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Time-Resolved Infrared Absorption Studies of Surface OH Groups on TiO_2 Particles Irradiated by UV Pulses

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The shift of vibrational frequency of surface OH groups on TiO_2 particles induced by UV pulse irradiation has been studied by time-resolved IR absorption spectroscopy. By the UV irradiation of the TiO_2 particles, the absorption intensity at 3696 cm^{-1} was decreased and that at 3654 cm^{-1} was increased. These changes were gradually recovered on a millisecond time scale. The transient changes were interpreted by a small (< 0.1 cm^{-1}) shift of a ν(O–H) band at 3677 cm^{-1}. The temperature jump triggered by the UV pulse caused the shift.

Photoinduced reactions over semiconductor particles such as TiO_2 play an important role in natural environments and also in technological applications.[1–3] Time-resolved IR spectroscopy is a powerful tool for studying the mechanism of the reactions, because it can be applied to the observations of photogenerated electrons[4–6] and also of molecular intermediates. In order to observe the kinetic phenomena related to the photoexcitation of solid surfaces, we built a time-resolved IR spectrometer.[6,7] By using the AC coupled amplification of an IR signal, a transient absorbance change as small as 10^{-6} was detectable over a wide range of delay times (50 ns–1 s). We believe that in situ observations on this time scale will provide rich information on reaction kinetics, because the kinetics are likely decelerated when they are linked to material transport across solid surfaces.

We have observed long-lived photogenerated electrons surviving on a millisecond time scale, and have proposed that these electrons escaped from the recombination assisted by the trapping of holes.[6,8] Surface hydroxyl groups on TiO_2 are thought to be an important intermediate which traps a hole,[1–3]

$$OH^- + h^+ \rightarrow OH^\bullet. \quad (1)$$

The vibrational frequency of the OH groups can be sensitive to their electronic states.[9,10] In the present study, we examined the transient response of the IR absorption in the OH stretching region triggered by UV pulse irradiation.

Experimental

Time-resolved IR absorption measurements were performed by a home built apparatus described previously.[6,7] Briefly, the cw IR light transmitted through the sample was analyzed with a dispersive monochromator (JASCO, CT50TF). The output light was transformed to an electric signal by photovoltaic InSb ($>$ 2000 cm^{-1}) and photoconductive MCT ($<$ 2000 cm^{-1}) detectors (Kolmar). The response of the IR absorption was obtained as a decay curve averaged in a digital sampling oscilloscope. Transient IR spectra at fixed delay times were reconstructed on a set of the experimentally observed decay curves at fixed wavenumbers. The spectral resolution of the monochromator was set at 32 cm^{-1}. The TiO_2 sample was photoexcited by the 355 nm pulses from a Q-switched Nd:YAG laser. The pulse width was 10 ns and the energy was 7 mJ/pulse. The sample was irradiated at 1 Hz, and typically an accumulation for 300 times was performed to obtain a decay curve. Steady-state IR measurements were performed with a FT-IR spectrometer (JASCO, FT/IR-610) with a MCT detector. The spectra were obtained by averaging 300 scans at a 4 cm^{-1} resolution.

The TiO_2 sample used in this study was TiO_4 standard catalyst, supplied by the Catalysis Society of Japan, which is known as Degussa P-25. It is a mixture of anatase (~80%) and rutile (~20%) particles.[11] The average diameter of the primary particles is 21 nm. The powder catalyst was fixed on a CaF_2 plate as a film and placed in a vacuum cell. Prior to the experiments, the TiO_2 sample on the plate was calcined in a 20 Torr (1 Torr = 133.33 Pa) O_2 atmosphere at 573 K and evacuated below 10^{-5} Torr to remove organic contaminants.

