J|A|C|S
COMMUNICATIONS

Direct Observation of Reactive Trapped Holes in TiO_2 Undergoing Photocatalytic Oxidation of Adsorbed Alcohols: Evaluation of the Reaction Rates and Yields

Yoshiaki Tamaki, Akihiro Furube,* Miki Murai, Kohjiro Hara, Ryuzi Katoh, and M. Tachiya

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

Received August 25, 2005; E-mail: akihiro-furube@aist.go.jp

TiO_2 is a highly active photocatalyst that has an antibacterial function and is used for applications such as air purification and surface self-cleaning. The photocatalytic activity of TiO_2 is mainly due to the oxidation power of photogenerated holes in its valence band. Hole transfer to a molecule adsorbed on the TiO_2 surface initiates the oxidation reaction, and the oxidized molecule changes into a final product through sequential chemical events. In photocatalytic reactions, TiO_2 reacts with an adsorbed molecule at the first step of oxidation using the holes; therefore, to understand the mechanism of photocatalytic reaction of TiO_2, it is very important to investigate the hole transfer processes.

Since the hole transfer processes are very fast, the reaction rates have been investigated by the transient absorption (TA) or transient reflecting grating methods, which have time resolutions of subpicoseconds.[1−3] However, the high charge carrier density arising from the intense laser excitation in these measurements complicates the electron−hole dynamics because of bulk recombination, which appears to dominate the process. Therefore, extraction of the oxidation reaction dynamics is difficult, and these techniques have not been successful in examining practical photocatalytic reactions that occur under low photon density condition from solar light or lamps. Thus, the mechanism of the photocatalytic reactions in TiO_2 has not been fully understood.

Moreover, the assignment of TA spectra of TiO_2 catalysts is difficult because of severe spectral overlap of transient species. Recently, we have successfully assigned TA bands of a nanocrystalline TiO_2 film to free electrons, trapped electrons, and trapped holes on the basis of precise measurements in a wide spectral range.[4] This has enabled us to discuss formation and decay dynamics of reactive species in TiO_2 quantitatively.

In this study, absorption of trapped holes formed in nanocrystalline TiO_2 films by UV irradiation was measured by highly sensitive femtosecond[5] and nanosecond[6] spectroscopy under low intensity excitation conditions to avoid fast electron−hole recombination. The rates and yields of photocatalytic oxidation of some alcohols on TiO_2 were successfully evaluated.

We used nanocrystalline anatase TiO_2 films on glass plates, the preparation method of which was reported elsewhere.[7] The reactants of the photocatalytic oxidation were methanol, ethanol, 2-propanol, and water. A TiO_2 film was placed in an optical quartz cell containing an air-saturated neat liquid of the reactant. Films were irradiated at 355 nm by 160-fs or 8-ns laser pulses to induce photocatalytic oxidation. The TA signals of all samples at the occurrence of the photocatalytic reactions were reproducible, so that accumulation of photocatalytic products was negligible.

The ground state absorption spectrum (Figure 1A) has its onset at around 380 nm, and the absorbance increases drastically with decreasing wavelength, indicating that selecting the excitation wavelength can control the charge carrier density. The trapped hole spectrum (also Figure 1A), which was obtained in our previous research,[4] has a characteristic peak at around 500 nm. Actually, when both electrons and holes are generated by excitation light, weak absorption of free electrons and trapped electrons can be detected at around 400 nm. Since the absorption of these electrons accounts only for 10% of the total absorbance, the trapped hole absorption dominates around this wavelength.

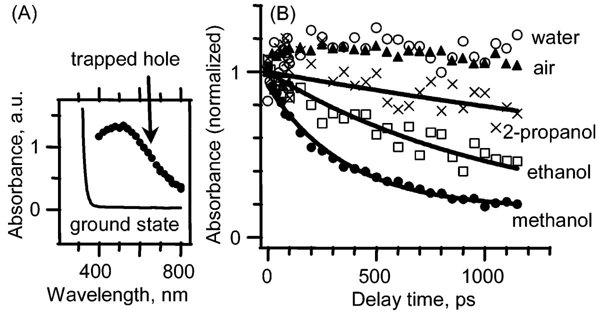

Figure 1. (A) Absorption spectra of TiO_2 nanocrystalline film in the ground state and of trapped holes in the film.[4] (B) Time profiles of transient absorption of TiO_2 in air, water, methanol, ethanol, and 2-propanol at 400 nm.

