



Review

Kinetics of the photocatalytic water-splitting reaction on TiO₂ and Pt/TiO₂ studied by time-resolved infrared absorption spectroscopy

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Abstract

The present account describes how the water-splitting reaction on TiO₂ (P-25) and Pt/TiO₂ catalysts is traced by time-resolved infrared (IR) absorption spectroscopy. The ac-coupled amplification of the IR signal allows detection of transient absorbance-change as small as 10⁻⁶ with a time-resolution of 50 ns. The TiO₂ or Pt/TiO₂ catalyst irradiated by a 355 nm UV-pulse at time = 0 presents a transient IR absorption which monotonically increases in intensity with decreasing wavenumber from 3000 to 1000 cm⁻¹. Photogenerated electrons trapped in shallow mid-gap states are proposed to cause the absorption. The decay kinetics of the electrons traced by monitoring the IR absorbance at 2000 cm⁻¹ is sensitive to vapor atmospheres. The electrons recombine with the complementary holes along a multi-exponential rate law in the catalysts placed in a vacuum. Dioxygen arriving from the gas-phase captures the electrons at delay time of 10–100 μs following the UV irradiation. In the presence of water vapor, holes in the TiO₂ catalyst are captured by an adsorbed reactant (probably hydroxyl species) within 2 μs and the recombination is obstructed thereafter. The excess electrons cannot transfer to another adsorbate to be reduced (probably proton) and hence reduce the catalyst itself. On the Pt/TiO₂ catalyst exposed to water, the electron transfer takes place at 10 μs or later, following the hole transfer completed within 2 μs. The hole transfer on Pt/TiO₂ is insensitive to the pressure of water vapor whereas the rate of the electron transfer is enhanced with the increasing pressure at 1–10 Torr. Transient response of an adsorbate vibration is also observed. The O–H stretching band of an adsorbed hydroxyl species at 3677 cm⁻¹ thermally shifted to the low-wavenumber side, when the TiO₂ catalyst is irradiated by the UV-pulse.

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1. Introduction

A photocatalytic cycle of reactions is initiated by the photoinduced electronic excitation in a semiconductor catalyst. A number of elementary steps suc-

cessively and competitively occur following the excitation, i.e. trap and recombination of excited charge carriers (electrons and holes), carrier attachment to adsorbed reactants, and reactions of the carrier-attached adsorbates to release products. The products further react with other entities on the catalyst or in the ambient phase, when final products are given via consecutive reactions. Determining the kinetics of those individual reactions is demanded to promote more

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advancements in practical applications of photoinduced functions such as the degradation of organic pollutants [1], dye-sensitized solar cells [2], artificial control of hydrophilicity [3], and water-splitting for hydrogen evolution [4].

Time-resolved infrared (IR) absorption spectroscopy is a promising method for the kinetic analysis of the photocatalytic reactions. Photoexcited electrons exhibit an IR absorption monotonically increased with decreasing wavenumber [5], while vibrations of polyatomic adsorbates give peculiar bands on a spectrum. The formation and consumption of the electrons, holes, reactants, intermediates, and products are thus to be traced simultaneously on a series of time-resolved IR spectra. Tamaru and coworkers originally demonstrated the ability of this method in analyzing the kinetics of thermally catalyzed reactions [6]. It was, however, difficult to trace individual steps of a photocatalytic reaction by time-resolved IR spectroscopy. The quantity of photogenerated carriers and chemical species is often limited far below the detection threshold of standard Fourier-transform spectrometers (10^{-4} in absorbance).

We construct a time-resolved IR spectrometer with an improved sensitivity to override the difficulty. Transient absorbance-change as small as 10^{-6} is detectable over a wide range of wavenumber ($4000\text{--}1000\text{ cm}^{-1}$) with a time-resolution of 50 ns. The present account describes what we found in the water-splitting reac-

tion on TiO_2 and Pt/TiO_2 catalysts by using the highly sensitive spectrometer.

2. Time-resolved IR spectrometer and catalysts

Fig. 1 illustrates our time-resolved IR spectrometer [7], which was made after [8]. Infrared light emitted from a MoSi_2 source is focused on the sample plate with ellipsoidal mirrors. Transmitted light is dispersed in a grating monochromator (JASCO) and the monochromatized IR output is transferred to electric signal in a MCT detector (Kolmar). The response of the photovoltaic MCT detector determines the time-resolution of the spectrometer to be 50 ns. The MCT output is amplified in ac-coupled amplifiers (NF Circuit and Stanford Research Systems) and accumulated in a digital oscilloscope (Lecroy) as a function of delay time.

