Direct measurement of picosecond interfacial electron transfer from photoexcited TiO_2 powder to an adsorbed molecule in the opaque suspension

Tsuyoshi Asahi, Akihiro Furube, Hiroshi Masuhara

Department of Applied Physics, Osaka University, Suita, Osaka 565, Japan

Received 12 April 1997; in final form 11 June 1997

Abstract

The excited state dynamics and interfacial electron transfer of an optically scattering TiO_2 powder suspension in alkaline water (pH = 10) with and without methyl viologen (MV^{2+}) as an electron acceptor was examined by means of femtosecond diffuse reflectance absorption spectroscopy using a femtosecond white-light continuum as a probe pulse. The spectral analysis of broad transient absorption bands directly proved plural trapping sites of electrons with different electronic structure and surface electron transfer from photoexcited TiO_2 particles to adsorbed MV^{2+} molecules in the few picoseconds to nanosecond timescale. © 1997 Elsevier Science B.V.

1. Introduction

Interfacial electron transfer plays a key role in the primary photochemical processes of metal oxide-based catalysts such as TiO_2. The timescale of the interfacial electron transfer and lifetime of photogenerated charge carriers in the catalysts determine the efficiency of heterogeneous photochemical reactions [1]. The development in the preparation of nanometer-sized semiconductor colloids allows us time-resolved spectroscopic studies on their dynamics and kinetics using conventional pump–probe techniques. Indeed, femtosecond and picosecond spectroscopic investigations on transparent aqueous TiO_2 colloids reveal the dynamics of charge carrier trapping and the following recombination in the time region of less than several tens of picoseconds [2–8], and the injection kinetics of an electron to molecules in solution or adsorbed on the surface in the picosecond

to sub-nanosecond time regime [9]. However, there are some experimental limitations for extending the ultrafast spectroscopic studies in general. First, TiO_2 nanoparticles are soluble in water only over a low pH range, and it is necessary to employ a stabilization agent such as poly(vinyl alcohol) in experiments above pH 3. Second, TiO_2 systems utilized most frequently in photocatalytic applications are not transparent solutions but powder or opaque suspensions. Therefore, time-resolved diffuse reflectance spectroscopy [10–15], in which the nonspecular reflected light of a probe beam is collected instead of the transmitted light, is considered to be fruitful for analyzing the dynamics of the various TiO_2 systems.

For instance, Colombo and Bowman recently reported the hole ejection from TiO_2 powder (P-25, Degussa) to SCN^- in an opaque aqueous suspension using a femtosecond diffuse reflectance spectroscopic technique [10]. In their experiments, however,

the wavelength of the probe beam was fixed at 620 nm, then characterization of the charge carriers was not provided. In order to reveal the nature of the transient species responsible for electron transfer, spectral information on the species is important and necessary. Furthermore, although some time-resolved spectroscopic studies on the dynamics and kinetics of the hole transfer from excited TiO_2 powder to molecules were reported [10,11], those on interfacial electron transfer to adsorbed molecules have not been examined, as far as we know.

In the present work, we have examined a TiO_2 powder suspension of alkaline water (pH 10) in the presence of MV^{2+} as an electron acceptor by means of femtosecond diffuse reflectance absorption spectroscopy using femtosecond white-light continuum as a probe beam. Spectral analysis of the broad transient absorption bands have directly proven a surface electron transfer from photoexcited TiO_2 powder to adsorbed MV^{2+} molecules in the picosecond timescale. New features of the electron trapping sites and the reactivity of surface sites are presented and discussed.

