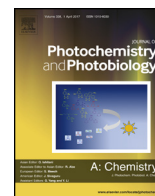




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Invited paper

Surface and bulk carrier recombination dynamics of rutile type TiO₂ powder as revealed by sub-ns time-resolved diffuse reflection spectroscopy

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ABSTRACT

The carrier dynamics of the semiconductor photocatalyst is the essential concern to clarify the detailed mechanisms of photocatalytic water splitting reactions, which is one of the key issues of artificial photosynthesis to produce solar fuels. In this present study, time-resolved transient diffuse reflection spectra of rutile type TiO₂ powder were recorded. Singular value decomposition against whole observed spectral data-set that was followed by global and target analysis has been performed for the first time. A series of examination revealed that the carriers generated in the bulk of TiO₂ particle and two distinctive surface carriers are decaying with their own lifetimes. Moreover, the comparison of the measurements both in vacuum and under oxygen atmosphere suggested that the lifetime of surface holes is several tens of nanoseconds. The factors that govern the activity of photocatalyst should be precisely addressed based on thus identified spectral and lifetime features of carriers. Therefore, the present investigation is expected to open the new door to give some good hints when designing more active photocatalysts.

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1. Introduction

Shortage of fossil fuels raises our increasing demand to develop alternative energy sources to support the sustainable growth of all human beings. Solar energy is one of the best candidates to fulfil such a requirement because it is clean and inexhaustible. The energy of sun-light that hits the surface of the earth for 1 h is equivalent to the gross amount of energy that human beings consume in one year [1]. One of the practical technologies to utilize the solar energy is “artificial photosynthesis” [2–6]. The artificial photosynthesis attracts keen attention in these days. It is defined as the process that uses water and CO₂ as raw materials and convert them into chemical resources with high energy using solar energy. The key process of the artificial photosynthesis is a so-called “the light reaction” that splits water and generates protons, electrons and molecular oxygen ($\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{e}^- + (1/2)\text{O}_2$). A number of researches on the light reaction using semiconductor

photocatalysts have been conducted [7–12]. The challenge of this technology is the improvement of the efficiency of solar energy to hydrogen conversion (STH). In order to improve the STH efficiency, it is necessary to increase the amount of light absorption from sunlight by decreasing the band-gap energy of the semiconductors [13]. It is also required to enhance the quantum efficiency of the light reaction. Although the improvement of the former condition has already been achieved by doping to the existing semiconductors as well as by bandgap engineering [14–16], a clear index has not yet been established on the improvement of the latter condition.

In order to tackle this issue, the analyses on the carrier dynamics of photocatalysts have currently been carried out for the purpose to clarify the factors to improve the quantum efficiency [17–24]. Furube et al. reported the carrier migration dynamics of various photocatalysts from 200 femtoseconds to several nanoseconds time regime by means of transient absorption spectroscopy that observes the diffuse reflectance [25,26]. Yamakata et al. explain the properties of both anatase and rutile type titanium dioxide (TiO₂) based on their carrier dynamics involving the long time-delay that extends over milliseconds [27]. Nevertheless, the

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carrier dynamics of the photocatalysts has not solved completely yet and the ideal structure of the photocatalysts is still not very clear. On the other hand, the energy and electron transfer processes in natural photosynthesis have been studied quite well and the detailed mechanisms of light-harvesting and energy transduction are well understood [28–30]. These mechanisms have been clarified using a method called global and target analysis. This is a well-established mathematical method that can simultaneously determine the spectral band shapes and their time evolution using a whole data set of observed time-resolved spectra [31]. Although a number of reports have already been made for the time-resolved absorption spectroscopic studies on the TiO₂ powder, it is amazing that none of them performed the global and target analysis.

In this present work, we have applied the same analysis protocols that have been established to analyse the time-resolved absorption spectra of natural photosynthesis to the studies of the semiconductor photocatalysts. We have clarified the carrier recombination processes in rutile TiO₂ powders that is well-known as a water oxidation catalyst using nanosecond to microsecond time-resolved diffuse reflection spectroscopy that was followed by global and target analysis. We believe that the extraction of the precise spectral waveforms and their time evolution profiles from the observed data-set is of great significance in determining the carrier dynamics.