The TiO_2 and Pt/TiO_2 catalysts were prepared with TiO_4 , a standard TiO_2 catalyst supplied by the Catalysis Society of Japan [9], generally known as Degussa P-25. Platinum particles of 1 wt.% were photodeposited from a H_2PtCl_6 aqueous solution when desired. The catalyst powder was fixed on a CaF_2 plate with a density of 2 mg cm^{-2} . The plate was placed in a stainless steel cell, in which the catalyst was calcined at 573 K in a 20 Torr O_2 atmosphere for hours prior to each measurement at 323 K.

The catalyst on the plate was irradiated by the third harmonic light of a Q-switched Nd:YAG laser

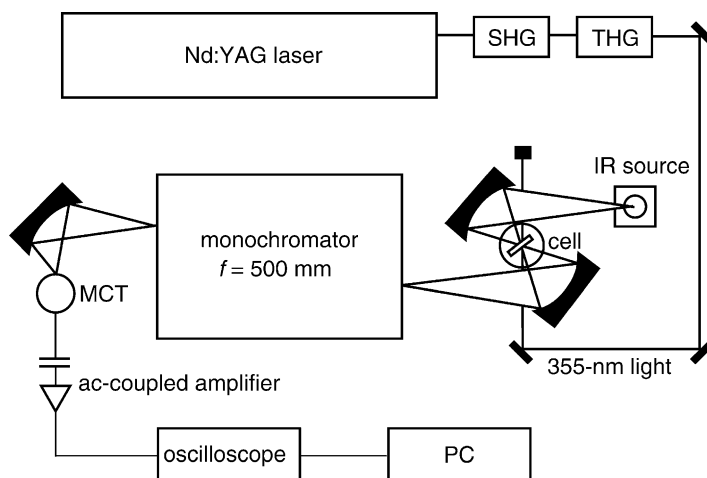


Fig. 1. The diagram of the time-resolved IR absorption spectrometer for kinetic measurements on photocatalysts.

(Spectron). The wavelength, time width, and energy of the pump pulse were 355 nm, 10 ns, and 3–12 mJ pulse⁻¹. The diameter of the irradiated spot on the plate was 6 mm. Transient absorbance-change as small as 10⁻⁶ was detected by signal averaging of 300 flashes at 0.1–1 Hz. The absorbance responses observed as a function of delay time were translated to transient absorption spectra at different time delays.

3. IR absorption by photoexcited electrons

When the TiO₂ catalyst was irradiated by the 355 nm (3.5 eV) pulse, structureless IR absorption temporarily appeared as shown in Fig. 2 [10]. The absorbance monotonically strengthened with decreasing wavenumber from 3000 to 1000 cm⁻¹ extending beyond the low-wavenumber limit of the spectrometer. Irradiation by 532 nm (2.3 eV) or 1064 nm (1.2 eV) light of the same pulse energy brought no response. The electronic excitation across the band gap (3 eV) caused the transient IR absorption. Transient absorption of a similar spectrum was observed on the Pt/TiO₂ catalyst [7]. Fig. 3 shows transient spectra obtained on Pt/TiO₂ at five time delays. The observed absorbance-change (Δabs) curves are fitted to a simple function of the wavenumber of IR light $\tilde{\nu}$ with a constant A ,

$$\Delta\text{abs} = A\tilde{\nu}^{-1.5} \quad (1)$$

The fit is good in the entire range of time delays examined, while the absorption intensity changes near

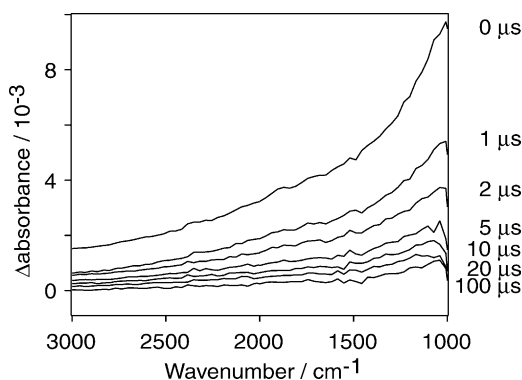


Fig. 2. Transient IR absorption spectra of the TiO₂ catalyst irradiated by the 355 nm pulse of 7 mJ. Seven spectra recorded at delay times of 0, 1, 2, 5, 10, 20, and 100 μs are displayed from [10].