2. Experimental

Colloidal solutions of TiO_2 were prepared in a similar manner to the published synthetic method [16]. The mixture of 60 ml of $Ti(OCH(CH_3)_2)_4$ (Wako) and 10 ml of 2-propanol (Nacalai Tesque) was added to 380 ml of distilled deionized water for longer than 10 min., while stirring vigorously. Within several minutes after the alkoxide addition, 3 ml of 70% nitric acid was poured into the hydrolysis mixture, still stirring vigorously. The mixture was then stirred for 6 h at about 80°C, resulting in a stable and transparent TiO_2 colloidal solution. The transparency suggests that the diameter of the colloids is less than 100 nm. After cooling of the acidic solution to room temperature, it was neutralized by NaOH, leading to the formation of white TiO_2 powder. It was soluble in acidic water ($<$ pH 3), resulting in a clear solution. This means that it is an aggregate of the nano-sized particles. The powder was washed by deionized water several times, and then dried under vacuum for several hours. The onset of optical absorption of the TiO_2 powder is about 390 nm, which

agrees with the 3.2 eV band gap of anatase TiO_2 [17]. Samples were suspended in deionized water. The optically scattering TiO_2 suspension of pH 10 was stirred to guarantee uniform distribution in the sample cell through the experiment. The pH value was adjusted by adding NaOH. MV^{2+} dichloride salt (Tokyo Kasei) was purified by recrystallization from ethanol.

The details of a fs diffuse reflectance spectroscopic system have been reported elsewhere [15]. Briefly, an excitation light source consists of a cw self mode-locked Ti:sapphire laser (Mira 900 Basic, Coherent), pumped by an Ar^+ laser (Innova 310, Coherent), and a Ti:sapphire regenerative amplifier system (TR70, Continuum) with a Q-switched Nd:YAG laser (Surelight I, Continuum). The fundamental output from the regenerative amplifier (780 nm, 3–4 mJ/pulse, 170 fs FWHM, 10 Hz) was frequency doubled (390 nm) and used as an excitation light source. The residual of the fundamental output was focused into a quartz cell (1 cm path length) containing H_2O to generate a white-light continuum as a probe beam. The transient absorption intensity was displayed as percentage absorption given by

$$\% \text{ absorption} = 100 \times (1 - R/R_0),$$

where R and R_0 represent the intensity of the diffuse reflected white-light continuum of a probe pulse with and without excitation, respectively. Typically, the spectral data were averaged over 300 measurements.

3. Results and discussion

Fig. 1 shows transient absorption spectra of the TiO_2 powder (1.5 g/10 ml) dispersed in water of pH 10 with and without MV^{2+}. Broad absorption spectra extending over the whole visible region were observed at 0 ps up to 6 ns after excitation without MV^{2+}. To our knowledge, any transient absorption spectra have not been reported for TiO_2 powder in the present early timescale, although there are considerable numbers of spectroscopic studies for the colloidal solution of TiO_2 nanoparticles. These data can be used for assignment of the present results, since the powder sample is considered to be an
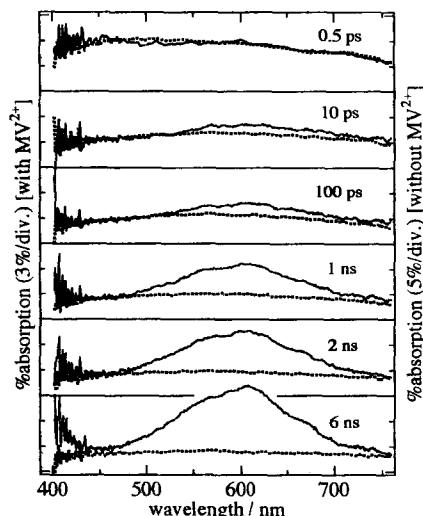
Fig. 1. Transient absorption spectra of the optically scattering TiO$_2$ powder (1.5 g/10 ml) dispersed in water of pH 10 without MV^{2+} (dotted lines) and with MV^{2+} (solid lines, [MV^{2+}] ≈ 0.7 mol/l). Excitation wavelength is 390 nm, and excitation intensity is about 3 mJ/cm^2.

aggregation of TiO$_2$ nanoparticles. Trapped electrons of a TiO$_2$ colloidal solution in the presence of poly(vinyl alcohol) as a hole scavenger show a broad absorption spectrum with a maximum around 500–650 nm, depending on the particle size and other conditions [8,17,18]. From the EPR measurement, the trapping sites are ascribed to surface Ti^{4+} centers near or at the surface [19]. A spectroscopic study on platinized TiO$_2$ referred a broad absorption band centered around 450 nm to be attributed to surface trapped holes [20]. Furthermore, it was recently demonstrated for acidic colloidal solution of TiO$_2$ that photogenerated conduction band electrons are trapped in less than 1 ps [2–5]. In the present spectroscopic experiment on the TiO$_2$ powder, both the transient absorption spectral shape and its time profiles are similar to those of the above solution. Then, we believe that the present experiment of the TiO$_2$ suspension reveals the dynamics of electron trapping near or at the surface followed by electron–hole recombination. Since the electronic spectrum with a maximum in the visible wavelength region is fully developed at 0.5 ps, electron trapping in the powder is inferred to take place in a few hundred femtoseconds.

