Photofuel Cells Using Allophane–Titania Nanocomposites

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Allophane–titania nanocomposite electrodes were prepared from titanium alkoxide sols dispersing the natural clay mineral allophane. Electrochemical measurements indicated that the oxidative degradation of glucose in the electrolyte enhanced the generation of electricity during UV irradiation. A higher short-circuit current was observed in the photofuel cell using the 0.10% allophane-containing titania electrode than that with the normal titania electrode. Allophane effectively adsorbed the glucose molecules and then transported them to the titania, on which their oxidation induced the electrogeneration.

Dye-sensitized solar cells employ dye-adsorbed titania as the working electrodes.[1] Such photocatalyst titania films are also useful as photofuel cell electrodes to generate electricity by oxidizing the fuel materials during UV irradiation.[2,3] The photofuel cell electrodes generally act in the liquid phase containing the fuel material. In such systems, the concentration of the fuel material on the photocatalyst surface is one of the parameters for improving the energy conversion efficiency.[4] A clay mineral, allophane, was reported to have a 3.5–5.0-nm-sized hollow spherical particle structure with 0.3–0.5-nm-sized defects on its surface and a significant ability to adsorb ionic or polar chemicals due to their amphoteric ion-exchange activity and high surface area.[5–7] The clay–titania composites are effective in degrading organic compounds[8–11] because the adsorbed molecules should be quickly transported to the titania surface.[12] However, hybridization of the general clay minerals with the photocatalysts decreased their photocatalytic activity because such clay minerals consist of relatively large-sized insulative particles. There is a possibility that the high dispersion of allophane nanoparticles on the photocatalyst surface allows the retention of semiconductivity and activity. We tried to prepare the allophane–titania nanocomposite electrodes by a simple sol–gel process and investigate the effect of their adsorption ability on the photofuel cell reactions.

The sol–gel reaction system was prepared by mixing $5.0 \, cm^3$ of titanium tetraisopropoxide, $25.0 \, cm^3$ of ethanol, $0.21 \, cm^3$ of water, and $0.21 \, cm^3$ of concentrated nitric acid as the catalyst for the sol–gel reaction. The allophane $(1.6SiO_2 \cdot Al_2O_3 \cdot 5\text{–}6H_2O)$ was extracted by elutriation of Kanuma soil from Tochigi, Japan, as already described.[12,13] The allophane was dispersed in the sol–gel systems of titanium tetraisopropoxide in which the Al/(Al + Ti) ratios were 1/100 (1.0% allophane) and 1/1000 (0.10% allophane). The sol–gel systems with and without allophane were agitated and allowed to react during ultrasonication for 1 day. Glass plates with the ITO transparent electrode were dip-coated with the sol–gel systems and then heated at 500 °C for 30 min in order to prepare the titania electrodes and allophane-containing titania electrodes, i.e., allophane–titania nanocomposite electrodes. The electrolyte solutions for the

photofuel cell reaction consisted of $0.20 \, mol \, dm^{-3}$ aqueous NaOH solution and that with 0.28 or $1.67 \, mol \, dm^{-3}$ of glucose.

The surface morphology of the electrode samples was observed using a field emission scanning electron microscope (Hitachi S-4100). The particle morphology of the flakes of the electrode surface layer was observed using a transmission electron microscope (JEOL JEM-2010). The crystalline phase was determined using an X-ray diffractometer (Rigaku RINT-2200V). The electrolyte solutions were allowed to soak into the space between the electrode sample and the counter Pt electrode. The FTIR spectra of the electrolyte solution containing 1.67 $mol \, dm^{-3}$ glucose were observed as a function of UV irradiation time using an FTIR spectrophotometer (Shimadzu IRPrestige-21) in order to examine the changes in concentrations of glucose and the products. The area of the irradiated electrode was $0.4 \, cm^2$. The I–V curves of the electrodes were measured in the electrolyte solutions with and without the $0.28 \, mol \, dm^{-3}$ glucose by a potentiostat (Hokuto Denko HSV-100) during UV irradiation. The area of the irradiated electrode was $100 \, cm^2$.

Figure 1 shows the SEM images of the titania and 1.0% allophane–titania composite films. These films consisted of 10–30-nm-sized particles and cannot be distinguished because the allophane particles are very small.[12] The EDX analysis revealed that the allophane particles were highly dispersed among the titania particles as previously shown.[12b] Figure 2 shows the
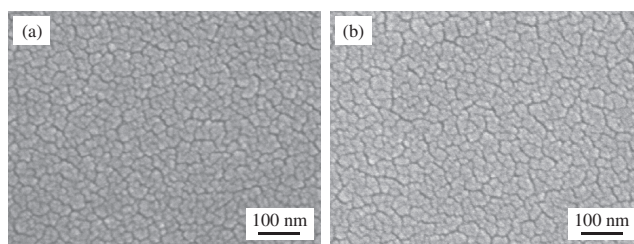