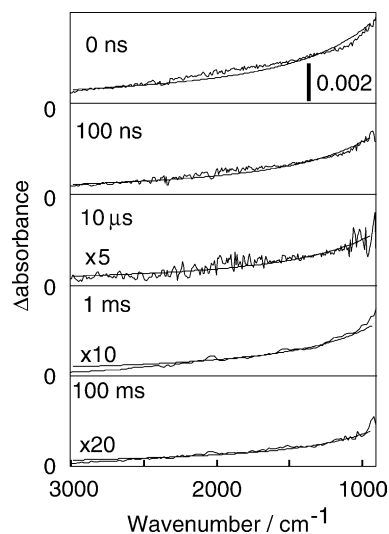


Fig. 3. Transient IR absorption spectra of the Pt/TiO₂ catalyst irradiated by the 355 nm pulse of 7 mJ. Five spectra recorded at delay times of 0, 100 ns, 10 μs, 1 and 100 ms are displayed. Observed data and fitted curves are shown from [7].

three orders of magnitude. The fitted curves are shown in Fig. 3.

Fig. 4 illustrates probable mechanisms of the IR absorption by electrons photoexcited in the conduction-band (CB). Monotonic absorption of IR light is often

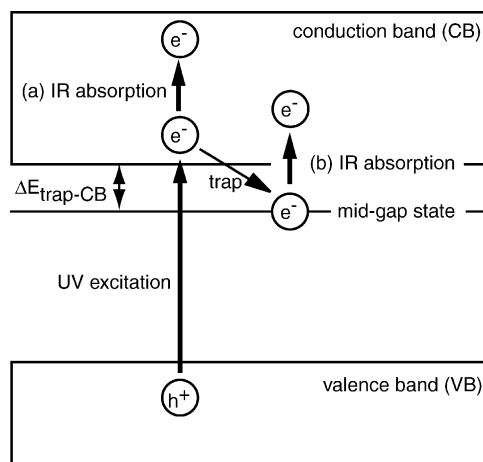


Fig. 4. Optical transitions of the electrons excited in TiO₂-based catalysts. (a) The intra-conduction-band (CB) transition of a free electron, and (b) the trapped-electron excitation to the CB. $\Delta E_{\text{trap-CB}}$ represents the gap between the mid-gap state and the CB.

observed on semiconductors and assigned to the optical transitions of charge carriers. Route (a) is the intra-CB transition of free electrons. Free electrons give absorption characterized by a monotonic spectrum formulated in $\tilde{\nu}^{-1.5}$, when the momentum required for the intra-band transition is provided by acoustic phonons [5,11]. Although the free electrons are trapped at mid-gap states within picoseconds [12], it is a reasonable assumption that a finite fraction of the trapped-electrons are thermally excited to the CB. The thermal energy kT at the sample temperature (323 K) is 0.03 eV. This is comparable to the reported ionization energy of the trap states, $\Delta E_{\text{trap-CB}}$, around 0.05 eV [13].

Another mechanism is the optical transition of the trapped-electrons to the CB, route (b). This is a parallel process to the transition from a donor level to the CB in a n-type semiconductors [5]. In this scheme, the energy of the absorbed photon is larger than the ionization energy of the trap, $\Delta E_{\text{trap-CB}}$. The intense absorption observed at 1000 cm^{-1} suggests that the ionization energy is less than 0.1 eV in our catalysts, being consistent to the reported value of 0.05 eV [13]. One more possible mechanism that the excited electrons scatter, not absorb, IR light is also pointed out [14].

Holes are created in the valence band (VB) complementarily to the electrons. However, the free hole transition in the VB, or the hole transition from mid-gap states to the VB is less probable to produce the IR absorption observed. Adsorbed hydroxyl species are thought to trap the holes and the energetic depth of the trapped holes to the VB is reported to be 1.5 eV [13]. This energy gap is too large to be thermally overridden at 323 K. The direct optical transition from the 1.5 eV-deep states to the VB cannot absorb the mid-IR light, either.

We thus propose that the electrons photoexcited and trapped in shallow mid-gap states can be quantified by the monotonic absorption of IR light, though identifying the contribution of the possible transitions to the observed absorption is difficult. The kinetics of the electrons consumed in the recombination with holes or in the reactions with adsorbates is traced in the decay of the IR absorption.

