



Electron–hole recombination in the bulk of a rutile TiO₂ single crystal studied by sub-nanosecond transient absorption spectroscopy

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ABSTRACT

The rate constant of electron–hole recombination in the bulk of a rutile TiO₂ single crystal was estimated to be $k_{\text{rec}} = 5 \times 10^{-13} \text{ cm}^{-3} \text{ s}^{-1}$ through sub-nanosecond time-resolved transient absorption spectroscopy. This value is more than four orders of magnitude smaller than the diffusion-limited rate constant ($k_{\text{rec}}^{\text{diff}} = 1.4 \times 10^{-8} \text{ cm}^{-3} \text{ s}^{-1}$) for a rutile TiO₂ crystal, suggesting low recombination reactivity between electrons and holes in the crystal.

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1. Introduction

Photocatalytic reactions of TiO₂ have been attracting much interest because of their applications in chemical processes including water splitting [1], degradation of environmental pollutants [2,3], and air purification [2,3]. The primary reaction process for TiO₂ photocatalysis is the photo-induced transfer of electrons, holes, or both from TiO₂ to reactants at surfaces. Slow recombination between electrons and holes leads to high photocatalytic activity, as demonstrated by Ohtani et al. [4]. Additionally, large surface areas of the catalysts can also contribute to enhanced photocatalyst performance, because primary photocatalytic reactions occur at surfaces.

Transient absorption (TA) spectroscopy is a powerful tool for studying primary reactions in TiO₂ photocatalysts [5,6]. We have studied photocatalytic reactions of TiO₂ over a wide wavelength range (400–2500 nm) with TA spectroscopy. We have assigned absorption spectral features attributed to holes and electrons in nanocrystalline TiO₂ films [7,8] and investigated the temporal changes in the spectra [9,10]. We recently studied the reaction of holes with alcohols through direct evaluation of the reaction rate constants [11] and quantum yields [12]. For nanocrystalline films, recombination occurs within several microseconds under weak excitation conditions, whereas the rate constant cannot be determined because the decay profiles do not obey second-order kinetics [7,8]. For nanoparticles dispersed in aqueous solvents, the second-order recombination kinetics between electrons and holes has been examined through TA spectroscopy, and the recombination rate constant k_{rec} is estimated to be $k_{\text{rec}} = 3.2 \times 10^{-11} \text{ cm}^{-3} \text{ s}^{-1}$ for 12-nm particles [13] and $k_{\text{rec}} = 1.8 \times 10^{-10} \text{ cm}^{-3} \text{ s}^{-1}$ for 2-nm particles [14].

The diffusion-limited recombination rate constant, $k_{\text{rec}}^{\text{diff}}$ of charge carriers can be estimated as

$$k_{\text{rec}}^{\text{diff}} = \frac{e}{\varepsilon \varepsilon_0} \mu \quad (1)$$

where e is the elementary charge, ε_0 and ε is the dielectric constant of free space and of a material, respectively and μ is the sum of the mobility of electrons and holes. The mobility of charge carriers in a smooth polycrystalline layer of anatase TiO₂ has been evaluated to be $\mu = 2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by means of a time-resolved microwave conductivity (TRMC) technique [15] and μ has been evaluated to be $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a rutile single TiO₂ crystal through THz time-domain spectroscopy [16]. Accordingly, using an ε value of 130, $k_{\text{rec}}^{\text{diff}} = 2.8 \times 10^{-8} \text{ cm}^{-3} \text{ s}^{-1}$ for an anatase crystal and $k_{\text{rec}}^{\text{diff}} = 1.4 \times 10^{-8} \text{ cm}^{-3} \text{ s}^{-1}$ for a rutile crystal. Although there have been no experimental results for the recombination rate constant for bulk crystals, the $k_{\text{rec}}^{\text{diff}}$ value estimated for bulk crystals is much larger than the recombination rate constant observed for nanoparticles experimentally. One possible explanation for this difference is that nanoparticles have smaller charge carrier mobility owing to their large surface areas, which might promote a large amount of traps for charge carriers at the nanoparticle surface. Another possibility is that the reactivity between electrons and holes is low, meaning that recombination is not diffusion-limited. This implies that small recombination rate constant can be obtained even for bulk crystals.