The TA of the TiO_2 film at 400 nm was recorded after femtosecond laser excitation (Figure 1B). Since the absorbance of the 1.5-μm-thick film was 0.3 at 355 nm, the excitation density was almost homogeneous in the film. A rise in absorption was observed within the time-resolution (200 fs) of our instrument (the rise profiles are not shown). In the case of the TiO_2 film in air, where there is no reactant for trapped holes, an additional rise in TA is observed up to 20 ps as a minor contribution after the instantaneous rise. As discussed in our previous report,[5] shallowly trapped holes relax into deeper trapping sites in this time range; hence, it is likely that a similar relaxation was observed in the time profile at 400 nm. As the TA in air does not decay up to 1 ns, electron−hole recombination is negligible, indicating that surface reaction dynamics of trapped holes can be selectively observed. For reference, TA data under higher excitation intensities are shown in Supporting Information.

The TA of the TiO_2 film in water is similar to that in air, meaning that the oxidation efficiency of water by trapped holes is very low. Yamakata et al.[8] investigated the photocatalytic oxidation of water by a nanocrystalline TiO_2 film by means of infrared TA from microseconds to milliseconds and confirmed the reaction of water with holes. Therefore, the photocatalytic oxidation rate of water is much slower than that of alcohols.

We monitored hole transfer to adsorbed molecules by observing the decay of hole absorption in the presence of alcohols. The TA for all alcohols decayed after excitation, clearly indicating that trapped holes reacted with the alcohols. As observed, the oxidation

10.1021/ja055866p CCC: $33.50 © 2006 American Chemical Society

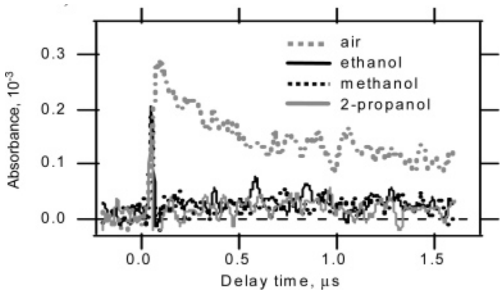

Figure 2. Transient absorption of TiO_2 nanocrystalline film in air, methanol, ethanol, and 2-propanol at 415 nm.

rates of these alcohols differ (Figure 1B). Note that the TA intensities just after excitation were the same before and after addition of alcohols, indicating that the photogenerated species were identical for all samples and ultrafast reaction did not occur. Also, experiments using another probe wavelength confirmed the observation of hole transfer (see Supporting Information).

For the data collected with the nanosecond TA spectrometer at 415 nm (Figure 2), geminate electron−hole recombination is responsible for the observed decay in air because of the absence of reactants. The TA is greatly reduced in the presence of alcohols; it can be regarded as constant in the microsecond time range, suggesting that the oxidation of adsorbed alcohols occurred within the pulse duration (8 ns). The ratio between the absorbance in alcohols (a constant value) and the maximum absorbance in air is 10%; from this ratio the oxidation yields are evaluated to be unity for all alcohols, considering that trapped holes contribute 90% of the total TA at 415 nm and that free and trapped electrons contribute 10%, as mentioned above.

To evaluate the oxidation rates, we analyzed the profiles shown in Figure 1B using a monoexponential function with a constant component (solid lines). The lifetimes of trapped holes in the films in methanol, ethanol, and 2-propanol are 300, 1000, and 3000 ps, respectively. The constant components were about 15% of the maximum absorbance in all cases, which is similar to the results of the nanosecond TA experiment. Thus, these constant components can be attributed to electrons absorbing at 400 nm. Thus, it was well-demonstrated that the combination of highly sensitive femtosecond and nanosecond spectroscopy under low density excitation conditions enables us to quantitatively investigate the dynamics of holes in the TiO_2 photocatalyst.

The dependence of the oxidation rates of alcohols is discussed next. Previously, recombination kinetics of electrons and holes in nanocrystalline TiO_2 films were examined by TA spectroscopy under conditions of low-density excitation.[4,9] These studies revealed that the recombination was very slow, with half-life periods from microseconds to milliseconds and that the kinetics were highly nonexponential, implying that this recombination is governed by the (rather complicated) diffusion of electrons and holes. On the other hand, the decay kinetics of the trapped holes shown in Figure 1B is monoexponential on the nanosecond order. Thus, the oxidation rates of the alcohols are not limited by the diffusion of the trapped holes. Hence, it is likely that the rate-limiting step in this experiment is hole transfer from trapping sites to alcohol molecules. In general, when the density of alcohols adsorbed on the TiO_2 film is much greater than that of trapped holes, quasi-first-order reactions can be observed.