4. Electron-hole recombination kinetics

The photoexcited electrons and holes recombine in the catalysts placed in a vacuum. Fig. 5 shows the

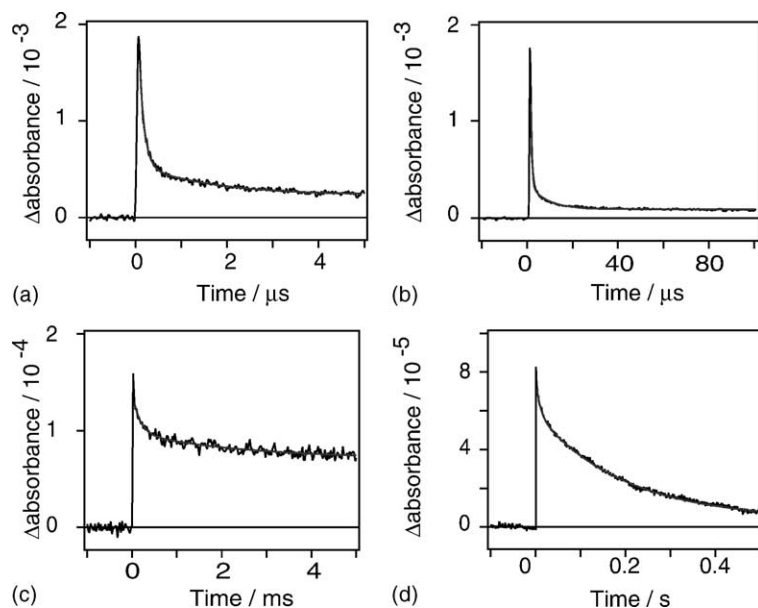


Fig. 5. The decay curve of the monotonic IR absorption on Pt/TiO₂ irradiated by the 355 nm pulse of 7 mJ at time = 0. The transient absorbance measured at 2000 cm^{-1} is shown. Segments (a–d) present the results separately observed on time scales of 0–5, 0–100 μs , 0–5 ms, and 0–0.5 s. Observed data and fitted curves are plotted as a function of time delay based on [7].

decay of the electrons in Pt/TiO₂ traced by the IR absorbance at 2000 cm⁻¹. The shape of the decay curves was insensitive to the UV-pulse energy ranging from 5 to 9 mJ. This strongly suggests the first-order kinetics of the decay. The curves in Fig. 5 are hence fitted to a multi-exponential function, and six life times of 1×10^{-7} , 2×10^{-6} , 5×10^{-5} , 9×10^{-4} , 1×10^{-2} , and 3×10^{-1} s are obtained [7]. To interpret the first-order decay, electron-hole pair concentration is assumed less than one pair per one TiO₂ particle, and carrier transfer among TiO₂ particles is ignored.

5. Reaction-induced decay kinetics of electrons

In the following sections, we focus on the reaction-induced decay kinetics of the trapped-electrons. Fig. 6 shows the decay of the electron absorption of the TiO₂ catalyst exposed to a 10 Torr O₂ atmosphere. The decay is accelerated in the presence of oxygen at time delays of 10–100 μs, while being independent of the gas-phase composition at 0–5 μs. The oxygen-induced quench of the electrons is ascribed to the reaction

with dioxygen arriving from the gas-phase,



The characteristic time of the reaction is estimated at tens of microsecond by comparing the two curves in Fig. 6. The order of the characteristic time is consistent with previous reports on electron transfer at TiO₂ surfaces [1]. The observed reactivity of the trapped-electrons is reasonable, when they are localized at Ti atoms exposed to the surface. Even if the electrons are trapped at bulk sites inaccessible by the oxygens, they are thermally excited to the CB as proposed in Section 3 and delocalized over the TiO₂ particle until captured.

A hole-capture reactant also affects the electron decay curve. Fig. 7 presents water-induced decay kinetics observed on the TiO₂. By exposing to 10 Torr H₂O, the electron decay is almost prohibited at delay times of 2 μs or later. This deceleration of the decay is ascribed to the quenching of the holes by water-induced adsorbates. A reaction with a hydroxyl anion,

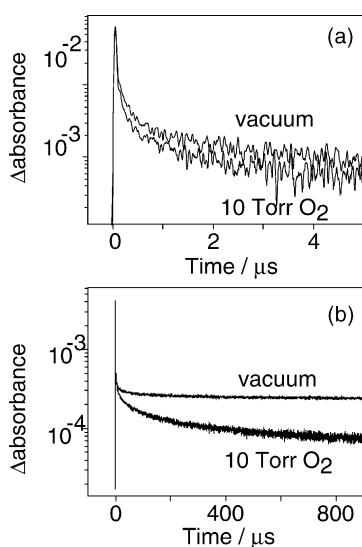


Fig. 6. The transient IR absorption intensity observed on TiO₂ irradiated by the 355 nm pulse of 7 mJ at time = 0. Two response curves were determined in the presence and absence of a 10 Torr O₂ atmosphere. The transient absorbance measured at 2000 cm⁻¹ is plotted as a function of time delay of (a) 0–5 μs and (b) 0–900 μs based on [10].

