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Photoelectrochemical Properties of TiO_2 Microcrystallites Incorporated in Sheet Silicates of Montmorillonite

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Photoelectrochemical properties of the titled material were investigated in a system of clay-modified electrodes. Photocurrent action spectra of the incorporated TiO_2 microcrystallites having ca. 15 Å diameter showed a blue shift from those of a TiO_2 single crystal electrode, indicating the operation of the quantum size effect at the TiO_2 microcrystallites. Photoelectrochemical activities for oxidation of several aliphatic alcohols were a little higher at the TiO_2 microcrystallites incorporated in the clay than the TiO_2 single crystal.

Photochemistry of extremely small semiconductor particles has gained popularities in recent years especially in view of the quantum size effect. So far a variety of sulfides, selenides, and phosphides have been investigated for their quantum size effects.1-3) It has also been reported that the size-quantized semiconductors exhibit high photocatalytic activities for several reactions in gas phase and in solutions containing stabilizing agents.3,4) Since photocatalytic activities of semiconductors are intimately related to their photoelectrochemical properties, the investigations on photoelectrochemical properties of semiconductor microcrystallites are of great significance, but to our knowledge little works have been done. In this paper, we would like to report for the first time photoelectrochemical properties of TiO_2 microcrystallites incorporated in sheet silicates of sodium montmorillonite, which will be denoted here as TiO_2/Clay.

The preparation of the TiO_2/Clay was carried out by referring to the procedure reported by Yamanaka et al.5) Titaniumtetraisopropoxide was dropwisely added to 1 mol dm^{-3} HCl to give a molar ratio of 0.25 of the former to HCl. After 3 h stirring, the resulting titania sol was mixed with aqueous suspension of 1 wt% sodium montmorillonite supplied by Kunimine Industrial Co. in such a way that the number of mol of TiO_2 was 40 times of the exchange capacity of the clay. The mixture was continuously stirred for 3 h at 50 °C, followed by centrifugation. After washing with de-ionized water for several times, the resulting TiO_2/Clay was dried in air. The weight ratio of TiO_2 to the clay was ca. 50%, and the size of the incorporated TiO_2 was estimated to be ca. 15 Å from the basal spacing of the TiO_2/Clay determined by X-ray diffractmetry. The surface area of the TiO_2/Clay was 347 m^2g^{-1}, as determined by a Shimadzu-Micromeritics surface area analyzer.

TiO_2/Clay-coated glassy carbon (GC) electrodes were prepared by using the published procedure of the preparation of clay-modified electrodes.[6)] The GC plates were polished with 0.03 µm alumina, followed by washing in an ultrasonic bath. Then they were coated with appropriate volumes of a 0.02 wt% TiO_2/Clay colloid, and were dried in air. As a reference to the TiO_2/Clay, a TiO_2 single crystal was used. The preparation of an well-etched single crystal electrode was already published.[7)]

The transmittance of the coated TiO_2/Clay was measured using a quartz plate as a substrate for coating. Illumination of the electrode was usually made by using a 500 W high pressure mercury arc lamp. In cases where photocurrent spectra were measured, a 500 W xenon lamp was used with combination of a monochrometer. The number of photons of the monochromatic light was determined by a calibrated Eppley thermopile.

An absorption spectrum of the TiO_2/Clay is given in Fig. 1 together with that of a TiO_2 powder prepared by agglomeration of TiO_2 microcrystallites of the sol. As shown in the figure, the spectrum of the TiO_2/Clay is blue-shifted from that of the TiO_2 powder, reflecting the quantum size effect of the TiO_2 microcrystallites incorporated in the clay. The sodium montmorillonite used did not show any remarkable absorption in the wavelength region given in the figure.

Figure 2 shows current-potential curves of a TiO_2/Clay-coated GC electrode in 0.1 M (M = mol dm^{-3}) Na_2SO_4, taken by the potential sweep method. By illumination photocurrents were induced by photosensitized oxidation of water. Then, the quantum efficiencies for anodic photocurrents of this electrode were measured at 0.8 V vs. SCE, and the results are included in Fig. 1. It is recognized from the results shown in Fig. 1 that the photocurrent spectrum of the TiO_2/Clay was in good agreement with its absorption spectrum. The photocurrent spectrum of the TiO_2 single crystal electrode is not shown here, but it had the onset at ca. 400 nm, being similar to those reported previously.[8)] Accordingly, the operation of the quantum size effect of the TiO_2/Clay-coated electrode in photosensitized oxidation of water is evident.

