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Effects of accumulated electrons on the decay kinetics of photogenerated electrons in Pt/TiO_2 photocatalyst studied by time-resolved infrared absorption spectroscopy

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Abstract

The effects of accumulated electrons on the decay kinetics of photogenerated electrons in Pt/TiO_2 photocatalyst were examined using time-resolved infrared (TR-IR) absorption spectroscopy. When the catalyst was irradiated by a UV pulse in the presence of methanol gas, the lifetime of the electrons was drastically elongated through the effective hole-consuming reaction by the adsorbed methoxy groups. When the catalyst was further irradiated by a second UV pulse in the presence of these long-lived electrons, the number of electrons generated by the second pulse was smaller than that generated by the first pulse though these pulse energies were the same. By increasing the interval between these two pulses, the number of electrons generated by the second pulse was gradually restored to equal that generated by the first pulse. These changes were ascribed to the enhancement of the rate of electron–hole recombination due to the long-lived electrons.

Keywords: Photocatalyst; Pt/TiO_2; Infrared absorption; Methanol; Kinetics

1. Introduction

Photocatalytic reactions have been intensively studied in recent years because of the potential use of solar energy conversions [1–4] and pollutant degradations [5–7] using solar energy. Photocatalytic reactions are induced by charge carriers generated by band-gap photoexcitation of semiconductors. In order to understand the mechanism of photocatalysts, the dynamic behaviors of the charge carriers should be observed using time-resolved techniques.

Time-resolved infrared (TR-IR) absorption spectroscopy is a powerful tool for probing these phenomena because photogenerated electrons in semiconductors have a strong absorption in IR region [8–11]. We have already demonstrated the ability of TR-IR in the study of the behavior of photogenerated charge carriers on platinized TiO_2 (Pt/TiO_2) in the course of photocatalytic reactions [12–14]. We found that photogenerated holes react faster than electrons with reactants on Pt/TiO_2 in water splitting [13,14] and methanol oxidation [12] processes. For example, the holes react with methoxy groups within the time resolution of our spectrometer (50 ns). This hole-consuming reaction proceeds effectively, and drastically prevents the competitive recombination with an electron. More than 50 times the number of electrons survived at 1 μs compared to the number observed to survive in a vacuum. These electrons did not decay at all in a microsecond time frame. The decay of the electrons was observed to take in the region of several seconds and was assigned to the electron-consuming reaction by methanol.

These results show that TR-IR provides considerable information about transient phenomena. Our interest is in understanding the behavior of charge carriers in steady-state conditions. The behavior of charge carriers in steady-state conditions is not always the same as that in transient experiments because the difference in electron- and hole-consuming reaction rates induces an imbalance in the density between electrons and holes in the reaction system. For example, in the case of methanol oxidation, the electrons are accumulated in the catalyst under successive UV irradiation [12]. These accumulated electrons sometimes affect the catalytic activities [15]. How the accumulated electrons induce a change in the behavior of carriers is a worthwhile subject for examination because this information would be helpful in choosing the best reaction conditions for high efficiency.

In this study, the effect of accumulated electrons on recombination kinetics was examined using the two-pump

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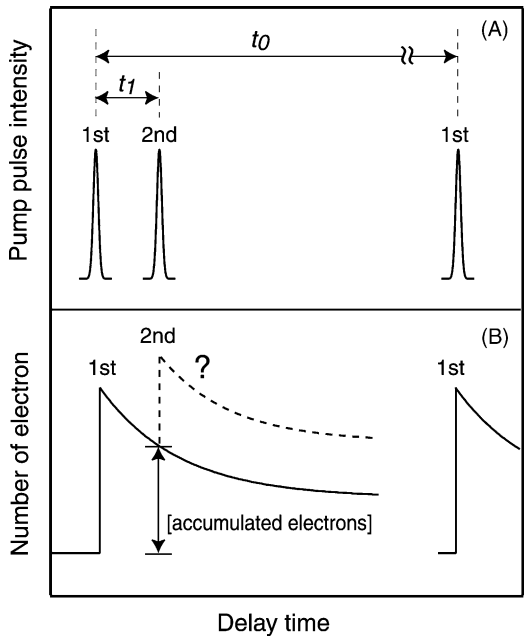

Fig. 1. Schematic diagram of the two-pump experiments. The catalyst was irradiated by pump pulses at the two intervals of t_0 and t_1 as shown in (A). The interval of t_1 is the delay time from the first- to the second-pump pulse, and t_0 is the interval between the first-pump pulses for repeated averaging. The t_0 should be long enough for the recovery of the changes induced by the second pulse. Schematic decay curves of electrons generated by the two-pump pulses are shown in (B). Our interest is the difference in the decay kinetics of electrons generated by the first- and second-pump pulses in the presence of accumulated electrons.

pulse irradiation technique (see Fig. 1). After the first-pump pulse irradiation, the catalyst was irradiated by the second pump pulse in the presence of the accumulated electrons generated by the first pulse. By changing the interval between the two-pump pulses (t_1), the number of accumulated electrons could be controlled and the effects on recombination could be examined.