The peak of the transient absorption spectra of the sample without MV^{2+} immediately after excitation is located at about 500 nm, while after 5 ps up to 6 ns it is shifted to about 600 nm. Moreover, time profiles of transient absorption consist of a rapid decay component with a time constant of a few ps and a slow decay one of several ns, as shown in Fig. 2. The results mean that at least two kinds of trapped electrons or holes, whose recombination dynamics are quite different from each other, are generated. The similar conclusion was already provided for the powder sample by Colombo and Bowman [4,10]. However, it is notable that their conclusion is based on the transient absorption experiment with a fixed probe wavelength (620 nm), and that the different electronic nature of these components have been confirmed by our ultrafast spectral measurements.

By adding MV^{2+} (about 0.7 M) to the TiO$_2$ suspension, a build-up of a new absorption band was clearly observed, as show in Fig. 1. The characteristic absorption band with a maximum at 605 nm is safely assigned to the band of MV$^+$ (λ_{max} = 605 nm, $\varepsilon_{600\ nm}$ = 11000 M^{-1} cm^{-1}) [21]. The time profiles of the transient absorptions at 600 and 450 nm are illustrated in Fig. 3. The risetime of MV$^+$ was estimated to be about 1.8 ns. It is well known that multi-photon excitation of water with a violet ultrashort laser pulse leads to the generation of aqueous solvated electrons, hence one possible formation process of MV$^+$ is a scavenging of the solvated electron by MV^{2+}. Also the solvated electrons may be formed by a direct electron injection from the excited TiO$_2$
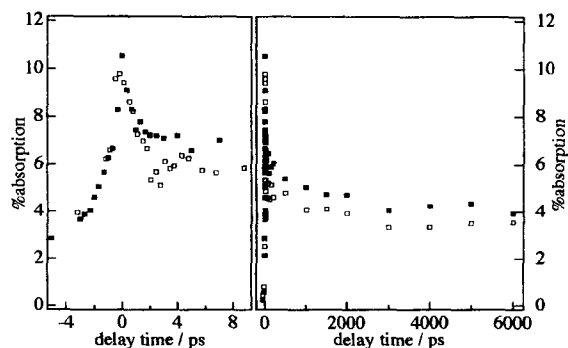

Fig. 2. Time profiles of the transient absorption of the optically scattering TiO$_2$ powder (1.5 g/10 ml) dispersed in water of pH 10 without MV^{2+} observed at 450 nm (□) and 600 nm (■).
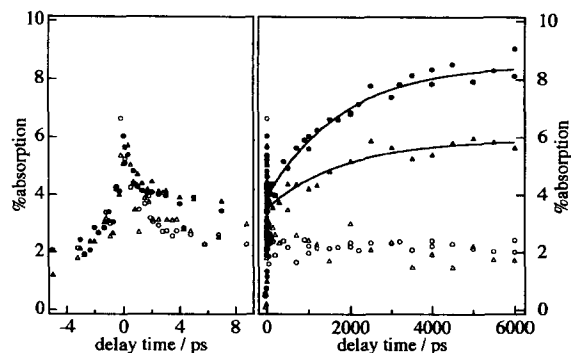
Fig. 3. Time profiles of the transient absorption of the optically scattering TiO_2 powder (1.5 g/10 ml) dispersed in water of pH 10 with MV^{2+}: $[MV^{2+}] \approx 0.7$ mol/l) observed at 450 nm (○) and 600 nm (●), and $[MV^{2+}] \approx 0.1$ mol/l observed at 450 nm (△) and 600 nm (▲).