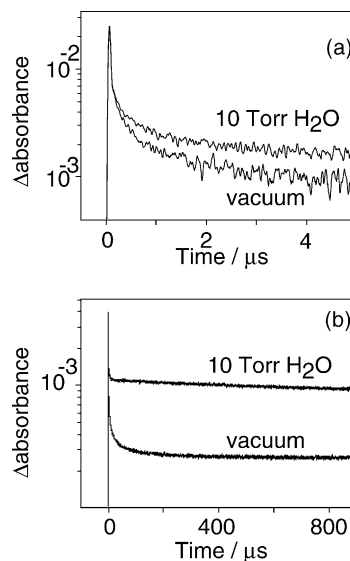


Fig. 7. The transient IR absorption intensity observed on TiO₂ irradiated by the 355 nm pulse of 7 mJ at time = 0. Two response curves were determined in the presence and absence of a 10 Torr H₂O atmosphere. The transient absorbance measured at 2000 cm⁻¹ is plotted as a function of time delay of (a) 0–5 μs and (b) 0–900 μs based on [10].

is thought as the initial step of the photooxidation of water [1]. Holes to recombine with the electrons are exhausted when reaction (3) is completed. Exposure to methanol vapor [15,16], a more effective hole-capture reagent than water, caused a more serious obstruction of the recombination. The constant IR absorbance at 2 μs or later indicates that water vapor cannot consume the electrons remaining on the catalyst. This agrees with the inability of the Pt-unloaded TiO_2 in the water-splitting reaction. The reduction step of the splitting,



requires the addition of Pt. The excess electrons accumulate in the catalyst and reduce Ti^{4+} cations. The TiO_2 catalyst changed from white to blue when irradiated by 355 nm pulses for several hours in the presence of water, as a result.

These results demonstrate that the trapped-electrons observed by IR absorption are reactive to adsorbates. A hole-capture reaction as well as an electron-capture reaction controls the decay of the electrons via the competition with the recombination reaction. On the other hand, previous studies on an n-CdSe single crystal [17] and TiO_2 particles [18] revealed that the adsorption of gas-phase reactants affects the recombination via bending the bands. Photoluminescence (PL) intensity on TiO_2 was diminished by the exposure to O_2 gas [18]. Adsorbed dioxygen molecules capture electrons regardless of UV irradiation to make a depletion layer in the substrate. The space charge layer enhances the intrinsic bend upward to the surface and promotes efficient separation of photogenerated electrons and holes. The PL via the radiative electron-hole recombination is thereby suppressed. This scheme predicts an increased population of the photoexcited electrons in an oxygen atmosphere. Adsorbed water, an electron donor, relaxed the upward bend in TiO_2 and increased the rate of recombination [18]. In our Figs. 6 and 7, the exposure to oxygen or water vapor increases or decreases the rate of electron decay being opposite to the prediction of the band-bend picture. We propose that the carrier separation driven by the bent band no longer determines the decay kinetics at 50 ns or later when the electrons and holes are localized at traps, whereas the bent band drives free electrons and free holes to separate in picoseconds.

6. Water-splitting reaction on Pt/ TiO_2

Platinized TiO_2 is known as a photocatalyst for the stoichiometric water-splitting reaction. We expect that both the hole-capture step (3) and the electron-capture step (4) of the reaction are traced on the IR decay curve. Fig. 8 shows decay curves of Pt/ TiO_2 in the absence and presence of water vapor [10]. Exposure to 10 Torr H_2O causes the hole-capture reaction and decelerates the decay at 0–2 μs on Pt/ TiO_2 . The water-affected curve in Fig. 8(a) reproduces the curve

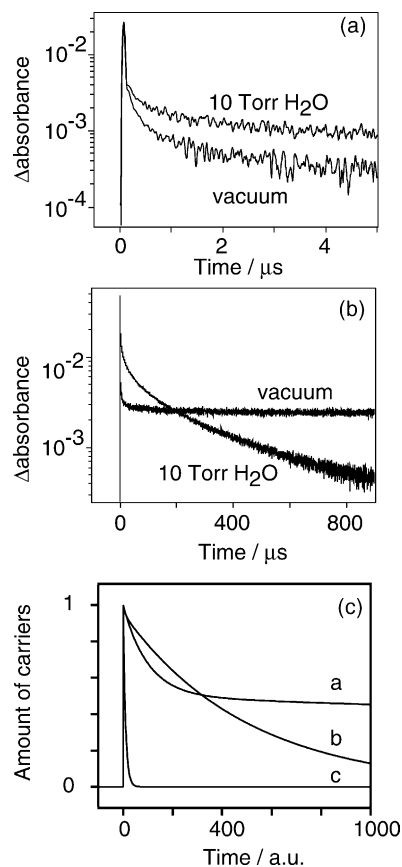
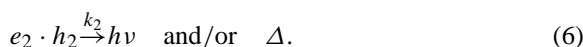
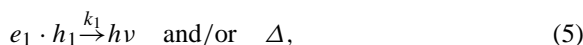