It was found that the photocurrents appeared only when the TiO_2/Clay layer was thin enough to allow penetration of ultraviolet lights, as will be noticed from the results shown in Fig. 3, where the dependence of the magnitude of anodic photocurrents on the amount of the coated TiO_2/Caly is given. The results seem to indicate that photoelectrochemical activities of the TiO_2/

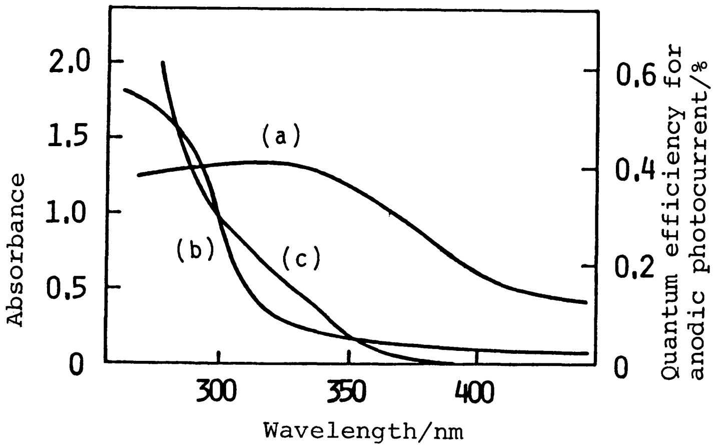

Fig. 1. Absorption spectra of (a) TiO_2 powder prepared by agglomeration of TiO_2 microcrystallites of the sol (4.0×10^{-4}M) and (b) TiO_2/Clay suspended in water to give 7.5×10^{-4} M TiO_2, and photocurrent spectrum of a TiO_2/Clay-coated GC electrode (c) measured in 0.1 M Na_2SO_4 at 0.8 V vs. SCE. The amount of coated TiO_2/Clay was 0.04 mg cm^{-2}.

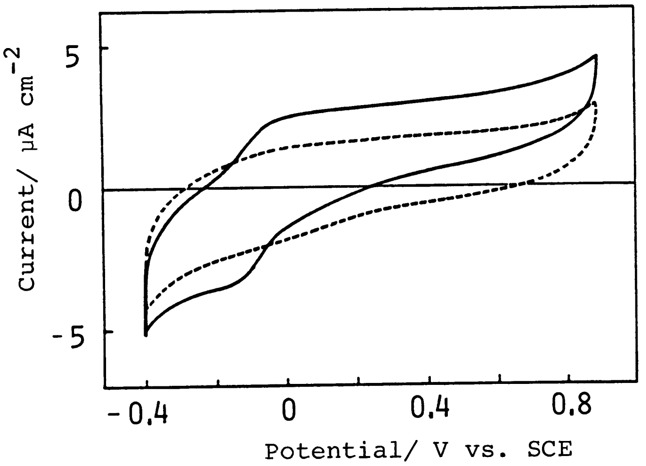

Fig. 2. Current-potential curves of a TiO_2/Clay-coated GC electrode in 0.1 M Na_2SO_4. (——) under illumination. (- - -) in the dark. dE/dt = 0.1 V s^{-1}.

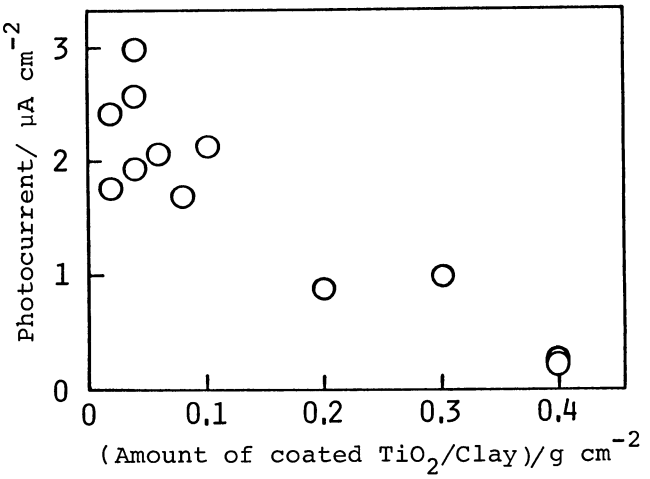

Fig. 3. Effect of the amount of coated TiO_2/Clay on photocurrents at 0.8 V vs. SCE in 0.1 M Na_2SO_4.

