Femtosecond Diffuse Reflectance Spectroscopy on Some Standard TiO_2 Powder Catalysts

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(Received April 17, 1997; CL-970287)

Transient diffuse reflectance spectroscopic analysis using a femtosecond white-light continuum as a probe pulse was applied to commercially available catalysts of TiO_2 powder; "standard TiO_2 catalysts" (JRC-TIO-2 and -4) supplied by the Catalysis Society of Japan. The ultrafast dynamics of photogenerated charge carriers under vacuum and air conditions was compared and discussed.

The utilization of small TiO_2 particles as photocatalysts has attracted a great deal of attention for degradation of toxic compounds, solar energy conversion, and so on.[1-5] In order to elucidate parameters that control the heterogeneous reactions, it is of crucial importance to investigate primary events in light-induced phenomena of TiO_2 particles, including trapping of photogenerated carriers and their recombination dynamics. Femtosecond and picosecond transient absorption studies on transparent TiO_2 colloidal solutions have revealed the charge carrier dynamics in an ultrafast time scale.[6-9] However, the TiO_2 catalysts utilized widely in photocatalysis applications are light scattering materials such as powder and suspensions, so that ultrafast spectroscopic studies on such systems have been quite limited.[10,11] Furthermore, the catalytic activities are strongly affected by environmental conditions, the surface nature, chemical compositions, and so on. Therefore, in situ analysis of photophysical and photochemical processes on such catalysts is extremely important and indispensable. For the purpose, time-resolved diffuse reflectance spectroscopy, where the diffuse reflected light from an opaque sample is used as an analyzing light, is very powerful. In this letter, we apply femtosecond diffuse reflectance spectroscopy to two types of "standard TiO_2 catalysts" (JRC-TIO-2 and -4) supplied by the Catalysis Society of Japan, and discuss the dynamics of trapped charge carriers in the TiO_2 particles.

Figure 1 shows transient absorption spectra of the TIO-4 and the TIO-2 powders in vacuum and in air measured by our femtosecond diffuse reflectance spectroscopic system using a femtosecond white-light continuum as a probe pulse.[12,13] Transient absorption intensity was displayed as %absorption defined as %absorption = 100 x (1 - (R / R_0)) where R and R_0 represented the intensity of the diffuse reflected light of a probe pulse with and without excitation, respectively. Excitation wavelength is 390 nm which is very close to the band gap energy of bulk anatase TiO_2. The samples were degassed in vacuum at 723 K for 5 h, heated in pure O_2 at 723 K for 4 h, and finally degassed to 1 x 10^{-5} Torr at 473 K. Some samples were measured after being exposed to air for 1 day, which we call here *sample in air*. Samples were contained in a quartz cell with 2 mm thickness. The broad transient absorption spectra are practically identical with those of the photogenerated electrons and holes in the TiO_2 particles.[7,8] In the studies on colloidal solution of TiO_2 nano-particles by femtosecond and picosecond transient