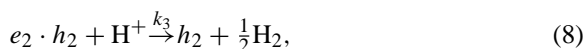
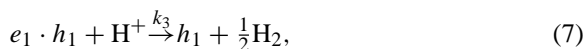
Fig. 8. The transient IR absorption intensity observed on Pt/ TiO_2 irradiated by the 355 nm pulse of 7 mJ at time = 0. Two response curves were determined in the presence and absence of a 10 Torr H_2O atmosphere. The transient absorbance measured at 2000 cm^{-1} is plotted as a function of time delay of (a) 0–5 μs and (b) 0–900 μs from [10]. Numerically simulated decay curves of electrons and holes are shown in (c). Curve a: total electron quantity in a vacuum, curve b: total electron quantity in a water vapor atmosphere, and curve c: total hole quantity in the water atmosphere.

of TiO₂, shown in Fig. 7(a), indicating that Pt particles do not affect reaction (3). The other important feature of the water-induced curve of Pt/TiO₂ is the enhanced decay at 10–900 μs. Two curves obtained in the presence and absence of water cross each other at 200 μs. This makes a clear contrast to the decay on the TiO₂ catalyst shown in Fig. 7. We ascribe the enhanced decay to the electron-capture reaction (4) activated by the Pt particles.

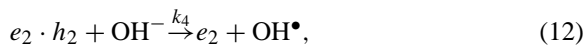
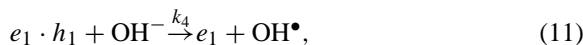
A simple kinetic model qualitatively reproduces the cross of the electron decay curves; the recombination reaction is represented with two components,



$e_1 \cdot h_1$ and $e_2 \cdot h_2$ are Pt/TiO₂ particles which contain an electron–hole pair. The pair in $e_1 \cdot h_1$ ($e_2 \cdot h_2$) recombines on the first-order law with a rate constant k_1 (k_2). The electron-capture reaction by a proton is explicitly formulated as,



where e_1 (e_2) and h_1 (h_2) represent particles containing an electron and a hole, respectively. The second-order rate constant, k_3 , is fixed in the four reactions. The hole-capture reaction by a hydroxyl anion,



is similarly assumed. The rate constant, k_4 , is fixed for the four reactions. The following rate equations are derived on the model,

$$\frac{d[e_1 \cdot h_1]}{dt} = -(k_1 + k_3' + k_4')[e_1 \cdot h_1], \quad (15)$$

$$\frac{d[e_2 \cdot h_2]}{dt} = -(k_2 + k_3' + k_4')[e_2 \cdot h_2], \quad (16)$$

$$\frac{d[e_1 + e_2]}{dt} = k_4'([e_1 \cdot h_1] + [e_2 \cdot h_2]) - k_3'[e_1 + e_2], \quad (17)$$

$$\frac{d[h_1 + h_2]}{dt} = k_3'([e_1 \cdot h_1] + [e_2 \cdot h_2]) - k_4'[h_1 + h_2], \quad (18)$$

where the large concentration of H⁺ and OH[−] is assumed constant. k_3' and k_4' replace $k_3[\text{H}^+]$ and $k_4[\text{OH}^-]$.

Panel (c) of Fig. 8 illustrates numerical solutions of the rate equations. The initial condition of the variables is $[e_1 \cdot h_1] = [e_2 \cdot h_2] = 0.5$ and $[e_1] = [e_2] = [h_1] = [h_2] = 0$ at time = 0. To simulate the decay in the vacuum, the rate constants are set at $k_1 = 0.01$, $k_2 = 0.0001$, and $k_3' = k_4' = 0$. Curve a shows the total electron population, $[e_{\text{total}}] = [e_1 \cdot h_1] + [e_2 \cdot h_2] + [e_1] + [e_2]$, as a double-exponential decay governed by k_1 and k_2 . In the presence of water, a rapid hole-capture with $k_4' = 0.1$ and a slow electron-capture with $k_3' = 0.002$ occur. Curve b presents $[e_{\text{total}}]$ calculated on the water-affected constants. Curves a and b make a cross and qualitatively reproduce the experimental observation in panel (b). The total concentration of holes, $[h_{\text{total}}] = [e_1 \cdot h_1] + [e_2 \cdot h_2] + [h_1] + [h_2]$, is quickly reduced to zero as shown by curve c. The holes to recombine with the electrons are exhausted in the reactions with OH[−], and the remainder electrons react with H⁺ on a single-exponential kinetics determined by k_3' . Consequently, the magnitude of the rate constants should follow the order,

$$k_4' > k_1 > k_3' > k_2, \quad (19)$$

to reproduce the cross.