In this study, we evaluated the charge recombination rate constant in the bulk of a rutile single crystal of TiO₂ to explore the origin of the slow recombination rate observed for TiO₂ nanoparticles. The recombination process was monitored by means of a sub-nanosecond, time-resolved TA spectroscopy technique under bulk excitation conditions. The obtained rate constant was more than four orders of magnitude smaller than that of the diffusion-limited rate constant, suggesting low reactivity between electrons and

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holes. This result implies that the slow recombination observed for nanoparticles is caused by low reactivity.

2. Experimental

Single crystals of TiO₂ were purchased from Nakazumi Crystal Laboratory. The crystal phase was rutile and the crystal face was (001). The specimen was 1 cm × 1 cm in area and 0.2 mm thick.

For TA measurements, the third harmonic (355 nm) of a Nd³⁺:YAG laser after pulse compression (Ekspla, SL311) was employed for excitation. The repetition rate of the laser was 10 Hz and the pulse duration was about 150 ps. A Xe flash lamp (Hamamatsu, L4642, 2-μs pulse duration) was used as a probe light source. The probe light was introduced into a Si photodiode (New Focus, 1601). For near-infrared wavelength measurements, an InGaAs photodetector (New Focus, 1611) was used. The signal from the detector was introduced into a digital oscilloscope (LeCroy, 6200 A). With this system, we could measure a small absorbance change (<10^{−3}) after 100 pulses, on average. The rise time of the overall system was about 400 ps. 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.

3. Results and discussion

Fig. 1 shows a TA spectrum of the rutile TiO₂ crystal recorded just after excitation with 355-nm light. The excitation intensity was $I_{\text{ex}} = 2.8 \text{ mJ cm}^{-2}$. The penetration depth L of 355-nm light is estimated to be 500 nm [17]; therefore, charge carriers were generated in the bulk crystal by excitation with this light. The observed spectrum is similar to one that was previously reported [18]. The spectrum of free charge carriers in semiconductor crystals is described by the power law λ^n , where $n = 1$ –3, that is concave shape [19]. However, the shape of the spectrum in Fig. 1 is convex, suggesting that the charge carriers were not in a fully free state. Nevertheless, this spectrum is substantially different from that observed for nanocrystalline TiO₂ films. In particular, a pronounced peak at 550 nm has been observed in the spectra of nanocrystalline TiO₂ films [7]. This peak is assigned to absorption due to surface-trapped holes. This spectral difference implies that holes were weakly trapped in the TiO₂ single crystal.

The absorption coefficient, ϵ_{abs} , of the charge carriers in TiO₂ can be estimated using the change in absorbance (ΔA) observed for TA

measurements, the excitation light intensity (I_{ex}) and quantum yield of charge separation (Φ_{CS})

$$\epsilon_{\text{abs}} = \frac{\Delta A}{\Phi_{\text{CS}} I_{\text{ex}}} \quad (2)$$

The Φ_{CS} value for the direct band-gap excitation of TiO₂ equals unity, as determined by photo-electrochemical measurements [20]. Thus, the absorption coefficient at 850 nm was estimated to be $600 \text{ M}^{-1} \text{ cm}^{-1}$. This absorption coefficient is similar to those previously observed for electrons of nanoparticles in aqueous solutions [21,22].

Fig. 2 shows decay profiles of the TA signal observed at 850 nm under several different excitation intensities. The decay occurred more rapidly with increasing excitation intensity, indicating that the decay was limited by the recombination between electrons and holes. Fig. 3 shows the absorbance just after excitation as a function of excitation intensities. The linear relationship observed here shows no ultrafast recombination which is unable to detect in the time resolution of our system.

The recombination of charge carriers in TiO₂ crystals might be affected by the presence of traps on the crystal surface because the mobility of charge carriers is reduced by trapping, even if the charge carriers are primary generated in the bulk of the crystal. The mobility of charge carriers in a rutile TiO₂ single crystal is reported to be $\mu = 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [16]. Thus, the diffusion time t_{diff} for an electron to travel from the bulk to the surface of the crystal can be estimated to be $eL^2/\mu kT = 100 \text{ ns}$, where L is the penetration depth of excitation light. This t_{diff} value is sufficiently larger than the decay time of the TA spectra observed in the present study (Fig. 2). Although some of charge carriers generated near the surface can reach to the surface during recombination time, recombination kinetics can be well fitted by the second-order kinetics as shown below. This implies that trapping process at the surface is not efficient. Thus, charge recombination mainly occurred in the bulk of the crystal in the present case.