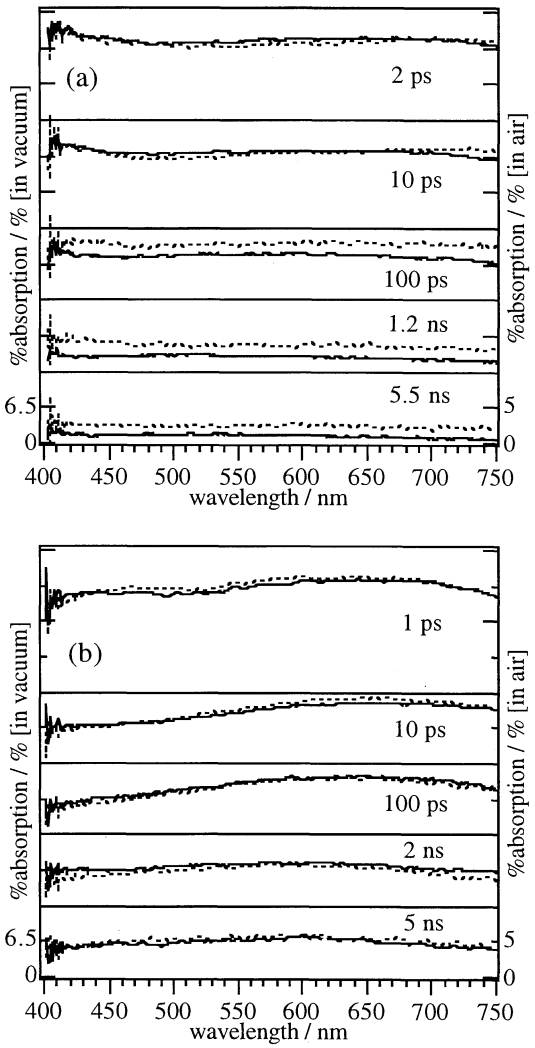

Figure 1. Transient absorption spectra excited with a 390 nm laser pulse (170 fs fwhm). (a) TIO-4 at excitation intensity 5 mJ cm^{-2} and (b) TIO-2 at excitation intensity 2 mJ cm^{-2} measured under vacuum (solid lines) and in air (broken lines).

absorption and EPR experiments, conduction band electrons are considered to be trapped at a surface Ti^{4+} center of the colloid within a few ps after excitation, and the trapped electrons give a broad absorption centered around 500-650 nm, depending on conditions.[7,8,14-18] The transient absorption spectral shape of the powder samples is much broader compared to that of the colloidal solution, and it changes with delay time after excitation. Hence, we consider that several types of trapped electrons with different lifetime are generated in these catalysts and their population and distribution change gradually even in a

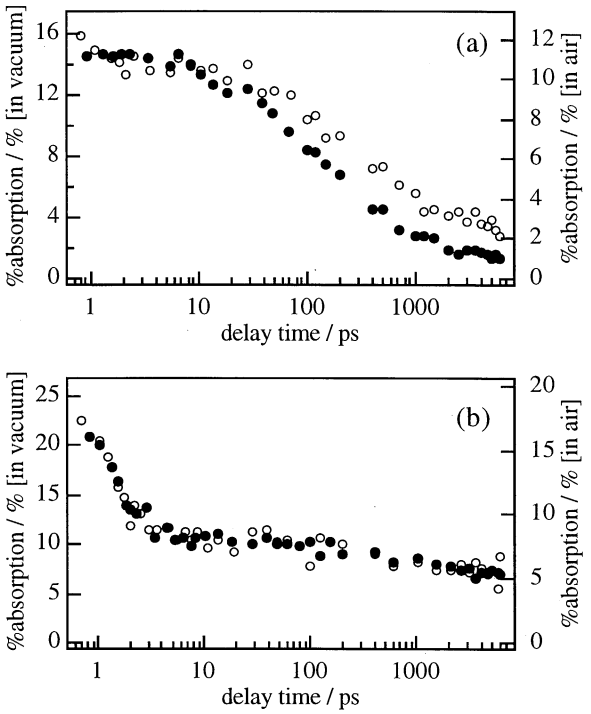

Figure 2. Time profiles of transient absorption at 600 nm of (a) TIO-4 and (b) TIO-2 measured under vacuum (●) and in air (○).

subnanosecond time region. They will include electrons trapped not only at the surface but also in defects of bulk, near the surface and the interfaces between the particles, although the nature is not clear at the present stage.

One finds that the shapes of transient absorption spectra and their time profiles are quite different between the two catalysts. Also, TIO-4 in air gave the different spectra and time profiles from those in vacuum, while any appreciable difference was not observed for TIO-2, as shown in Figure 1. This means that the charge carrier dynamics in TIO-4 is eventually ascribed to the surface or related ones. On the other hand, for TIO-2, electron-hole recombination dynamics in the bulk should be mainly observed. The results seem to agree with the differences of relative photocatalysis activity and of surface area between the two catalysts.[19,20] Although both catalysts are mainly composed of the anatase form of TiO_2, TIO-4 was prepared by chemical vapor deposition from $TiCl_4$, while TiO-2 was done by calcination of the residue from the evaporation of aqueous solution of $TiO(SO_4)_2$. The former is a highly insoluble assembly (about 1 μm diameter) of nanocrystals of 30 nm diameter, and the latter is a particle of several hundreds nm diameter. Also, the catalytic reactivity of TIO-4 is much higher than that of TIO-2.[19,20]