The oxidation and reduction steps in the water-splitting reaction are thereby distinguished along the reaction time. Photogenerated holes quickly oxidize water within 2 μs, whereas the electrons reduce water at 10–900 μs. There are several possible reasons for the hydroxyl oxidation preceding the proton reduction. Holes in the VB of TiO₂ are thermodynamically below the O₂/H₂O redox potential by 2 eV, while electrons in the CB are above the H⁺/H₂ potential only by 0.1–0.2 eV [1]. The large drop for the hole transfer favors the oxidation step. The intrinsic upward bend of

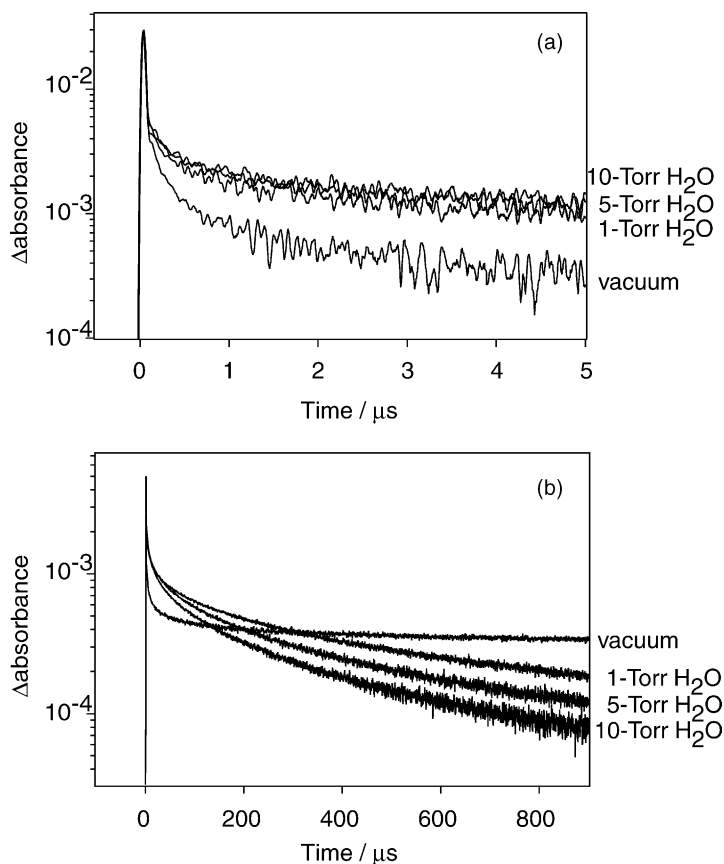


Fig. 9. The transient IR absorption intensity observed on Pt/TiO₂ irradiated by the 355 nm pulse of 7 mJ at time = 0. The response curves were measured in the presence of a water atmosphere at 0, 1, 5, or 10 Torr. The transient absorbance measured at 2000 cm⁻¹ is plotted as a function of time delay of (a) 0–5 μ s and (b) 0–900 μ s based on [19].

the VB can also drive holes to the surface and promote reaction (3). Proton migration from the TiO₂ substrate to Pt particles may delay reaction (4).

The hole-capture reaction showed no pressure dependence of water vapor. The electron decay curves obtained at 1, 5, and 10 Torr of water vapor are identical at 0–5 μ s in Fig. 9 [19]. This indicates that the adsorbates to capture the holes are saturated on the catalyst surface exposed to the 1 Torr H₂O atmosphere, and supports the accepted proposal that hydroxyl anions react with the holes in the initial stage of the water-splitting reaction. On the other hand, the electron-capture reaction observed at 10–900 μ s exhibits a positive dependence on the water pressure. The positive order suggests that physisorbed water species enhance in the electron-capture reaction.