The second-order recombination kinetics can be described by

$$\frac{d[N]}{dt} = -k_{\text{rec}}[N]^2 \quad (3)$$

where $[N]$ denotes the density of the generated charge carriers. The equation can be solved as

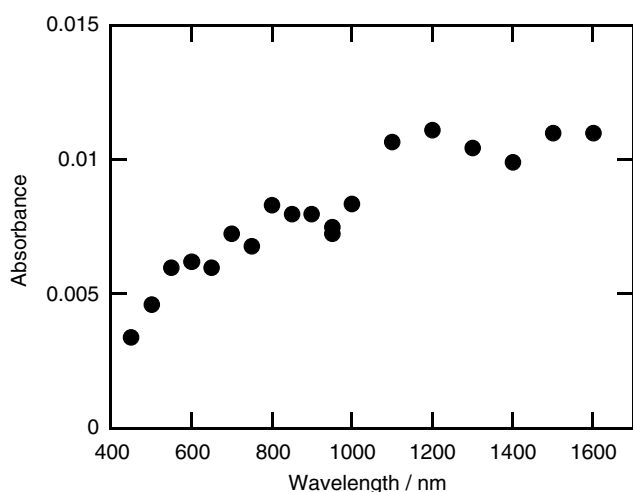


Fig. 1. Transient absorption spectrum of a rutile TiO₂ single crystal excited by 355-nm light.

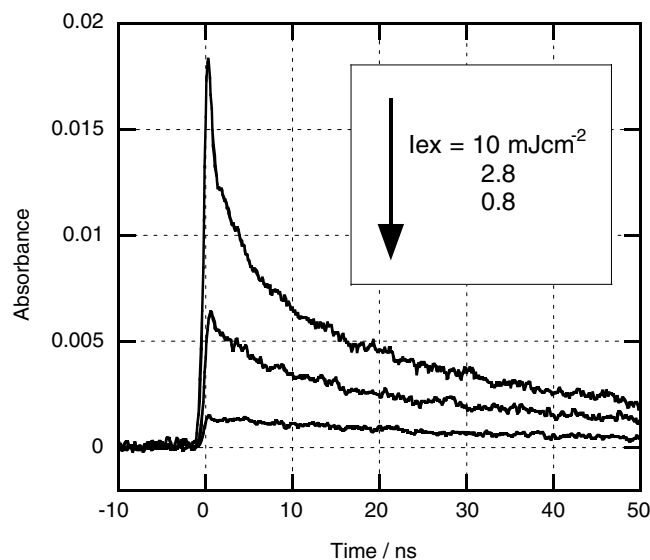


Fig. 2. Decay profiles of transient absorption in a rutile TiO₂ single crystal under various excitation intensities.

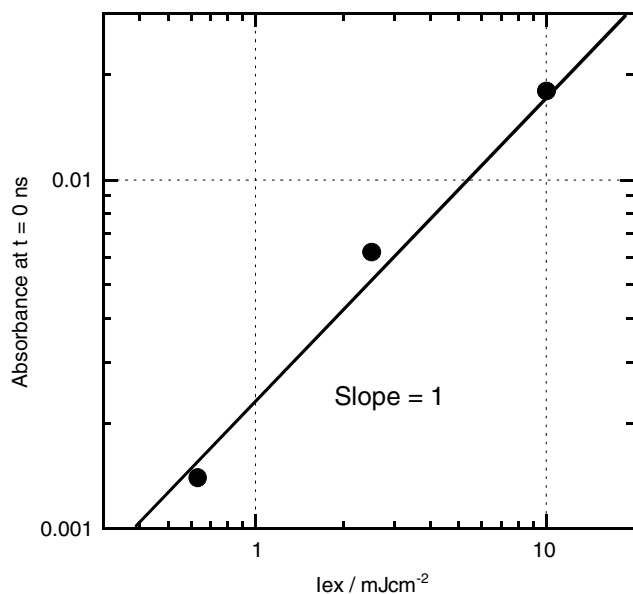


Fig. 3. Transient absorption signals from Fig. 2 observed just after excitation as a function of excitation intensity.