2. Experimental

The decay kinetics of photogenerated electrons were observed using the home-built TR-IR spectrometer described previously [10,16]. Briefly, the IR probe light from the $MoSi_2$ was focused on the sample and the transmitted light was monochromatized by a grating monochromator (JASCO, CT50TF). The output IR intensity was measured with a photovoltaic MCT detector (Kolmar). A signal at a fixed wavenumber was amplified in AC-coupled amplifiers. Time-dependent transmitted IR intensity was accumulated and directly converted to a decay curve in a digital sampling oscilloscope. The time resolution of this spectrometer was limited by the response of the MCT detector to 50 ns. The spectral resolution was set at 32 cm^{-1} and 20 scans were averaged.

The Pt/TiO_2 catalyst was prepared with TIO4 (P-25), a standard TiO_2 catalyst supplied by the Catalysis Society of Japan [17]. Platinum was deposited at 1 wt.% by photodeposition from a H_2PtCl_6 aqueous solution. The catalyst was fixed on a CaF_2 plate in a density of 2 mg/cm^2. The catalyst on the plate was photoexcited by 355 nm light with 10 ns width from third harmonic generation of a Q-switched Nd:YAG laser (Spectron, SL401). The pulse energy was set to 0.5 mJ/pulse. In the two-pump pulse experiments, the desired laser pulses were produced by the hand-made pulse controller. The intervals of pump pulses of the same energy (t_0 and t_1 in Fig. 1) could be changed at steps of 0.1 s. In this experiment, t_0 was fixed at 100 s and t_1 was changed.

3. Results and discussion

Fig. 2 shows the transient IR absorption at 2000 cm^{-1} after the 355 nm UV pulse irradiation on Pt/TiO_2 in the presence of 10 Torr methanol gas. This transient IR absorption was assigned to the IR absorption by the electrons generated by the band-gap photoexcitation [10,18]. The decay of the transient IR absorption was thus attributed to the decay kinetics of photogenerated electrons in Pt/TiO_2. As reported previously [12], the behavior of charge carriers on Pt/TiO_2 catalyst in 10 Torr (1 Torr = 133.3 Pa) methanol gas is as follows. The holes are exhausted within 50 ns due to the effective hole-consuming reaction by the adsorbed methoxy groups. The decay of electrons was observed in the region of several seconds and assigned to the electron-consuming reaction by the adsorbed methanol. The decay curve (a) in Fig. 2 shows the decay of electrons generated by the first-pump pulse. This decay is attributed to the electron-consuming reaction as mentioned above

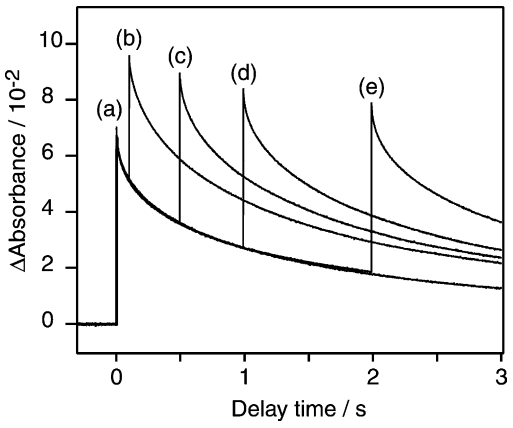

Fig. 2. The decay of photogenerated electrons on Pt/TiO_2. The catalyst was irradiated by two-pump pulses at several intervals. The energies of these pulses were 0.5 mJ. (a) The catalyst was irradiated only by the first-pump pulse at time = 0. (b)–(e) The catalyst was irradiated by both first- and second-pump pulses. The interval between these pulses was changed, namely 0.1, 0.5, 1 and 2 s, respectively.

because the holes that can recombine with the electrons are not present in this time region [12].