Clay appear only if TiO_2 particles that are in contact with the GC substrate are illuminated. The smallness of anodic photocurrents shown in Fig. 2 and that of the quantum efficiency of anodic photocurrents shown in Fig. 1 must be resulted from the existence of silicate layers of 9.6 Å which block direct electrical communication between the electrode substrate and the incorporated TiO_2 particles. TiO_2 particles held at edges at the interlayer spacings and/or those on the silicate layers are thought to be mostly involved in photosensitized oxidation of water.

To examine photoelectrochemical activities for other reactions, photosensitized oxidation of aliphatic alcohols was investigated using nonaqueous alcohol solutions into which $LiClO_4$ was dissolved as an electrolyte. It was found that there are a little different activities between the TiO_2/Clay-coated electrode and the TiO_2 single crystal electrode. If the ratio of anodic photocurrents at 0.8 V vs. SCE for oxidation of alcohols to that for oxidation of methanol is plotted as a function of the number of carbons, the results shown in Fig. 4 were obtained. At the TiO_2 single crystal electrode the magnitude of anodic photocurrents steadily decreased with an increase in the number of carbons, but at the TiO_2/Clay-coated electrode the photocurrent decrease seems to stop at the number of carbons of five beyond which the photocurrents became eventually constant.

There may be a variety of factors which are related to bringing about the observed different behaviors between the TiO_2/Clay and

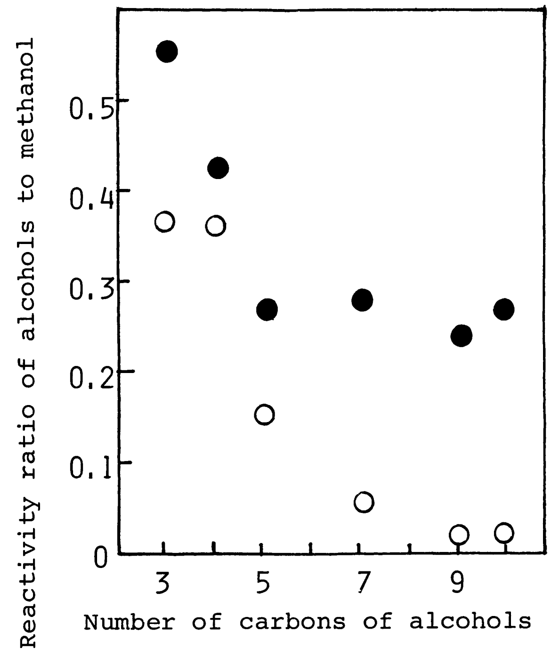

Fig. 4. Dependence of the reactivity for oxidation of aliphatic alcohols on their number of carbons, obtained at 0.8 V vs. SCE. (○) TiO_2 single crystal. (●) TiO_2/Clay-coated electrode.

the TiO_2 single crystal electrodes, but at least the difference in energetic correlations of the semiconductors to the reactants seems to be very important. It is recognized from the observed blue shift of the absorption spectrum of the TiO_2/Clay that this material had a greater bandgap than TiO_2(rutile) bulk materials. Truely, as will be reported in a separate paper,[9] the energy structure of the TiO_2/Clay, determined by analyzing transient photocurrents of irradiated semiconductor suspensions in the presence of an electron scavenger and a hole scavenger, was different from that of the TiO_2 bulk materials in such a way that the valence bandedge of the former material was ca. 0.34 V more positive than that of the latter. Since it is known that alcohols having a greater number of carbons are less reactive for oxidation, the more positive valence bandedge is favorable for oxidation of these alcohols.

It may be speculated that the clay support must have some favorable effect on the generation of the apparent high activities of the TiO_2 microcrystallites. Considering that aliphatic alcohols are apt to be easily incorporated into the interlayer spacings of the clay,[10] the alcohols must have high adsorbabilities to the clay, resulting in the apparent high activities for electrochemical oxidation. In the present study, however, the activities were determined in nonaqueous alcohol solutions, so the contribution of the high adsorbabilities if any would not be significant. In conclusion, the observed high activities of the TiO_2 microcrystallites for oxidation of several primary alcohols seem to be resulted at least in part from the relatively high oxidizing power of this material.

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