Photochemical Properties of TiO_2 Microcrystallites Prepared in Nafion

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TiO_2 microcrystallites of different sizes were prepared in Nafion and the energy diagrams of these were determined from the onset potential of photocurrents due to oxidation of tartrate ions and the bandgap energy which was estimated from absorption spectra. The smallest particle prepared in the present study had the diameter less than 2 nm and the bandgap energy of 3.95 eV. Photocatalytic activities of the TiO_2 microcrystallites prepared in Nafion for photodecomposition of acetic acid were very low compared to those of TiO_2 microcrystallites prepared in clay interlayers and were comparable to those of the latter photocatalysts obtained in the presence of SO_4^{2-}, suggesting that sulfonate groups of Nafion made the photocatalytic activity of TiO_2 microcrystallites decrease.

The preparation and photophysical properties of size-quantized semiconductor particles have been actively investigated.[1–4] Since these semiconductor microcrystallites have very large specific surface areas, they may be useful as photocatalysts. Judging from results obtained on photocatalytic activities of size-quantized TiO_2,[5–7] the size-quantized particles seem to exhibit the activities greater than those expected from the greatness of the surface area. Anpo[5] et al. investigated the activities of TiO_2 for photocatalytic hydrogenation of CH_3CCH in a gas-phase as a function of the particle size of the photocatalyst and suggested that the size-quantization of the semiconductor results in the enhancement of the photocatalytic activities, but the particle sizes of the photocatalysts which they used were fairly large from the viewpoint of size-quantization. The smallest particle they used was 3 nm at most. It seems important to evaluate the size-quantization of TiO_2 of much smaller particles, because bulk TiO_2 has large effective masses of electrons and positive holes in a relative sense and the size-quantization must become appreciable with the particle size smaller than ca. 5 nm in such case, as judged, for example, from the equation derived by Brus.[3]

Then it was the primary purpose of the present study to prepare TiO_2 particles of appreciable size quantization and to investigate their photocatalytic activities. To prepare very small TiO_2 particles of different sizes, Nafion was used as a support. It has been demonstrated that Nafion is useful both as a stabilizing agent for semiconductor microcrystalline colloids[8] and as a support for fixing semiconductor particles.[9] In the former case, the semiconductor colloids are prepared in the presence of Nafion, while in the latter cation-exchanged Nafion is first prepared, which is then converted to semiconductors with reactions in gas phase, as demonstrated, for example for PbS microcrystals of 1.6 nm.[9] The usefulness of Nafion will be demonstrated also in this paper. As will be shown below, a very large size-quantization of ca. 1 eV was operative at TiO_2 prepared in Nafion, but the use of Nafion as the support was unfavorable in obtaining high photocatalytic activities for photodecomposition of acetic acid. The principal reason for this will be discussed based on control experiments using size-quantized TiO_2 particles prepared in the interlayer spacings of sodium montmorillonite.

Experimental

TiO_2 microcrystallites were prepared in Nafion in a manner similar to that reported for the preparation of TiO_2 microcrystallites in the interlayer spacings of sodium montmorillonite (Kunimine Industrial Company, Kunipia G).[7] Titanium tetraisopropoxide was dissolved in 2-propanol to give 1.8 wt% and the resulting solution was added to 1 $mol\,dm^{-3}$ HCl so as to make the molar ratio of HCl to titanium tetraisopropoxide 4:1. The mixed solution was agitated at 50 °C for 6, 8, and 15 h, respectively, for the purpose of aging to result in TiO_2 colloids of different sizes. Then 5 wt% Nafion in alcoholic solution (Aldrich, Nafion 117) was added to the TiO_2 sols in such a way that the molar ratio of 1/4 Ti^{4+} to the sulfonate group of Nafion ($[1/4\ Ti^{4+}]/[SO_3^-]$-Nafion) was 8, followed by agitation at 50 °C for 2 h. Under acidic conditions, the TiO_2 microcrystals must be protonated to result in positive charges on the surface because the pH giving the point of zero charge of TiO_2 is 6.7.[10] Then the prepared TiO_2 microcrystals must be electrostatically bound to sulfonate groups of Nafion. It is not known whether or not the prepared TiO_2 microcrystals were in pores of Nafion or on the polymer surfaces, but this did not bring about any serious problems in the present study, because the prepared TiO_2 microcrystals were stable for over three months, as judged from the occurrence of no appreciable change in absorption spectra. The resulting TiO_2 with the aging time of, for example, 6 h will be denoted in this paper as TiO_2/Nafion (aging time 6 h). Besides these, 3.5 wt% titanium tetraisopropoxide dissolved in 2-propanol was prepared and immediately after the addition of 1 $mol\,dm^{-3}$ HCl solution to it, the Nafion solution in the same ratio of Ti^{4+} to the sulfonate groups of Nafion as described above was added. The resulting mixture was agitated at 50 °C for 2 h. The TiO_2 prepared in this way will be denoted as TiO_2/Nafion (aging time 0 h).