Methanol molecules are reported to adsorb more preferentially than surface OH groups,[10] and the largest density of the OH group on TiO_2 is 4.5/nm^2.[11] Hence, the binding site density of methanol on TiO_2 is larger than 4.5/nm^2. Methanol chemisorbs as methoxy form on the Ti site,[12] whose density on TiO_2 can be counted as 7.0/nm^2 on the (001) surface and 10.3/nm^2 on the (101) surface,[13] indicating high occupancy (>64% and >44%, respectively) of the surface Ti sites by methoxy. These densities will be enough for the quasi-first-order reaction. We expect that a similar situation is valid for other surfaces and imperfect surfaces with defects. For ethanol and 2-propanol, since the TiO_2 films were immersed in the neat alcohols, it is inferred that chemisorbed alcohols with high densities react with trapped holes as alkoxy form.

The reason for the different oxidation times for different alcohols is unclear at the present stage. Oxidation reactions of alcohols can be regarded as electron transfer from alkoxy species to adjacent surface holes (unoccupied surface states just above the valence band). The rates of electron transfer would be determined, for one thing, by the free energy change, that is, by the ionization potential of the alkoxy forms. The ionization potentials of alcohols in the gas phase are 10.85 eV for methanol, 10.65 eV for ethanol, and 10.42 eV for 2-propanol.[14] The valence band edge of anatase TiO_2 is located at 6.9 eV below the vacuum level.[15] Therefore, the electron transfer from these alcohols to surface holes does not occur energetically. Unfortunately, the ionization potentials of alkoxy forms adsorbed on TiO_2 have not been reported to our knowledge. As other factors controlling the electron-transfer rate, adsorption manners of alkoxy forms (e.g., their orientation with respect to the surface), dynamical motions of the alkoxy forms, and surrounding alcohols may be responsible. Clarification of the reaction mechanism is a future challenge.

Rates and yields of oxidation reactions of absorbed alcohols were successfully evaluated by measuring absorption of reactive trapped holes in nanocrystalline TiO_2 films. With the present method, the absorption of trapped holes that are common in every photocatalytic oxidation can be observed; therefore, this method is applicable to studies on oxidation reactions of molecules for which oxidized forms are experimentally hard to detect.

Acknowledgment. This work was supported by the COE development program of Ministry of Education, Culture, Sports, Science and Technology of Japan. Y.T. is a NEDO Fellow.

Supporting Information Available: Supplemental experimental results. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Furube, A.; Asahi, T.; Masuhara, H.; Yamashita, H.; Ampo, M. *Res. Chem. Intermed.* **2001**, *27*, 177−187.
(2) Yang, X.; Tamai, N. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3393−3398.
(3) Morishita, T.; Hibara, A.; Sawada, T.; Tsuyumoto, I. *J. Phys. Chem. B* **1999**, *103*, 5984−5987.
(4) Yoshihara, T.; Katoh, R.; Furube, A.; Tamaki, Y.; Murai, M.; Hara, K.; Murata, S.; Arakawa, H.; Tachiya, M. *J. Phys. Chem. B* **2004**, *108*, 3817−3823.
(5) Tamaki, Y.; Furube, A.; Katoh, R.; Murai, M.; Hara, K.; Arakawa, H.; Tachiya, M. *C. R. Chim.*, in press.
(6) Yoshihara, T.; Murai, M.; Tamaki, Y.; Furube, A.; Katoh, R. *Chem. Phys. Lett.* **2004**, *394*, 161−164.
(7) Hara, K.; Horiguchi, T.; Kinoshita, T.; Sayama, K.; Sugihara, H.; Arakawa, H. *Sol. Energy Mater. Sol. Cells* **2000**, *64*, 115−134.
(8) Yamakata, A.; Ishibashi, T.; Onishi, H. *J. Mol. Catal. A: Chem.* **2003**, *199*, 85−94.
(9) Green, A. N. M.; Chandler, R. E.; Haque, S. A.; Nelson, J.; Durrant, J. R. *J. Phys. Chem. B* **2005**, *109*, 142−150.
(10) Wang, C.; Groenzin, H.; Shultz, M. J. *Langmuir* **2003**, *19*, 7330−7334.
(11) Bahnemann, D. W.; Hilgendorff, M.; Memming, R. *J. Phys. Chem. B* **1997**, *101*, 4265−4275.
(12) Wang, C.; Groenzin, H.; Shultz, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 8094−8095.
(13) Vittadini, A.; Selloni, A.; Rotzinger, F. P.; Grätzel, M. *Phys. Rev. Lett.* **1998**, *81*, 2954−2957.
(14) Robinson, J. W. *Handbook of Spectroscopy*; CRC Press: Cleveland, OH, 1974; Vol. 1, pp 257−511.
(15) Snook, J. H.; Samuelson, L. A.; Kumar, J.; Kim, Y.; Whitten, J. E. *Org. Electron.* **2005**, *6*, 55−64.

JA055866P