

Communications to the Editor

Single Charge Accumulation Dynamics on Photocatalytic TiO_2 Particles in Ethanol Slurries by Time Domain Reflectometry

Seiichiro Nakabayashi and Akira Fujishima*

Department of Synthetic Chemistry
Faculty of Engineering, University of Tokyo
Hongo, Bunkyo-kyu, Tokyo 113, Japan

Kenichi Honda

Division of Molecular Engineering
Kyoto University, Sakyo-ku, Kyoto 606, Japan

Received June 4, 1984

Recently, many kinds of photocatalytic reactions at semiconductor surfaces have been studied.¹ The reaction mechanism of the photocatalytic process is not well understood, however, some progress in this direction has been made. For example, Grätzel et al. studied the electron and/or hole transfer rate observed by the laser flash photolysis technique,² and Bard et al. reported quasi-Fermi level floating during the photocatalytic reaction by a slurry electrode system.³ In this article, we present results of a new technique, time domain reflectometry (TDR), for studying the mechanism of the photocatalytic reactions occurring in suspension of TiO_2 powder in ethanol. The advantages of this technique are its ability (1) to observe a system without a color change during the reaction and (2) to make in situ measurements.

Since fundamentals of the TDR technique have been reported elsewhere,⁴ only a short explanation of the technique will be given. Generally speaking, TDR is a pulse method to measure the electrical properties of a sample by means of a terminated coaxial cable. Instruments based on TDR have been used for years for cable testing. Recently, TDR was applied to evaluate the dielectric properties of materials^{4c,d} and the rate of intervalence electron transfer of a mixed-valence compound.^{4a,b}

The experimental system is shown schematically in Figure 1a. In the TDR system, the voltage step pulse propagates from the pulse generator through a coaxial cable to the sampling oscilloscope, where the signal is monitored by the sampling oscilloscope. The voltage pulse then travels to the sample cell, which is equipped with a blocking double-comb electrode (BDCE) that serves as a sensor of changes in the electrical properties of the TiO_2 suspension. The voltage pulse is reflected at the BDCE by impedance mismatch, which results in an echo signal that is propagated backward to the pulse generator. This echo signal contains information about the electrical properties of the TiO_2 suspension and is observed by the sampling oscilloscope.

The concept of the BDCE is schematically shown in Figure 1b. The BDCE consists of two comb-shaped electrodes made of aluminum which are electrically isolated from the suspension by a thin insulator film. The BDCE was made on a quartz substrate by a photoetching procedure. The spaces between teeth of the

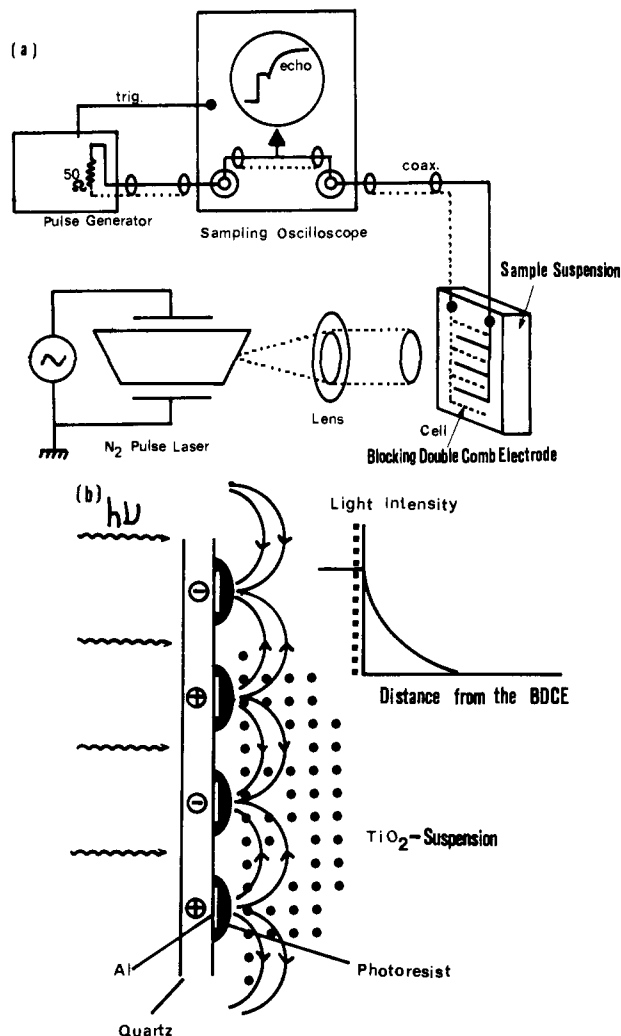


Figure 1. Experimental system (a), and structure of the blocking double-comb electrode (BDCE) (b). The inset at the upper right in (b) is the schematic profile of the irradiation intensity from the BDCE.