Results and Discussion

Figure 1 shows the transient IR spectra of the TiO_2 particles upon 355 nm UV pulse irradiation observed in vacuum. Immediately after the irradiation, the absorption intensity at 3696 cm^{-1} was decreased, while that at 3654 cm^{-1} was increased. These spectral changes were gradually recovered with the elapsing time within 100 ms. Vibration bands observed at 3700–3600 cm^{-1} are assigned to the O–H stretching of the surface OH groups.[12,13] The spectra in Fig. 1 showed that some of the OH groups were affected by the UV pulse irradiation.

The UV irradiation produces electrons and holes in the conduction and valence bands of TiO_2, respectively. The holes are thought to react with the OH groups as reaction (1) and to affect the frequency of the ν(O–H) band.[14] The UV pulse irradiation also heats the sample, and the rise in temperature induces a band shift to the low frequency side through anharmonic coupling with low-frequency modes.[15] The question is whether the changes of ν(O–H) in Fig. 1 were induced by the attachment of the photogenerated holes or by the thermal effect. The temporal profile of the intensity at 3696 cm^{-1} is compared with the sample temperature and the population of the photogenerated electrons in Fig. 2. IR emission was observed at 1200–900 cm^{-1} on the TiO_2 sample irradiated by the UV pulse.[6] It was ascribed to the thermal emission caused by the temperature jump. On the other hand, the IR absorption observed at 4000–900 cm^{-1} was assigned to the electrons photogenerated by the band gap excitation.[6,8] The temporal profile of the absorption intensity at 3696 cm^{-1} was quite similar to that of the emission at 900 cm^{-1} (sample temperature) and much different from that of the absorption at 2000 cm^{-1} (photogenerated electron population). The parallel behavior of the intensity at 3696 cm^{-1} absorption and the sample temperature strongly suggests the thermal origin of the observed shift. Furthermore, the decay profile of the intensity at 3696 cm^{-1} was dependent on the film thickness of the TiO_2. For example, the photoinduced change observed on a film of 5 mg/cm^2 (Fig. 1) remained at 50 ms, whereas it was completely decayed on another film of 3 mg/cm^2 within 20 ms (Fig. 2). The decay of the photogenerated carriers can not depend on the thickness, while the cooling rate can.

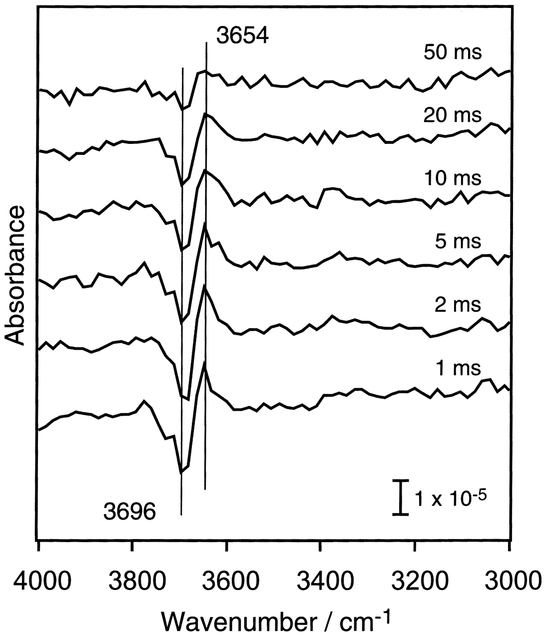

Fig. 1. Transient IR absorption spectra of the TiO_2 catalyst irradiated by 355-nm pulse. Six spectra recorded at delay times of 1, 2, 5, 10, 20, and 50 ms are displayed. Each spectrum was measured at a resolution of 32 cm^{-1} with 4 cm^{-1} intervals.