Photocatalytic activities of the TiO_2/Nafion (aging time 0

h) prepared in this way were compared with those of TiO_2 microcrystallites prepared in the clay interlayers, which will be denoted as TiO_2/clay, and with those of TiO_2 bulk powder (rutile modification) prepared by agglomeration of TiO_2 sols. The preparation of these materials was reported previously.[11] Prior to use as the photocatalyst, the TiO_2/Nafion sol was centrifuged at 3500 rpm for 15 min, followed by washing with distilled water several times. It was difficult to determine the specific surface area of TiO_2 included in the TiO_2/Nafion, because the evaporation of the solvent of the TiO_2 sol for the preparation of the sample resulted in very thin platelets of resins. The specific surface area of the TiO_2/clay and the TiO_2 powder was 350 $m^2 g^{-1}$ and 160 $m^2 g^{-1}$, respectively. To determine the amount of TiO_2 in the TiO_2/Nafion (aging time 0 h), 66.1 mg of the dry TiO_2/Nafion was put in a test tube, together with 3 g ammonium sulfate and 6 ml sulfuric acid, followed by heating to dissolve out the TiO_2. The resulting Ti^{4+} solution was subjected to absorption spectroscopy at 410 nm using tiron as a complexing agent.[12] The amount of TiO_2 in the TiO_2/Nafion determined in this way was 15.7 wt%, and that of TiO_2 in the TiO_2/clay was 50 wt% as previously reported.[11] When the TiO_2/Nafion was used as the photocatalysts, not the dry one but wet one prepared by the centrifugation at 3500 rpm for 15 min was used. The content of TiO_2 in this sample was 2.6 wt%.

The TiO_2 particles of the TiO_2/Nafion was observed by a Hitachi H-9000 high resolution transmission electron microscope. For this purpose, samples were prepared by dropping a small amount of the TiO_2/Nafion solution onto carbon-evaporated copper mesh (3 mm diameter) by using a microsyringe, followed by drying. In a similar way, TiO_2/Nafion-coated glassy carbon electrodes were prepared for photoelectrochemical measurements. Photocurrent-potential curves were obtained by employing the lock-in technique, because appreciable cathodic currents in the dark appeared at the onset potential of anodic photocurrents. Absorption spectra of the TiO_2/Nafion were measured in 2-propanol and aqueous solution using a Shimadzu MPS-5000 UV-visible spectrophotometer.

Photocatalytic experiments were carried out using a quartz tube of 16 mm diameter and 180 mm height in which 10 ml of 3 mol dm^{-3} CH_3COOH, and 5 mg photocatalysts in the TiO_2 base was mixed. Prior to illumination of the TiO_2 suspension with a 500 W high pressure mercury arc lamp, the suspension was bubbled by Ar gas for 2 h. The products in gas phase were CH_4 and CO_2, and these were determined by gas chromatography using a Porapak Q column and argon carrier gas.

Results and Discussion

Photochemical Properties. Figure 1 shows absorption spectra of the TiO_2/Nafion sol of the aging time of 0, 6, and 15 h, together with those of the TiO_2/clay and the TiO_2 powder suspended in water. The TiO_2/Nafion sols were diluted to 1/50 with 2-propanol. The greatest blue shift was observed at the TiO_2/Nafion (aging time 0 h) and the degree of the blue shift was decreased with an increase in the aging time. The bandgap of TiO_2 in the TiO_2/Nafion was determined by applying the following equation to the obtained absorption spectrum.

$$(\alpha h\nu) = A(h\nu - E_g)^{n/2}, \qquad (1)$$

where α is the absorption coefficient, and $n=1$ holds in the direct transition and $n=4$ for indirect transition. It is not always clear whether the absorption threshold of TiO_2 is determined either by the direct transition or