BDCE are about 0.3 mm. The lines of electric force between the teeth of the BDCE are most dense near the quartz substrate where the irradiated photons are absorbed by the TiO_2 particles. This light absorption profile from the BDCE into the suspension is schematically shown at the upper right of Figure 1b. The TiO_2 suspension in the cell was photoexcited through the BDCE by a N_2 pulse laser with a 50-Hz pulse repetition rate. The photocatalytic system consisted of a suspension of 2.6 g of TiO_2 powder (P-25, Aerosil) in 200 mL of ethanol containing 0.1 M Na_2SO_4 and 500 mg of poly(vinyl alcohol) to stabilize the suspension. The cell was totally sealed from the ambient atmosphere, and dissolved oxygen was removed under vacuum. Two types of photocatalytic reactions were studied: Type 1 proceeds without an electron acceptor, and type 2 proceeds with an electron acceptor, 10^{-3} M methylviologen (MV^{2+}).

The experimental procedure consisted of measuring shifts of the TDR echo signals due to the photoinduced reaction. This was accomplished by measuring the change of the TDR signal 10 ns after the onset of the reflection of the electronic echo. This point in time corresponded to the rising part of the echo; the plateau value of the echo was found to be constant as the reaction proceeded.

(1) (a) Bard, A. J. *J. Phys. Chem.* **1982**, *86*, 172. (b) Sakata, T.; Kawai, T.; Hashimoto, K. *Chem. Phys. Lett.* **1982**, *88*, 50. (c) Sato, S.; White, J. M. *Chem. Phys. Lett.* **1980**, *72*, 83.

(2) (a) Duonghong, D.; Ramsden, J.; Grätzel, M. *J. Am. Chem. Soc.* **1982**, *104*, 2977. (b) Humphry-Baker, R.; Lillie, J.; Grätzel, M. *J. Am. Chem. Soc.* **1982**, *104*, 422.

(3) (a) Dunn, W. W.; Aikawa, Y.; Bard, A. J. *J. Electrochem. Soc.* **1981**, *128*, 222. (b) Ward, M. D.; White, J. R.; Bard, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 27.

(4) (a) Bunker, B. C.; Kroeger, M. K.; Richman, R. M.; Drago, R. S. *J. Am. Chem. Soc.* **1981**, *103*, 4254. (b) Bunker, B. C.; Drago, R. S.; Kroeger, M. K. *J. Am. Chem. Soc.* **1982**, *104*, 4593. (c) Rellner-Feldegg, H. *J. Phys. Chem.* **1969**, *73*, 616. (d) Cole, R. H. *J. Phys. Chem.* **1975**, *79*, 1459.

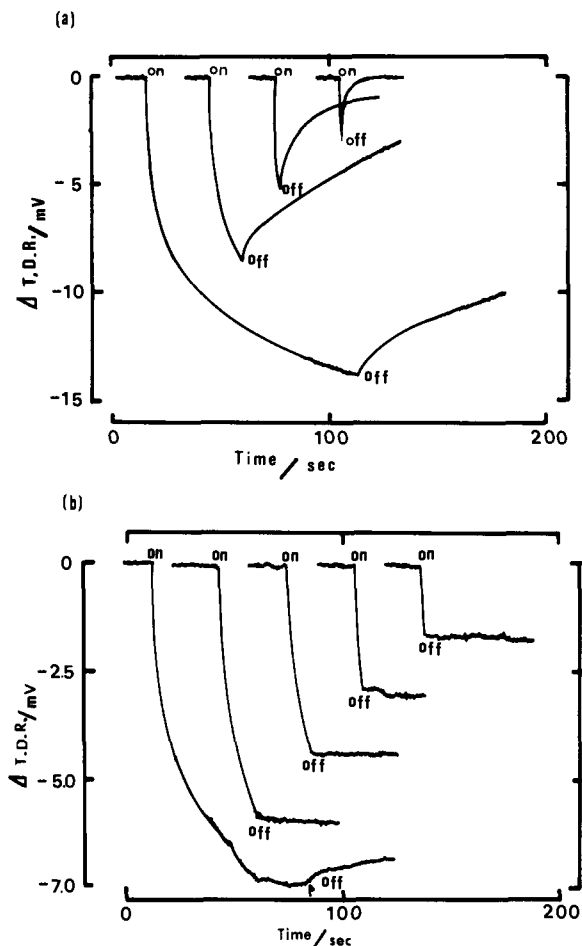


Figure 2. Time-dependent profile of the TDR signal; "on" and "off" in the figures show the starting and end point of the irradiation, respectively. MV^{2+} was added in (a); no MV^{2+} was added in (b).

Typical results are shown in Figure 2a,b which correspond to two cases: when an electron acceptor (10^{-3} M MV^{2+}) was added to the alcohol and when no electron acceptor was added, respectively. In both cases, the photoexcited reaction caused the TDR signal to be shifted -10 mV from its initial value. However, at the end of the photoexcitation, the behavior of the TDR signals was totally different for the suspensions with and without the electron acceptor. For example, in the case for which the acceptor was present, the TDR signal returned to the initial level (Figure 2a) and the time constants of the growth depended on the total time of irradiation. However, when an electron acceptor was absent a growth of the TDR signal was not observed (Figure 2b).