Next, the effects of accumulated electrons on the decay kinetics of electrons were examined. We define the accumulated electrons as the electrons remaining on the catalyst at just before the second pulse irradiation. Curves (b)–(e) in Fig. 2 show the decay of electrons on Pt/TiO_2 observed with different intervals (t_1) of two-pump UV pulses. In the presence of accumulated electrons, the number of photogenerated electrons was changed. As shown in Fig. 2, the number of electrons generated by the first- and second-pump pulses were different. In detail, the signal intensity generated by the first pulse shown in curve (a) was 7.0×10^{-2} in absorbance, but that by the second pulses after 0.1 s as curve (b) was 4.3×10^{-2}, in the presence of the accumulated electrons of 5.1×10^{-2} in absorbance. The number of electrons generated by the second pulse was gradually recovered by decreasing the number of accumulated electrons. After a 100-s delay from the first-pump pulse, the number of generated electrons was completely restored.

We further studied the decay kinetics of electrons proceeding after the second pulse irradiation in detail. Fig. 3 shows the changes of electron density in microsecond time frame induced by the first and second pump pulse irradiation. The baseline of these curves was defined as the level just before the second pulse irradiation. As seen from the decay curve (a), there were at least two decay components, i.e. one component was recombined within 50 ns and the other did not decay at all in the microsecond time frame. We refer to the number of these electrons surviving in microseconds time frame as the number of surviving electrons. Both components existed irrespective of the presence of the accumulated electrons as shown in Fig. 3. However, the number of surviving electrons was dependent on the number of

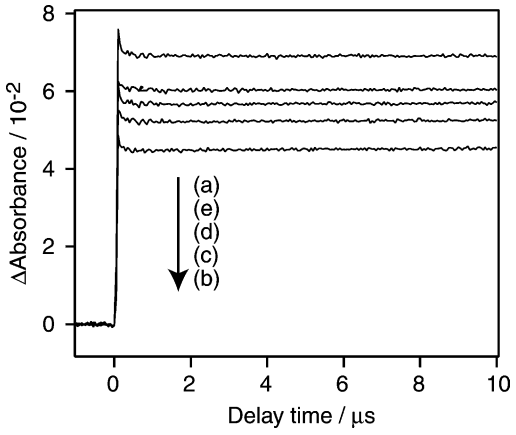

Fig. 3. The decay profiles of electrons generated by the first- and second-pump pulses. The energies of these pulses were 0.5 mJ. (a) The decay of electrons generated by the first pulse. (b)–(e) The decay of electrons proceeded after the second-pump pulse irradiation. The interval between the first- and second-pulses was changed, namely 0.1, 0.5, 1 and 2 s, respectively. The baseline of these curves was defined as the level just before the second pulse irradiation.

accumulated electrons, with the former number decreasing when accumulated electrons were present. By increasing the delay time of the second pump pulse, the number of surviving electrons gradually recovered as seen by the curves of (b)–(e). The reduction of the surviving electrons was ascribed to the effects on the electron–hole pair recombination proceeding within 50 ns, since the pump pulse energies of first- and second-pump pulses were the same.

These features observed in Fig. 3 concerning the number of surviving electrons can be well reproduced by the simple model of second-order decay kinetics. In the time region where the electron-consuming reaction is negligible, the decay kinetics of electrons is controlled by the recombination and hole-consuming reaction by methoxy groups. The rate of recombination ($r_{\text{recombination}}$) can be described as

$$r_{\text{recombination}} = k_{\text{recombination}}[\text{e}][\text{h}], \tag{1}$$

where $k_{\text{recombination}}$ is the rate constant for recombination. [e] and [h] represent the number of electrons and holes in the reaction system. The rate of hole-consuming reaction (r_{reaction}) by the methoxy groups is described as

$$r_{\text{reaction}} = k_{\text{reaction}}[\text{methanol}][\text{h}] = k'_{\text{reaction}}[\text{h}], \tag{2}$$

where k_{reaction} is the rate constant for the reaction. [methanol] the number of adsorbed methoxy groups. When [methanol] is much larger than [h], the term of k_{reaction}[methanol] can be replaced with a constant k'_{reaction}. Then the rate equations of electrons and holes are derived as follows:

$$-\frac{\text{d[e]}}{\text{d}t} = k_{\text{recombination}}[\text{e}][\text{h}], \tag{3}$$

$$-\frac{\text{d[h]}}{\text{d}t} = k_{\text{recombination}}[\text{e}][\text{h}] + k'_{\text{reaction}}[\text{h}]. \tag{4}$$