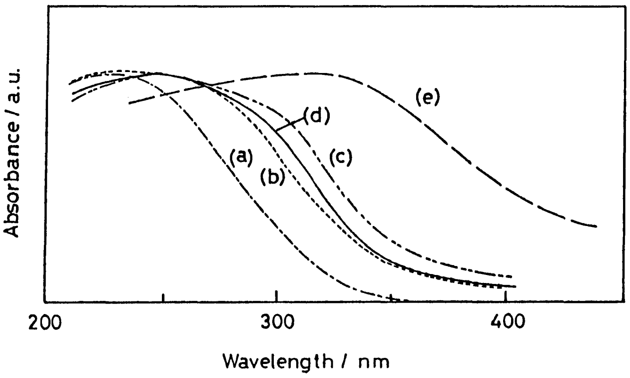

Fig. 1. Absorption spectra of TiO_2/Nafion (aging time 0 h (a), 6 h (b), 15 h (c)) in 2-propanol, TiO_2/clay (d), and TiO_2 powder (e) suspended in water. The amount of suspension: TiO_2/Nafion 0.4 $mg\,ml^{-1}$, TiO_2/clay 0.1 $mg\,ml^{-1}$, and TiO_2 0.3 $mg\,ml^{-1}$.

Table 1. Bandgap Energies, Absorption Threshold, and Potentials at the Conduction Bandedges at pH 0 of Several TiO_2 Microcrystallites

	Aging time	Bandgap[a)]	Absorption threshold	E_{CB} at pH 0
	h	eV	nm	V vs. SCE
TiO_2/Nafion	0	3.95	313	−0.75
	6	3.75	330	−0.7
	8	3.68	337	−0.69
	15	3.65	339	−0.54
TiO_2/clay		3.83	324	−0.64[b)]
TiO_2/powder		3.07	397	−0.28[b)]

a) The value calculated from direct forbidden equation, $(\alpha h\nu)^2=K(h\nu-E_g)$. α: Absorption coefficient, E_g: Bandgap. b) Based on data reported in Ref. 11.

the indirect one. According to literatures,[13] the direct transition gives the bandgap of 3.06 eV while that of the latter 3.10 eV.

Plots of $\alpha h\nu$ vs. $h\nu$ of the absorption spectra of the TiO_2 bulk powder prepared in the present study gave E_g=3.07 eV and n=0.99, indicating that the direct transition occurs in its phototransition. By applying Eq. 1 to the absorption spectra of the TiO_2/Nafion with n=1, the bandgaps shown in Table 1 were obtained. The bandgap of the TiO_2/clay was previously estimated to be 3.58 eV from the blue-shift in the fluorescence maximum, but its value estimated by using Eq. 1 was 3.83 eV. As shown in Table 1, the bandgap values were influenced by the aging time of the TiO_2/Nafion. However, the observations by TEM did not differentiate the particle size of the TiO_2 prepared by using the different aging time. TiO_2 particles (aging time 0 h) could be recognized as a faint circles having lattice imaging of ca. 2 nm or less in diameter. The same was true for the aging time of 8 and 16 h. Furthermore, during the TEM observations, it was noticed that some particles of ca. 1 nm disappeared. This is probably due to the dose of electron beams. By reference to the lattice spacing of (1 1 1) plane of the evaporated Au particles in the TEM picture obtained under the same conditions, the line-to-line distance of the lattice imaging was determined to be 0.322±0.004 nm and 0.259±0.004 nm, which must correspond to the lattice spacing of the (1 1 0) and (1 0 1) in the rutile modification, respectively.

We believe that the particle size smaller than 2 nm was prepared in this study and it was varied a little depending on the aging time. This interpretation is supported by the finding that the absorption threshold of the TiO_2/Nafion (aging time 6 h) was almost the same as that of the TiO_2/clay in which the size of TiO_2 is estimated to be ca. 1.5 nm from the interlayers distance of the TiO_2/clay. The particle size (R) of semiconductor microcrystals can be estimated from Eq. 2[3] if its banndgap is known.

$$E^* = E_g + \hbar^2\pi^2/2R^2(1/m_e + 1/m_h) - 1.8e^2/\varepsilon R, \qquad (2)$$

where E^* and E_g are the bandgap of size-quantized particles and that of the bulk materials, respectively, and m_e and m_h are the effective mass of an electron and positive hole of the semiconductor bulk. By applying E_g=3.07 eV, m_e=9 m_0,[6] and m_h=2 m_0[6] (m_0: electron mass) to Eq. 2, we obtain the particle sizes of 1.01, 1.14, 1.2, and 1.23 nm for the aging time of 0, 6, 8, and 15 h, respectively. It has been pointed out that the usefulness of Eq. 2 is questioned[14] for such small particles of ca. 2 nm or less, but the bandgap values estimated here seem to give indications of very smallness of the TiO_2 particles prepared in this study.