Most interestingly, the decay of transient absorption of TIO-4 in air, observed at 600 nm, became much slower than that in vacuum, as shown in Figure 2a. This means that the deactivation of the trapped electrons in the time scale is reduced by adsorption of oxygen or water molecules at the surface. It is suggested that the observed absorption spectra of TIO-4 are not owing to trapped electrons just at the surface but to those in a surface layer since electrons at the surface should be rapidly scavenged by the molecules. There will be several interpretations on the present result. For example, formation of a potential barrier owing to the adsorbed molecules keeps the electrons in the surface layer.[21] Holes in the surface layer are trapped by adsorbed water molecules, resulting in suppression of hole-electron recombination. In order to make the mechanism clear, the effect of environmental condition and surface modifications should be investigated, which is now in progress.

In conclusion, it is clearly shown that femtosecond diffuse reflectance spectroscopy is very powerful for analyzing primary photophysical and photochemical processes of TiO_2 catalysts. The present result clearly demonstrates that the electronic nature and the dynamics of trapped electrons generated by photoexcitation of the catalysts are sensitively affected by the synthetic procedure and the resulting physical and chemical properties.

The present work is supported by a Grant-in-Aid for Scientific Research on Priority Areas on "Photoreaction Dynamics" from the Ministry of Education, Science, Sports, and Culture, Japan (06239101).

References

1 P. V. Kamat, *Chem. Rev.*, **93**, 267 (1993).
2 M. A. Fox and M. T. Dulay, *Chem. Rev.*, **93**, 341 (1993).
3 A. Hagfeldt and M. Grätzel, *Chem. Rev.*, **95**, 49 (1995).
4 M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, *Chem. Rev.*, **95**, 69 (1995).
5 M. Anpo, Y. Kubokawa, K. Ito, and K. Honda, *in "Hikarishokubai"* (Y. Kubokawa, K. Honda, and Y. Saito, Eds.) Chap. 1, Asakurashoten, Tokyo (1988).
6 D. E. Skinner, D. P. Colombo, Jr., J. J. Cavaleri, and R. M. Bowman, *J. Phys. Chem.*, **99**, 7853 (1995).
7 N. Serpone, D. Lawless, R. Khairutdinov, and E. Pelizzetti, *J. Phys. Chem.*, **99**, 16655 (1995).
8 G. Rothenberger, J. Moser, M. Grätzel, N. Serpone, and D. K. Sharma, *J. Am. Chem. Soc.*, **107**, 8054 (1985).
9 K. R. Gopidas, M. Bohorquez, and P. V. Kamat, *J. Phys. Chem.*, **94**, 6436 (1990).
10 D. P. Colombo, Jr., K. A. Roussel, J. Saeh, D. E. Skinner, J. J. Cavaleri, and R. M. Bowman, *Chem. Phys. Lett.*, **232**, 207 (1995).
11 D. P. Colombo, Jr. and R. M. Bowman, *J. Phys. Chem.*, **99**, 11752 (1995).
12 T. Asahi, M. Matsuo, and H. Masuhara, *Chem. Phys. Lett.*, **256**, 525 (1996).
13 T. Asahi, M. Matsuo, H. Masuhara, and H. Koshima, *J. Phys. Chem.*, A **101**, 612 (1997).
14 R. F. Howe and M. Grätzel, *J. Phys. Chem.*, **89**, 4495 (1985).
15 R. F. Howe and M. Grätzel, *J. Phys. Chem.*, **91**, 3906 (1987).
16 U. Kölle, J. Moser, and M. Grätzel, *Inorg. Chem.*, **24**, 2253 (1985).
17 D. Bahnemann, A. Henglein, J. Lillie, and L. Spanhel, *J. Phys. Chem.*, **88**, 709 (1984).
18 D. Bahnemann, A. Henglein, and L. Spanhel, *Faraday Discuss. Chem. Soc.*, **78**, 151 (1984).
19 Y. Murakami, *in "Preparation Catayst III,"* p.775. Catalysis Society of Japan, Tokyo (1983).
20 H. Yamashita, Y. Ichihashi, M. Harada, G. Stewart, M. A. Fox, and M. Anpo, *J. Catal.*, **158**, 97 (1996).
21 M. Anpo, K. Chiba, M. Tomonari, S, Coluccia, M. Che, and M. A. Fox, *Bull. Chem. Soc. Jpn.*, **64**, 543 (1991).