to water. However, the absorption band of solvated electrons ($\lambda_{max} = 720$ nm, $\varepsilon_{700 \text{ nm}} = 18500$ $M^{-1} cm^{-1}$) [22] was not observed. We performed a similar transient absorption experiment on MgO (1.5 g/10 ml) suspension with MV^{2+} (about 0.7 M), where MgO is a light scattering material, but no apparent transient absorption signal was obtained. Then, the contribution of solvated electrons to the MV^+ formation process is considered to be negligible in the present experiment. We examined the TiO_2 sample with a lower concentration (about 0.1 M) of MV^{2+}, but the risetime was independent of the concentration. On the other hand, the yield of MV^+ at 5 ns was reduced to only 60% in spite of about one-order difference of the concentration of MV^{2+}. Therefore, it is concluded that the formation of MV^+ observed here is attributed to a reduction of MV^{2+} adsorbed on the surface by the trapped electron in the TiO_2 powder.

In spite of the clear observation of the formation of MV^+, a new decay component of trapped electrons corresponding to the interfacial electron transfer was not found in the observed wavelength region. This will be explained by the following two factors. One is the large difference in extinction coefficients between the trapped electrons of TiO_2 and MV^+. If the extinction coefficient of the trapped electron at 600 nm is similar to that of acidic TiO_2 colloidal solution, namely about 1200 M^{-1} cm^{-1} [18], one finds that this value is ten times smaller than that of MV^{2+}. The other is eventually ascribed to the inho-

mogeneity of the surface nature of the TiO_2 powder; namely, only a part of the long-lived electrons can react with adsorbed MV^+ molecules and the transient absorption spectrum at 6 ns in Fig. 1 is a superposition of the MV^+ band and the transient absorption spectrum of the TiO_2 powder at 6 ns.

It is notable here that besides the electron transfer on a nanosecond time scale, a much faster reduction process of MV^{2+} was observed. In the transient absorption spectra of Fig. 1, the absorption of MV^+ is observed 10 ps after excitation and the amount is comparable to that at 100 ps. There was no significant difference in the transient spectra immediately after excitation with and without MV^{2+}, so MV^{2+} reduction by the short-lived electron with an absorption peak at 500 nm may occur, competing. with the rapid (a few ps) charge recombination (see Fig. 2). The rate constant of the electron transfer is estimated to be larger than 10^{11} s^{-1}. An interesting feature of the fast reduction process is the pH effect on the rate constant. At pH 4, while the slow formation process of MV^+ disappeared completely, the fast one remained. The pH effect on the slow reduction process is in good agreement with early studies on the photoreduction of MV^{2+} in a TiO_2 colloidal solution ($[MV^{2+}] = 10^{-3}$ M) by Duonghong et al. [23]. They showed that the rate constant of the interfacial electron transfer increased by more than 3 orders of magnitude over a pH range from 3 to 8. One of the explanations is that there exists a number of different reaction sites, which can transfer an electron to the adsorbed MV^{2+} with different time constants, at the surface of the TiO_2 particles. This may be related to the trapped electrons with the different lifetime and absorption maximum as described above. However, it is not yet clear at present whether this difference in the reactivity is caused by a reduction potential of the trapped electrons or by the adsorption manner of MV^{2+} on the surface and the local environmental condition. Detailed studies on the rapid reduction of MV^{2+} and the pH effect are now in progress and will be published elsewhere.

It is shown here that the dynamics of trapped electrons in the heterogeneous TiO_2 powder could be characterized not only by their decay dynamics but also by the absorption spectrum. The present result is the first clear experimental evidence of the interfacial electron transfer from photoexcited TiO_2

powder to adsorbed MV^{2+} molecules in an opaque aqueous suspension in the time region from the sub-picosecond to nanosecond. A spectral analysis of the broad transient absorption spectra using femtosecond diffuse reflectance spectroscopy has been proven to be powerful for investigations on the surface dynamics of electron transfer and electron-hole recombination of the heterogeneous systems in the picosecond to nanosecond time region.

Acknowledgements

References

[1] A.L. Linsebigler, G. Lu, J.T. Yates Jr., Chem. Rev. 95 (1995) 735; M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341.