Photocurrent-potential curves were measured at the TiO_2/Nafion-coated glassy carbon electrodes in 0.1 mol dm^{-3} $LiClO_4$ containing 0.01 mol dm^{-3} sodium potassium tartrate as a sacrificial reagent at pH 2. The adjustment of pH was made using $HClO_4$. Since appreciable dark currents flowed at the onset potential of anodic photocurrents, the onset potential of anodic photocurrents was determined by using the lock-in technique. Photocurrent-potential curves obtained are given in Fig. 2. It is believed that the observed photoanodic currents resulted from oxidation of the sacrificial reagent at TiO_2 microcrystallites which were in contact with the glassy carbon electrode substrate. It is recognized by correlating Fig. 2 with Fig. 1 that the greater the blue-shift in the absorption spectra, the more negative the onset potential of anodic photocurrents. E_{CB} values shown in Table 1 were obtained for four kinds of TiO_2/Nafion prepared in this study by assuming that the onset potential of anodic photocurrents roughly gives the energy level (E_{CB}) of the bottom of the conduction bands, and that the E_{CB} varies with solution pH at the rate of −60 mV/pH.

Photocatalytic Properties. We have already reported[11] that the TiO_2/clay exhibited higher photocatalytic activities for photodecomposition of n-carboxylic acids such as acetic acid, propionic acid and n-butyric acid than the bulk powder, and that the difference in the photocatalytic activities between the TiO_2 bulk powder and the TiO_2/clay in those cases seemed to exceed the surface area difference between these catalysts. High catalytic activities of size quantized semiconductors exceeding the surface area difference between those and bulk powders have also been suggested by Anpo[5] for hydrogenation of methyl acetylene on TiO_2. Then very high activities were expected for the TiO_2/Nafion. To examine the photocatalytic activities of the TiO_2/Nafion (aging time 0 h), the photodecomposition of acetic acid to yield methane[15–17] was investigated. Figure 3 shows the production rate of methane as a function of solution pH for the TiO_2/Nafion, TiO_2/clay, and TiO_2

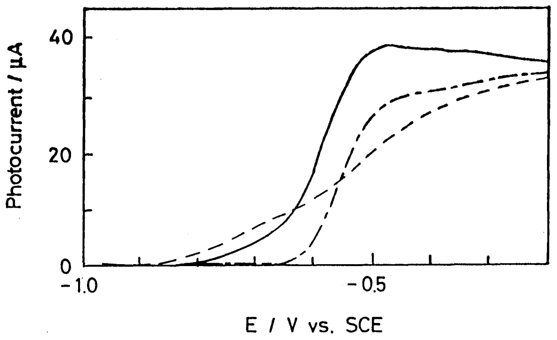

Fig. 2. Photocurrent vs. potential curves of TiO_2/Nafion-coated electrodes in 0.1 mol dm^{-3} $LiClO_4$ containing 0.01 mol dm^{-3} potassium sodium tartrate as a sacrificial reagent at pH 2. Aging time: (----) 0 h, (——) 6 h, (— - —) 15 h. Scan rate: 5 mV s^{-1} Light source: 500 W super high pressure mercury lamp.