These results are explained as follows. The photocatalytic reaction that occurs in the TiO_2 suspension causes changes in electrical properties of the suspension, i.e., the impedance of the BDCE, and then this change is detected by the TDR signal. The electrical properties of the suspension may be determined by several factors including (1) the concentration and mobility of the free carriers in the TiO_2 particles, (2) the distribution and concentration of ions around the particles, and (3) the conformation of the solvent dipoles at the particle surface. Initially, electron-hole pairs are created in the TiO_2 particles by the photoexcitation, and the concentration of the free carriers in the TiO_2 is increased. The changes in the free carrier concentration in the semiconductor particle will affect the surface potential of the particle and then the distribution of ions around the particle, which causes the change in the dielectric property of the suspension.^{5,6} However, the concentration of the ions in the sus-

pension is approximately constant because the nonreactive electrolyte (Na_2SO_4) is present. The change in the surface potential will also affect the conformation of the dipoles of the solvent molecules. Therefore, the impedance of BDCE and the TDR signal are controlled mainly by the concentration of the carriers in the particles.

Holes created by the photoexcitation are transferred to the solvent ethanol, and then the electrons accumulate in the particle, if an electron acceptor is not present in the suspension. When an electron acceptor MV^{2+} is present, the electron accumulation will be decreased, but the accumulation can still occur if the hole-transfer rate is faster than the electron-transfer rate to the electron acceptor. After the cessation of the irradiation, the discharge of the accumulated electrons in the particle is more rapid if MV^{2+} is present. The rate of discharge is controlled by the diffusion of MV^{2+} in the ethanol to the surface of the particles. Then, the rate of discharge is slower for long-term than short-term irradiation because the length of the diffusion layer of MV^{2+} is increasing (i.e., the concentration gradient of MV^{2+} is decreasing) as the photocatalytic reaction proceeds. From this explanation, it is the accumulated electrons in the TiO_2 particle that shift the TDR signal.

To our knowledge, this is the first experiment in which TDR has been applied to study photochemical reactions, especially photocatalytic reactions occurring on semiconductor particles.

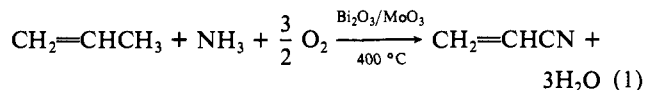
Registry No. TiO_2 , 13463-67-7; MV^{2+} , 4685-14-7; ethanol, 64-17-5.

Homogeneous Models for Propylene Ammoxidation. 1. Tungsten(VI) Imido Complexes as Models for the Active Sites

Dominic M.-T. Chan,* William C. Fultz,
William A. Nugent, D. Christopher Roe, and
Thomas H. Tulip

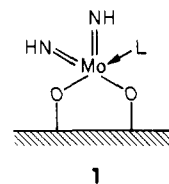
Contribution No. 3405
Central Research and Development Department
E. I. du Pont de Nemours and Company
Experimental Station, Wilmington, Delaware 19898
Received September 10, 1984

The ammoxidation of propylene is a major industrial process by which eight billion pounds of acrylonitrile are produced annually. In this process, a mixture of propylene, ammonia, and air is passed over a heterogeneous bismuth molybdate catalyst (eq 1). Intense interest in the mechanism of this transformation¹



reflects its rather low yield (ca. 65%) when compared with other oxidation reactions (e.g., ca. 90%) for oxidation of propylene to acrolein).

On the basis of studies on heterogeneous systems,¹ the active sites in propylene ammoxidation were proposed^{1d} to have structure 1. At various points in the catalytic cycle, the coordinated group



(5) Schwan, H. P.; Schwarz, G.; Maczuk, J.; Pauly, H. *J. Phys. Chem.* **1962**, *66*, 2626.

(6) (a) Chew, W. C.; Sen, P. N. *J. Chem. Phys.* **1982**, *77*, 4683. (b) Chew, W. C.; Sen, P. N. *J. Chem. Phys.* **1982**, *77*, 2042.

(1) For reviews on the mechanism of propylene ammoxidation, see: (a) Keulks, G. W.; Krenzke, L. D.; Notermann, T. M. *Adv. Catal.* **1978**, *27*, 183-225. (b) Haber, J.; Bielanski, A. *Catal. Rev.—Sci. Eng.* **1979**, *19*, 1-41. (c) Gates, B. C.; Kutzer, J. R.; Schuitt, G. C. A. "Chemistry of Catalytic Processes"; McGraw-Hill: New York, 1979; pp 325-389. (d) Burrington, J. D.; Kartisek, C. T.; Grasselli, R. K. *J. Catal.* **1983**, *81*, 489-498.