holes recombine with electrons. This heterogeneous reaction suggests that the TiO_2 surface is not fully covered with alcohol molecules. Thus, only molecules situated near holes undergo reaction. Such phenomena have been observed for the reaction of holes with sugars and polyols [11].

4. Conclusion

Reactions of holes in nanocrystalline TiO_2 films were studied with the transient absorption spectrometer that we developed. No reactions of holes with liquid acetonitrile, water or toluene were observed. Reactions of alcohols with holes were observed for small-sized alcohols, whereas reactivity decreased as the size of the alcohol molecule increased. This result may be due to the adsorption of fewer molecules on the surface, resulting in lower activity. We believe that the technique presented here can be used to evaluate the photocatalytic activities of TiO_2 materials prepared by various methods.

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