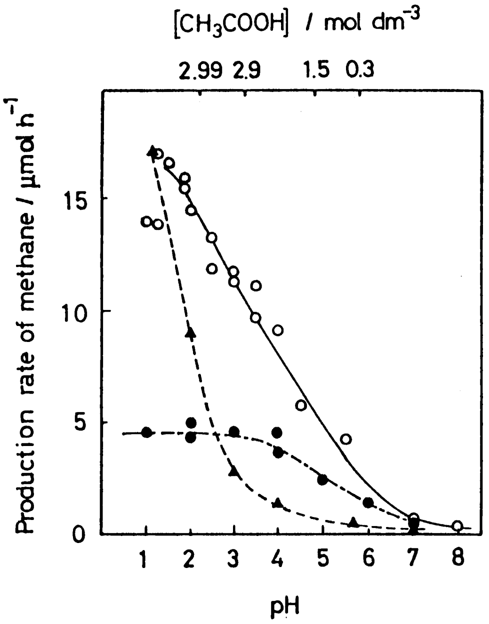

Fig. 3. Effect of pH on the production rate of methane in the photodecomposition of acetic acid. Photocatalyst: TiO_2/Nafion (aging time 0 h ●), TiO_2/clay (○), TiO_2 powder (▲). The concentration of acetate was varied by changing pH of acetic acid solution with fixing the total concentration to 3 mol dm^{-3}. 5 mg TiO_2 (10 mg for TiO_2/clay: 190 mg for wet TiO_2/Nafion) was suspended in 10 ml of the solutions. Light source: 500 W super high pressure mercury lamp.

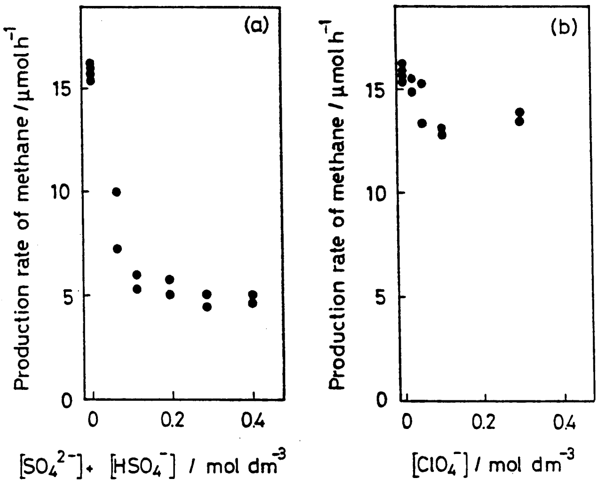

Fig. 4. Effect of sulfate and perchlorate anions on the production rate of methane in the photodecomposition of 3 mol dm^{-3} acetic acid. (a) addition of sulfuric acid (b) addition of perchloric acid. Solution pH was fixed to 1.95 with $NaHSO_4$ and $NaClO_4$. Other conditions were the same as in Fig. 3.

powder photocatalysts. All the photocatalysts showed remarkable pH dependence of the photocatalytic activities and the activities were higher at lower pH, being in agreement with results which were already reported.[15,16] In the case of the TiO_2/Nafion photocatalyst, however, the increase in the activity with decreasing pH was not seen at pH<4, and almost constant and low activities were obtained in this pH region. In contrast, the TiO_2/clay in that pH range exhibited higher activity than that of the TiO_2 powder, as expected from the previous study. If it is assumed that size-quantized semiconductors usually show high photocatalytic activities, the observed very low activity at the TiO_2/Nafion seems to suggest that the Nafion used for holding TiO_2 microcrystallites have some unfavorable effect in the appearence of the photocatalytic activity. It was discovered that the high activity of the TiO_2/clay was distinctly lowered by the addition of SO_4^{2-} to 3 mol dm^{-3} acetic acid, as shown in Fig. 4, though the addition of ClO_4^- did not result in a serious decrease in its photocatalytic activity.

The unfavorable effect of the SO_4^{2-} addition on the photocatalytic activities was already shown in previous study,[17] but discussion on this effect was not made. Considering that the addition of ClO_4^- did not cause a remarkable decrease in the methane production rate, the suppression of the methane production rate caused by the addition of H_2SO_4 seems to be related to higher adsorbability of HSO_4^- and SO_4^- on surface active sites (Ti^{4+}) of TiO_2.[18] Then the idea is evolved that the sulfonate groups of Nafion make strong interaction with TiO_2 microcrystallites at pH below 4. The sulfonate group must be bound to positively charged sites of TiO_2 which serve as the active sites for adsorption of acetate ions as the reactant.[15]

According to the results shown in Fig. 3, the methane production rate at the TiO_2/Nafion was decreased with increasing pH above 4. The apparent low activity observed at pH>4 must result from a scarcity of positively charged sites where the adsorption of acetate ions occurs.[15] When the positively charged surface sites become less abundant, the interaction of them with the sulfonate groups of Nafion should become less, resulting in the disappearence of the unfavorable effect of the Nafion support on the production rate of methane.

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