Figure 1. SEM images of the (a) titania and (b) 1.0% allophane–titania composite films.
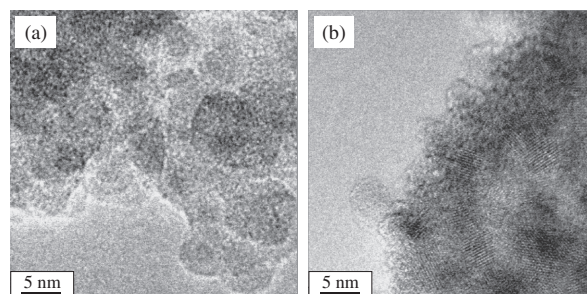

Figure 2. TEM images of the (a) allophane and (b) the 1.0% allophane–titania composite powders.
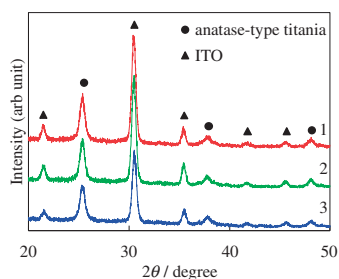
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Figure 3. XRD patterns of the (1) titania film and the allophane–titania composite films containing (2) 0.10% and (3) 1.0% allophane.

TEM images of the allophane and 1.0% allophane–titania composite powders. The allophane consisted of ca. 5-nm-sized porous particles. In the image of the composite, the ca. 10-nm-sized particles, which exhibited lattice fringes, should indicate the titania particles. Many small particles of allophane were dispersed on the titania surface.

Figure 3 shows the XRD patterns of the titania and allophane–titania composite films. The peaks at 25.3, 37.8, and 48.1° assigned to anatase-type crystals were observed in all the films. Their crystallite sizes were estimated using Sherrer's equation to be 22 nm for the titania, 18 nm for the 0.10% allophane–titania composite, and 16 nm for the 1.0% allophane–titania composite. The sizes were smaller for the allophane-containing films than for the only titania film. This result indicates that the allophane particles prevented the crystal growth of the titania because the allophane particles strongly bonded to the titanium alkoxide polymers and the titania gel particles.[12] This phenomenon is similar to the effect of the organic dyes which strongly interact with the titanium species in the sol–gel systems and prevent the reorientation of the titanium alkoxide polymers.[4,14] The dispersion of allophane particles influenced the particle growth and crystallization process of titania.

The photocatalytic degradation of glucose and the resulting CO_2 production were observed on the titania and allophane–titania composite electrodes during UV irradiation by FTIR measurements. The CO_2 was resolved as CO_3^{2-} in the present basic solutions. Figure 4 shows the time course of the concentrations of glucose and CO_3^{2-} estimated from the absorbance at 1030 and 1420 cm^{-1}, respectively.

The glucose concentration decreased with an increase in UV irradiation time. The decrease in glucose concentration by adsorption onto the electrodes can be negligible because the film thickness was ca. 400 nm and the total surface area of the films was very small. The amount of the eosin Y adsorbed on all the films (10 cm^2) was ca. 5×10^{-5} mol. In the previous study, hybridization of 1.0% allophane with the titania powder sample increased its adsorption ability by 10%.[12b] The degradation rate was fast in the order of using the 0.10% allophane–titania composite, titania, and 1.0% allophane–titania composite electrodes, indicating their photocatalytic activity. The allophane particles can adsorb glucose and the partial oxidation products and donate them to the titania. The photocatalytic activity was enhanced by adding a small amount of allophane due to the effective adsorption and degradation relay.[12] However, a larger amount of allophane decreased the photocurrent due to depressing the photocatalytic function of the titania.
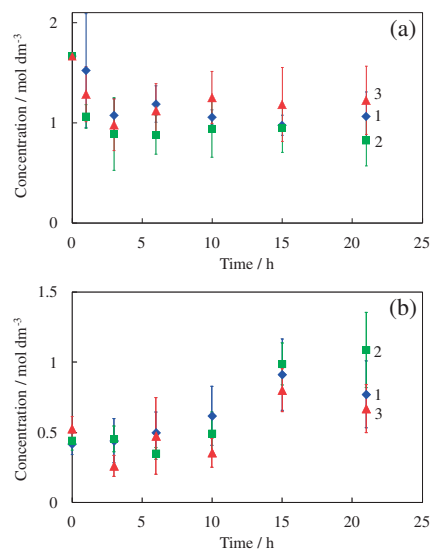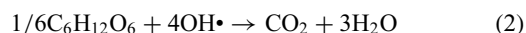

Figure 4. Changes in concentrations of (a) glucose and (b) CO_2 during photocatalytic degradation using the (1) titania electrode and the allophane–titania composite electrodes containing (2) 0.10% and (3) 1.0% allophane.