$$\frac{1}{[N]} = k_{\text{rec}}t + \frac{1}{[N]_0} \quad (4)$$

where $[N]_0$ denotes the density of generated charge carriers at time $t = 0$ after excitation. $[N]_0$ can be evaluated as

$$[N]_0 = \frac{\Phi_{\text{CR}} I_{\text{ex}}}{L} \quad (5)$$

Fig. 4 shows the reciprocal absorbance as a function of time for the TA decay recorded at $I_{\text{ex}} = 2.8 \text{ mJ cm}^{-2}$. The linear relationship observed here clearly shows that the decay obeyed second-order kinetics. Thus, the recombination rate constant can be estimated as $k_{\text{rec}} = 5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. This value is obviously more than four orders of magnitude smaller than that of the diffusion-limited rate constant ($k_{\text{rec}}^{\text{diff}} = 1.4 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$) estimated for rutile TiO_2 single crystals. This large difference is attributed to the low reactivity of between electrons and holes.

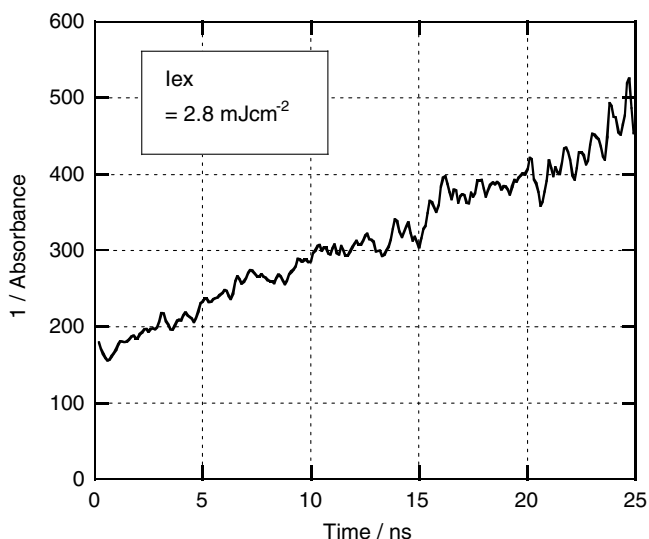


Fig. 4. Reciprocal absorbance as a function of time for the TA decay recorded at $I_{\text{ex}} = 2.8 \text{ mJ cm}^{-2}$.

The cause of the observed low reactivity between electrons and holes is not clear. Possibly, lattice deformation induced by charge carriers contributed to this reduced reactivity. Charge carrier transport in TiO_2 has been described by using a small polaron model, namely charge carriers interact with crystal lattice [16]. We recently discussed the origin of absorption spectra due to holes in nanocrystalline TiO_2 films [8], and we noted that holes located on an oxygen atom produce a characteristic absorption in the visible wavelength range upon deformation of the crystal lattice. As shown in Fig. 1, the spectrum obtained in the present study indicated that the charge carriers were not fully freely moving, suggesting that charge carriers, probably holes, were trapped by induced lattice deformations in the bulk of crystal. These deformations may have acted as a barrier for the holes' recombination with electrons.

For nanocrystalline TiO_2 films, charge carrier recombination occurs on the microsecond timescale under weak excitation conditions [7]. The rate constant of the recombination is difficult to evaluate because the decay does not obey second-order kinetics. Recently, the effective mobility of charge carriers in nanocrystalline TiO_2 films was evaluated to be $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ through time-resolved microwave conductivity (TRMC) measurements. The mobility evaluated by TRMC is reduced by some reasons [23], namely, the value of mobility is lower limit. In nanoparticles, holes are trapped at the surface and therefore the minimum time required for recombination under low excitation intensity conditions can be estimated from the diffusion time in the particle. In such instances, the diffusion time t_{diff} can be expressed as $t_{\text{diff}} = er^2/\mu kT$, where r is the particle radius. By using $r = 10 \text{ nm}$, $\mu = 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $T = 293 \text{ K}$, we estimated the recombination of electrons and surface-trapped holes in one particle to be completed within 4 ns. This timescale is much faster than the microsecond recombination observed for nanocrystalline TiO_2 films. This implies that the recombination rate is determined by the reactivity between electrons and holes, and is not determined by mobility of charge carriers, which is consistent with the present TA results.

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