Steady-state IR absorption was observed on a TiO_2 sample at various temperatures. Figure 3 shows the FT-IR spectra of the OH stretching region of the TiO_2 powder recorded in the vacuum. Five peaks were identified at 3730, 3691, 3677, 3664, and 3640 cm^{-1} on the spectrum recorded at 323 K. These peaks were assigned to the surface OH groups in different environments.[12,13] Figure 3 also shows the subtracted spectra recorded at different temperatures. When the temperature was increased from 323 to 573 K, the five bands decreased in intensity due to the recombinative desorption of the surface OH groups as water molecules. The transient spectral changes at 3696 and 3654 cm^{-1} observed in Fig. 1 were not reproduced

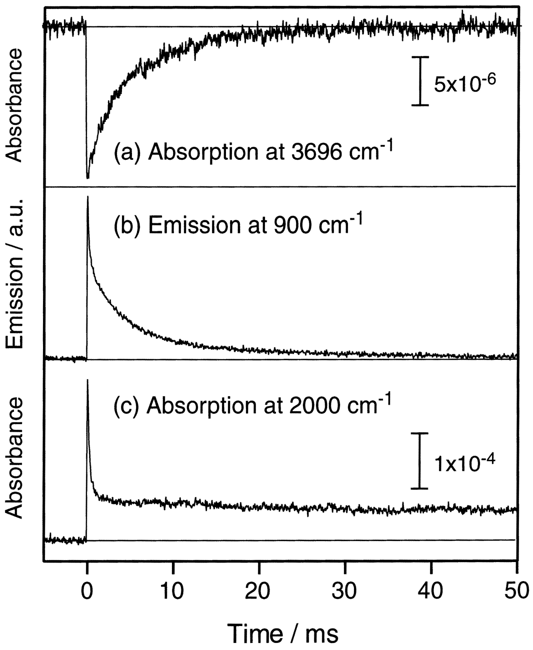

Fig. 2. Temporal profiles of the UV induced changes on TiO_2 particles, (a) the peak top intensity of the surface OH group at 3696 cm^{-1}, (b) the IR emission from the sample at 900 cm^{-1}, (c) the absorbance at 2000 cm^{-1} assigned to the photogenerated electrons.

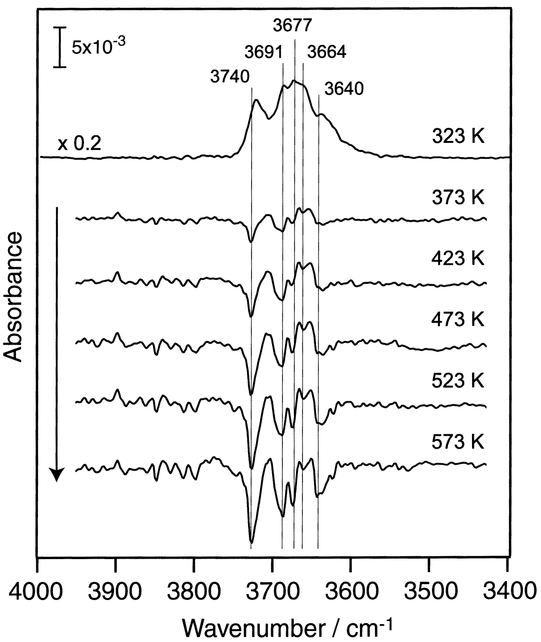

Fig. 3. FT-IR spectrum of the surface OH groups on TiO_2 catalyst measured at 323 K, and the subtracted spectra between the measured one at 323 K and those recorded at the elevated temperatures from 323 to 523 K. These spectra were obtained at a 4 cm^{-1} resolution.

in the subtracted spectra in Fig. 3. All five peaks decreased in intensity in Fig. 3. These results suggest that the temperature jump caused by the UV irradiation was much smaller than the temperature increments examined, as shown in Fig. 3.

We propose that a wide ν(O–H) band slightly shifted to the low wavenumber side, in order to interpret the spectra in Fig. 1. A numerical simulation well reproduced the result obtained in Fig. 1. Figure 4 shows the simulated subtracted spectra which depended on the peak shifts due to the change of temperatures. A gaussian band centered at 3675 cm^{-1} of a 50 cm^{-1} width is assumed to make a small shift to the lower frequency side. The peak position, 3675 cm^{-1}, is the center of the two positive and negative peaks at 3696 and 3654 cm^{-1}. It agrees with the steady-state peaks at 3677 cm^{-1}. The FWHM of the bands in Fig. 3 was 15–20 cm^{-1}. Thus, the 50 cm^{-1} width is reasonable for a band observed by the TR-IR spectrometer at the 32 cm^{-1} resolution.