7. O–H vibration on UV-irradiated TiO₂

Infrared spectroscopy possesses an advantage of observing molecular vibrations, as mentioned in Introduction. In this last section, the transient response of O–H stretching bands is examined [20]. Fig. 10 shows the transient IR spectra of the TiO₂ catalyst pumped by the 355 nm pulse in a vacuum. The absorbance at 3696 cm⁻¹ is decreased while that at 3654 cm⁻¹ is increased upon the UV irradiation. These features are recovered within 100 ms. The absorption of the non-irradiated catalyst observed by a standard FT-IR spectrometer (JASCO) is inserted in the figure for comparison. Bands at 3740, 3691, 3677, 3664, and 3640 cm⁻¹ are of the O–H stretching mode of different hydroxyl species [21,22]. The

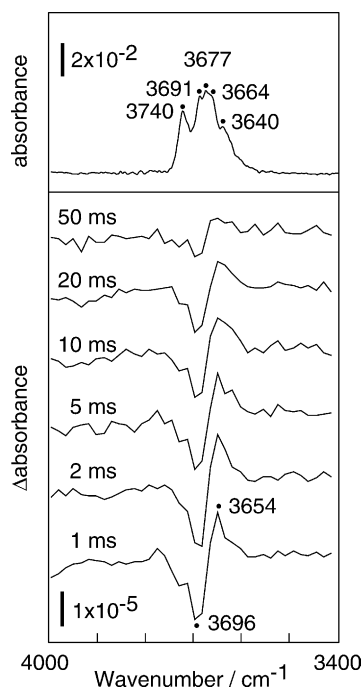


Fig. 10. Transient IR absorption spectra of the hydroxyl species on the TiO₂ catalyst irradiated by the 355 nm pulse of 7 mJ at time = 0. Six spectra recorded at time delay of 1, 2, 5, 10, 20, and 50 ms are displayed from [20]. The steady-state absorption of the hydroxyl species observed by a FT-IR spectrometer is inserted in the upper panel.

time-resolved spectra indicate that the UV irradiation temporarily affects some of the hydroxyl species. Detailed analysis of the transient spectra revealed that a temperature jump triggered by the irradiation causes a small shift of the band at 3677 cm⁻¹. The hydroxyl radical assumed in reaction (3) are absent in the spectra. Its residence time or population may be beyond the time-resolution or sensitivity of our spectrometer.

8. Summary and prospects

The present account describes how the water-splitting reaction on the TiO₂ (P-25) and Pt/TiO₂ catalysts is traced by time-resolved IR absorption spectroscopy. The ac-coupled amplification of the IR signal allows detection of transient absorbance-change as small as 10⁻⁶ with a time-resolution of 50 ns. The TiO₂ and Pt/TiO₂ catalysts irradiated by the 355 nm UV-pulse at time = 0 present the transient IR ab-

sorption assigned to photogenerated electrons trapped in shallow mid-gap states. The decay kinetics of the electrons is sensitive to vapor atmospheres and traced by monitoring the IR absorbance at 2000 cm⁻¹. The electrons recombine with the complementary holes along a multi-exponential rate law in a vacuum. On the Pt/TiO₂ catalyst exposed to water vapor, photogenerated holes react with an adsorbate to be oxidized (probably hydroxyl species) within 2 μs following the UV irradiation, whereas photogenerated electrons are transferred to another adsorbate to be reduced (probably proton) at 10 μs or later. The hole-capture step is insensitive to the pressure of water vapor while the rate of the electron-capture step is enhanced with the increasing pressure. The O–H stretching band of an adsorbed hydroxyl species at 3677 cm⁻¹ thermally shifted to the low-wavenumber side, when the TiO₂ catalyst is irradiated by the UV-pulse.

We believe that time-resolved IR absorption spectroscopy provides a general way of monitoring excited charge carries and chemical species relevant to photocatalysis, because conduction-band electrons absorb mid-IR light in a broad range of semiconductors [5]. Another advantage of this IR-based method is freedom from scattering of probe light, which often cause a problem in visible spectrometry of μm-sized particles. Indeed, NaTaO₃-based catalysts, which achieve an excellent quantum efficiency (>50%) in the water-splitting reaction [23], present IR absorption of a similar spectrum [24]. The spectrometer combined with a liquid cell is capable of observing photochemical responses at TiO₂-solution interfaces [25]. It is now ready to examine various photocatalysts including thin TiO₂ films useful in practical applications [26], multi-component oxides aimed at utilizing the full spectrum of the solar light [27–29], etc. The degradation of organic pollutants like alcohols, aldehydes, phenols, carboxylic acids, and nitriles is another important object of future study. Identification of short-lived reaction intermediates by their vibrations is highly demanded as a result of the time-resolved IR spectrometry.

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