The effects of the accumulated electrons was considered by changing the initial value of the carriers ($[\text{e}]_0$ and $[\text{h}]_0$) as

$$[\text{e}]_0 = [\text{e}]_{\text{second}} + [\text{e}]_{\text{accumulated}}, \tag{5}$$

$$[\text{h}]_0 = [\text{h}]_{\text{second}}, \tag{6}$$

where $[\text{e}]_{\text{second}}$ and $[\text{h}]_{\text{second}}$ are the number of electrons and holes generated by the second pulse, and $[\text{e}]_{\text{accumulated}}$ the number of accumulated electrons. The initial conditions of the variables was set to $[\text{e}]_{\text{second}} = [\text{h}]_{\text{second}} = 1$, and $[\text{e}]_{\text{accumulated}}$ was changed from 0 to 1. The rate constants of $k_{\text{recombination}}$ and k'_{reaction} were fixed to be 0.05 for simplicity (these values do not affect the features in Fig. 4). These rate equations were numerically solved. In Fig. 4, the change of electron density induced by the second pulse irradiation ($[\text{e}]-[\text{e}]_{\text{accumulated}}$) was plotted for comparison with Fig. 3. As seen from the figure, a certain number of electrons survived after the recombination proceeded within a time period of 10 a.u. By increasing the number of accumulated electrons from 0 to 1, the rate of recombination was accelerated and the number of surviving electrons decreased. Increasing the number of accumulated electrons in the simulation corresponds to decreasing the time interval between two-pump

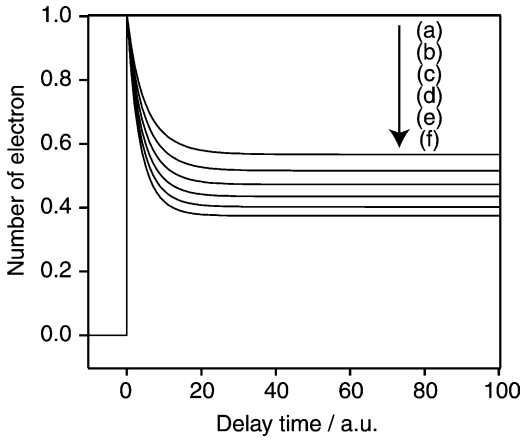

Fig. 4. Numerically simulated decay curves of photogenerated electrons in Pt/TiO_2. The effect of the accumulated electrons on the decay kinetics was examined. (a)–(f) Accumulated electrons were increased from 0 to 1.0 at steps of 0.2.

pulses in the experiment. Thus, the observed decrease in the number of surviving electrons (Fig. 3) was reproduced by this simulation. It is noted that the number of electrons generated by the second pulse was smaller than that generated by the first pulse in the experiment (Fig. 3). This is because the time resolution of the apparatus was not good enough to trace quantitatively the recombination kinetics that proceeded within 50 ns after the photoexcitation.

We have demonstrated that the existence of accumulated electrons enhances the rate of recombination. This phenomenon occurs when the density of the charge carriers is higher than one pair per particle. Thus, we have to be careful about the electron accumulation when we discuss the kinetics of photogenerated charge carriers. In the case of pump-probe experiments, the electrons were accumulated and the lifetime of the electron becomes short when the lifetime of electrons was longer than the intervals of laser repetition. Electrons would be accumulated even under irradiation with CW light. For example, if a catalyst is irradiated with 355 nm light of a 1 mW/cm^2 power density, 10^4 photons falls on a catalyst particle of a 25 nm diameter per second. Electrons in the presence of methanol gas would be readily accumulated under the irradiation, since the lifetime of the electrons was longer than 1 s as observed in Fig. 2. The quantum yield of the reaction would depend on light power density in this case.

4. Conclusion

We adopted TR-IR absorption spectroscopy with two-pump pulse excitations of a photocatalyst for the elucidation of the decay kinetics of photogenerated electrons under steady-state reaction conditions. The decay kinetics of electrons on Pt/TiO_2 in the presence of methanol gas was examined. When the catalyst was irradiated by the first UV pulse, the lifetime of electrons was drastically elongated. This result was interpreted by the effective hole-consuming reaction by the methoxy groups. The second pump pulse irradiation in the presence of these accumulated electrons produced photogenerated electrons, but the number of electrons was smaller than that generated by the first pulse. The increment of the accumulated electrons further reduced the number of electrons generated by the second pulse. This result was ascribed to the enhancement of the rate of recombination by the accumulated electrons. A numerical simulation reproduced this feature.

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