When the band position was shifted from 3675 cm^{-1} to the low-wavenumber side, a negative peak and a positive peak appeared on the subtracted spectrum at 3696 and 3654 cm^{-1}, respectively. As the peak shift was increased from 0.2 to 1.0 cm^{-1}, the amplitude of the negative and positive peaks became larger, while their positions remained unchanged. This feature was what we observed in Fig. 1. We confirmed that this feature was also reproducible by the simulation with the lorentzian band shape instead of the gaussian band shape, though the positions and amplitudes of the negative and positive peaks were a little different from those in Fig. 4.

Then, we roughly estimated the shift caused by the UV irradiation. In this simulation, the peak height of the parent band was fixed to 1 in absorbance. When the peak position shifted by 1 cm^{-1}, the peak height of the subtracted spectra became 0.03. In the experimentally observed spectra, the peak top intensity of the parent band at 3677 cm^{-1} was 0.05 in the steady-state spectrum (Fig. 3), and the photoinduced absorbance change was 1.5×10^{-5} (Figs. 1 and 2), i. e., 0.03% of the parent peak intensity. There was an almost linear relationship between the band shift and the absorbance change, as indicated in Fig. 4. The experimentally observed absorbance change in Fig. 1 thus corresponds to a frequency shift as small as 0.01 cm^{-1}.

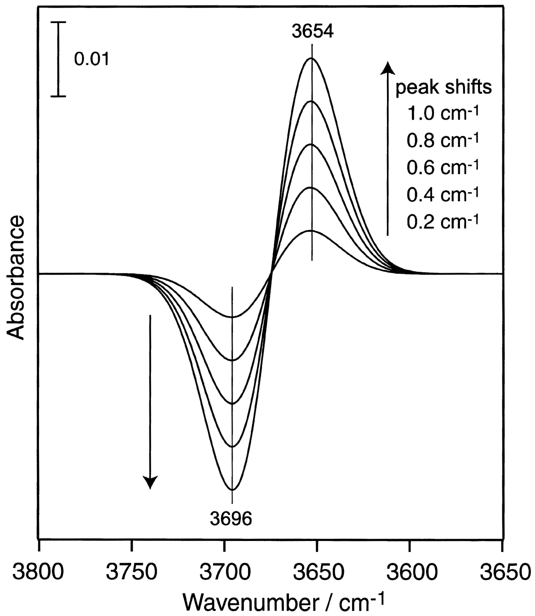

Fig. 4. Simulated subtracted IR spectra of the surface OH group. A gaussian spectrum centered at 3675 cm^{-1} of the 50 cm^{-1} width is assumed to make the small shifts to 3674 cm^{-1} at the step of 0.2 cm^{-1}. The peak top height of the parent bands was fixed at 1.0 in absorbance.

The surface OH groups are thought to trap photogenerated holes and to be oxidized to OH radical species.[1–3] However, the hole trapping by the OH groups was not evidenced in the TR-IR measurements. Instead, a thermally induced ν(O–H) shift was detected. Arguing against the many reports which have observed the hole-attached OH radical species,[14,16] Howe and Grätzel[17] proposed that the holes attach to lattice oxygen anions instead of to the OH groups. Our result may support their proposal. On the other hand, the hole-attached species, if they exist, may be observed by increasing the pump laser power and by improving the heat conductivity to suppress the thermally induced change of the spectrum.

Conclusion

We demonstrated the ability of time-resolved IR spectroscopy in observing the kinetics of the surface OH groups on TiO_2 particles. The UV pulse irradiation caused a small jump of sample temperature. A ν(O–H) band at 3677 cm^{-1} thermally shifted to the low wavenumber side by 0.01 cm^{-1}.

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