2. Experimental section

Rutile type TiO₂ was purchased from Wako Pure Chemical Industries (99.9% grade) and used as received. An analysis using scanning electron microscopy (SEM) revealed that the mean particle diameter of the TiO₂ powder was approximately 200 nm and the BET surface area was 7 m²/g (see Fig. 1). Before the time-resolved reflection measurements, the powder of rutile TiO₂ was placed in a quartz cuvette (2 mm optical path lengths) and evacuated (1×10^{-2} Torr) at 473 K for 1 h. The details of sub-ns pump-probe spectroscopic system is described elsewhere [29]. Fig. 2 shows a schematic drawing of the set-up of sub-ns time-resolved diffuse reflection spectroscopy system. It is composed of a Ti:Sapphire regenerative amplifier (Spectra Physics Hurricane-X, 100 fs pulse duration at 800 nm) and a sub-ns pump-probe time resolved spectrophotometry systems. 355 nm pump-pulse (<200 fs pulse duration) was generated by the fourth harmonic generation of the output of optical parametric amplifier (OPA-800C, Spectra Physics). The broad band probe-pulse is generated as a supercontinuum light by means of nonlinear process through the photonic crystal fiber that is pumped by a sub-ns (500 ps) Nd:YAG laser at 1064-nm. Diffuse reflection of the probe pulse was

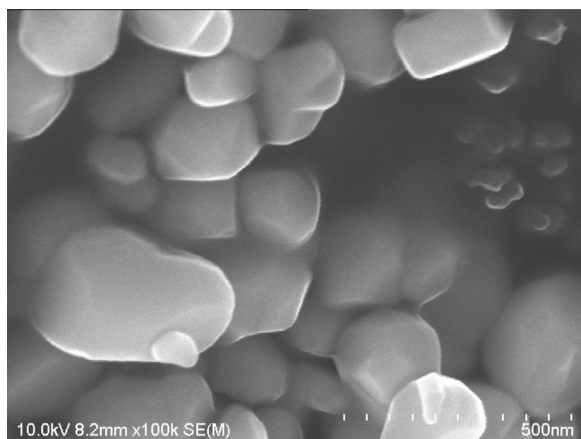


Fig. 1. SEM image of TiO₂ powder that was used in this investigation.

collected and collimated using an objective lens (20×, N.A. 0.40, Mitsutoyo Co.). Thus collimated light was focused into the optical fiber using an off-axis parabolic mirror and then connected to a spectrometer that is coupled to a CMOS linear diode array detector. The time delay between pump and probe pulses was adjusted electronically (Ultrafast systems, EOS). All measurements were performed at room temperature. Transient absorption intensity was displayed as a percentage of absorption that is converted from reflectance using a following formula.

$$\%Absorption = 100 \times \left(1 - \frac{R}{R_0}\right)$$

Here R_0 is reflectance before the pump-pulse irradiation and R is reflectance after the pump-pulse irradiation.

3. Results and discussion

Fig. 3(a) shows the contour plot of the time-resolved absorption spectra of the rutile TiO₂ (Wako Pure Chemical Industries). In what follows transient reflectance is converted to percentage absorption using a formula described in the experimental section for the purpose of easier understanding. A broad signal is observed immediately after the pump-pulse irradiation, and then this signal decays over delay time. Fig. 3(b) shows the time profiles of the transient absorption signals monitored at 400 nm (green), 600 nm (red) and 900 nm (blue). While the broad transient reflection signal represented by the kinetics at 600 nm decays within a few tens of ns, the sharp signal at 400 nm decays in μ s order. The sharp peak at 400 nm should be originated from the thermal relaxation or the “deactivated carriers”. The former process should show decay that is faster than the μ s time-scale for the TiO₂ particles in submicrometer order used in this work, because the thermal diffusivity of rutile-type TiO₂ is reported to be 3.17×10^{-6} m²/s [32,33]. Therefore, the origin of the sharp signal at 400 nm would be the “deactivated carriers”, which corresponds to the transition of the electron (hole) from the deep level of a trap to the conduction (valence) band. The time profile monitored by 600 nm probe light involves both fast and slow decay components. This is evidenced by the deviation of the fitting curve based on the single exponential decay dynamics from the observed temporal profile in the time regime from 10 ns to 500 ns as shown in Fig. 3(b). On the other hand, Katoh, et al. had reported that the decay profiles of the transient absorption signal at 850 nm of single crystals of rutile TiO₂ could be well fitted by the second-order kinetics [34]. Although the second order kinetics model is also applicable to analyze the time profile in our sample, it is found that the time constants determined by the fitting using the second-order kinetics model show contradiction between the signals monitored at 900 nm and 600 nm. As shown in Fig. 3(b) the normalized time profile monitored at 900 nm shows the deviation from that at 600 nm. This is a good indication that the rate constants to describe the temporal behavior at 600 nm and 900 nm kinetics are different to each other, although both data can well be fitted using the second-order kinetics model (see also Fig. S1 in Supporting information). Therefore, we have applied the multiple exponential decay dynamics in this study for the sake of explaining the temporal behavior of the whole observed data-set. Fig. 4 shows the excitation power dependence of the difference absorbance at 600 nm immediately after photoexcitation. Since the intensity of the initial transient signal increases linearly with increase of the pump light intensity, it is suggested that nonlinear optical processes are not involved in the transient absorption measurements within the limit of the present excitation intensities. Therefore, the fast decay component can be assigned to the carrier recombination in the bulk (*vide infra*). This assignment at the same

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