[2] D.E. Skinner, D.P. Colombo Jr., J.J. Cavaleri, R.M. Bowman, J. Phys. Chem. 99 (1995) 7853.

[3] D.P. Colombo Jr., K.A. Roussel, J. Saeh, D.E. Skinner, J.J. Cavaleri, R.M. Bowman, Chem. Phys. Lett. 232 (1995) 207.

[4] D.P. Colombo Jr., R.M. Bowman, J. Phys. Chem. 99 (1995) 11752.

[5] N. Serpone, D. Lawless, R. Khairutdinov, E. Pelizzetti, J. Phys. Chem. 99 (1995) 16655.

[6] J.Z. Zhang, R.H. O'Neil, T.W. Roberti, J.L. McGowen, J.E. Evans, Chem. Phys. Lett. 218 (1994) 479.

[7] J.Z. Zhang, R.H. O'Neil, T.W. Roberti, J. Phys. Chem. 98 (1994) 3859.

[8] G. Rothenberger, J. Moser, M. Grätzel, N. Serpone, D.K. Sharma, J. Am. Chem. Soc. 107 (1995) 8054.

[9] N. Serpone, D.K. Sharma, J. Moser, M. Grätzel, Chem. Phys. Lett. 136 (1987) 47.

[10] D.P. Colombo Jr., R.M. Bowman, J. Phys. Chem. 100 (1995) 1996.

[11] R.B. Draper, M.A. Fox, J. Phys. Chem. 94 (1990) 4628.

[12] F. Wilkinson, J. Chem. Soc. Faraday Trans. II 82 (1986) 2037; F. Wilkinson, C.J. Willsher, P.A. Leicester, J.R.M. Barr, M.C.J. Smith, J. Chem. Soc. Chem. Commun. (1986) 1216.

[13] N. Ikeda, K. Imagi, H. Masuhara, N. Nakashima, K. Yoshihara, Chem. Phys. Lett. 140 (1987) 481; N. Ikeda, H. Koshioka, H. Masuhara, K. Yoshihara, Chem. Phys. Lett. 150 (1988) 452.

[14] N. Fukazawa, H. Fukumura, H. Masuhara, Chem. Phys. Lett. 222 (1994) 123; N. Fukazawa, H. Fukumura, H. Masuhara, J. Prochorow, Chem. Phys. Lett. 220 (1994) 461; S. Hashimoto, N. Fukazawa, H. Fukumura, H. Masuhara, Chem. Phys. Lett. 223 (1994) 493.

[15] T. Asahi, M. Matsuo, H. Masuhara, Chem. Phys. Lett. 256 (1996) 525; T. Asahi, M. Matsuo, H. Masuhara, H. Koshima, J. Phys. Chem. A 101 (1997) 612.

[16] B. O'Regan, J. Moser, M. Anderson, M. Grätzel, J. Phys. Chem. 94 (1990) 8720.

[17] H. Tang, H. Berger, P.E. Schmid, F. Lévy, Solid State Commun. 92 (1994) 267.

[18] U. Kölle, J. Moser, M. Grätzel, Inorg. Chem. 24 (1985) 2253.

[19] R.F. Howe, M. Grätzel, J. Phys. Chem. 89 (1985) 4495; J. Phys. Chem. 91 (1987) 3906.

[20] D. Bahnemann, A. Henglein, J. Lillie, L. Spanhel, J. Phys. Chem. 88 (1984) 709; D. Bahnemann, A. Henglein, L. Spanhel, Faraday Discuss. Chem. Soc. 78 (1984) 151.

[21] E.M. Kosower, J.L. Cotter, J. Am. Chem. Soc. 86 (1964) 5524; P.A. Trudinger, Anal. Biochem. 36 (1970) 222.

[22] D.N. Nikogosyan, A.A. Oraevsky, V.I. Rupasov, Chem. Phys. 77 (1983) 131.

[23] D. Duonghong, J. Ramsden, M. Grätzel, J. Am. Chem. Soc. 104 (1982) 2977; M. Grätzel, A.J. Frank, J. Phys. Chem. 86 (1982) 2964.