The amount of CO_3^{2-} was great in the same order as that of the glucose degradation rate. The 0.10% allophane–titania composite electrode exhibited a higher performance than the others. This result indicates that the glucose was oxidized during the photocatalytic reaction process. However, the increment in CO_3^{2-} concentration was smaller than the decrement in glucose concentration. The partial oxidative products of glucose such as carboxy, carbonyl, and alcoholic compounds should be easily adsorbed on the allophane and titania surface.[13,15–18] Therefore, they were not detected in the water phase. It was difficult to determine such organic compounds on the electrode surface due to their very small amounts.

Hydroxy ions are oxidized by holes and form hydroxyl radicals on the titania under basic condition. The glucose molecules should be oxidized by the hydroxyl radicals on the titania and produce CO_2 and H_2O. H_2O should be reduced with oxygen by the electrons on the counter electrodes. These reactions can be expressed as follows:

Titania electrode:

$$4OH^- + 4h^+ \rightarrow 4OH\bullet \tag{1}$$

$$1/6C_6H_{12}O_6 + 4OH\bullet \rightarrow CO_2 + 3H_2O \tag{2}$$

Counter electrode:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \tag{3}$$

The moderate concentration of the fuel material on the photocatalyst surface is an important parameter for improving the energy conversion efficiency. Also, the active species, hydroxyl radicals, should be concentrated on the photocatalyst surface. The allophane and titania surface should be negatively charged under the present condition. The holes are consumed to produce the hydroxyl radicals, and then the hydroxy ions are presumed to be supplied to the titania surface by the allophane. The reaction rate became slower with the elapse of time because the oxygen concentration in the solution was very low. The rise in the CO_2
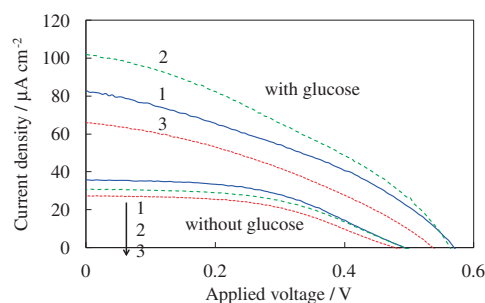
Figure 5. *I–V* curves of the (1) titania electrode and the allophane–titania composite electrodes containing (2) 0.10% and (3) 1.0% allophane observed using the electrolyte solutions with and without glucose during UV irradiation.

Table 1. IPCE values for the above electrodes (1)–(3) using the electrolyte solutions with and without glucose during 340-nm irradiation

	1	2	3
With glucose	13.7%	14.9%	11.3%
Without glucose	10.5%	9.5%	8.4%

production was delayed because the second reaction on the titania electrode consisted of several partial oxidation steps.

Figure 5 shows the *I–V* curves of the titania and allophane–titania composite electrodes observed during UV irradiation. The incident photon-to-current efficiency (IPCE) values for the electrodes are shown in Table 1. The photocurrent due to water splitting was observed using glucose-free electrolyte solution. The short-circuit current decreased with an increase in the amount of allophane in the titania electrode using glucose-free electrolyte solution. This indicates that the electronic conductivity in the electrode reflected the photoelectric conversion efficiency even though the photocatalytic activity was best enhanced by adding 0.10% allophane. The short-circuit current values observed using the glucose-containing electrolyte solution were significantly larger than those observed using the glucose-free solution. This indicated that the oxidation of the glucose enhanced the generation of electricity. The highest short-circuit current values were observed using the 0.10% allophane-containing titania electrode because the allophane increased the concentrations of the organic materials on the electrode surface without decreasing its electronic conductivity. The larger amount of allophane decreased the photocurrent due to decreasing the electronic conductivity in the electrode. Allophane particles should be highly dispersed in the titania in order to effectively function as an adsorbent and prevent their aggregation causing action as an insulator. The thinness and porous structure of the films in the present electrodes decreased their parallel resistance and the open-circuit voltage even though the theoretical value is ca. 1.2 V.[4]

The photocurrent action spectra were also measured using the above electrodes although they are not shown. The threshold values of these spectra were around 400 nm, the same as the absorption edge of the titania, indicating that the photocurrent was generated by the excited electrons in the titania.[19] The photocurrent values in the spectra for the above electrodes also corresponded to the short-circuit current values obtained from the *I–V* curves.

The allophane–titania nanocomposite electrodes were prepared from the allophane-dispersing titanium alkoxide sol by the sol–gel method. CO_2 was observed as a photocatalytic product from the oxidative degradation of glucose on the electrodes during UV irradiation. The oxidation of the glucose enhanced the generation of electricity. The higher photocurrent values were clearly observed in the 0.10% allophane-containing electrode than in the normal titania electrode because the allophane increased the concentrations of the organic materials on the electrode surface without decreasing the electronic conductivity of the electrode. The photocatalytic activity was enhanced by adding a small amount of allophane due to the effective adsorption and degradation relay, which promoted the consumption of holes and suppressed the electron–hole recombination.

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