



Reaction in photofuel cells using allophane–titania nanocomposite electrodes



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ARTICLE INFO

Article history:

Received 2 April 2013

Received in revised form 27 August 2013

Accepted 1 September 2013

Available online 9 September 2013

Keywords:

Photocatalysis

Photofuel cell

Titania

Allophane

Starch

ABSTRACT

Allophane–titania nanocomposite electrodes for photofuel cells were prepared from titanium alkoxide sols dispersing the natural clay mineral allophane. The electrochemical measurements indicated that the oxidative degradation of starch in the solutions and suspensions enhanced the generation of electricity during UV irradiation. CO₂ was observed as the degradation product. A higher photocurrent was observed using the allophane–titania nanocomposite electrode adsorbing a greater amount of the starch molecules. Allophane increased the capacity of the electrode to adsorb the starch molecules, even from the suspensions. This brought the molecules close to the titania nanoparticles, on which their oxidation induced the generation of electricity.

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1. Introduction

The electronic application of photocatalysts is developing in various fields such as photovoltaic cells due to their semiconducting properties. Photocatalyst titania films are widely studied as dye-sensitized solar cell electrodes and are approaching their practical use [1–3]. They are also useful as photofuel cell electrodes to generate electricity assisted by oxidizing the fuel materials during UV irradiation [4–9]. Photofuel cell is based on the mechanism of solar cell, in which the available energy depends on the conduction band potential of the semiconductor. In the solar cells using aqueous electrolyte solutions, electrons are circulated by water splitting and its reverse reaction. Such solar cells exhibit low photoelectric conversion efficiency due to the charge recombination and back electron transfer. The organic compounds added to the electrolyte solutions prevent the backward processes due to efficient consumption of the electrons and holes. Oxidative degradation of fuel materials promotes the electron circulation rather than generates electricity from their combustion energy. 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 [10,11]. A method to

increase the concentration is the use of the appropriate adsorbents.

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 [12–17]. The clay–titania composites are effective in degrading organic compounds [18–22] because the adsorbed molecules should be quickly brought to the titania surface [23]. 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 retention of the semiconductivity and activity.

We previously prepared allophane–titania nanocomposite thin films on the glass plates coated with ITO (Indium Tin Oxide) transparent electrodes as the working electrodes of the photofuel cells by the sol–gel method [24]. 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 brought them close to the titania nanoparticles, on which their oxidation induced the electrogeneration.

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Such liquid phases are required to be highly concentrated solution or suspension of the fuel materials of slightly soluble polymers because the polymers originating from plant wastes are preferred for utilization as the materials. In this study, starch was used as a fuel material in order to evaluate the degradation reaction in its solutions and suspensions as the pre-stage using cellulose compounds. We investigated the photocatalytic oxidative degradation of the starch solutions and suspensions in the photofuel cells using allophane–titania nanocomposite electrodes and their energy conversion properties. The effect of the adsorption ability of allophane on the photofuel cell reactions was also examined.

2. Experimental

2.1. Materials

Ethanol (C_2H_5OH), titanium tetraisopropoxide ($Ti(OCH(CH_3)_2)_4$), nitric acid (HNO_3), hydrochloric acid (HCl), sodium hydroxide ($NaOH$), sodium carbonate (Na_2CO_3), and methylene blue (MB , $C_{16}H_{18}N_3S$) (Wako, S or reagent grade) and starch ($(C_6H_{10}O_5)_n$) (Yoneyama, reagent grade) were used without further purification. The water was deionized and distilled. Glass plates coated with the ITO transparent electrode ($60\text{ mm} \times 25\text{ mm}$) (AGC Fabritec) were soaked in hydrochloric acid (1.0 mol dm^{-3}) for 1 h and then rinsed with water. The allophane ($1.6SiO_2 \cdot Al_2O_3 \cdot 5-6H_2O$) was extracted by elutriation of Kanuma soil from Tochigi, Japan, as previously described [23,25,26].

2.2. Sample preparation

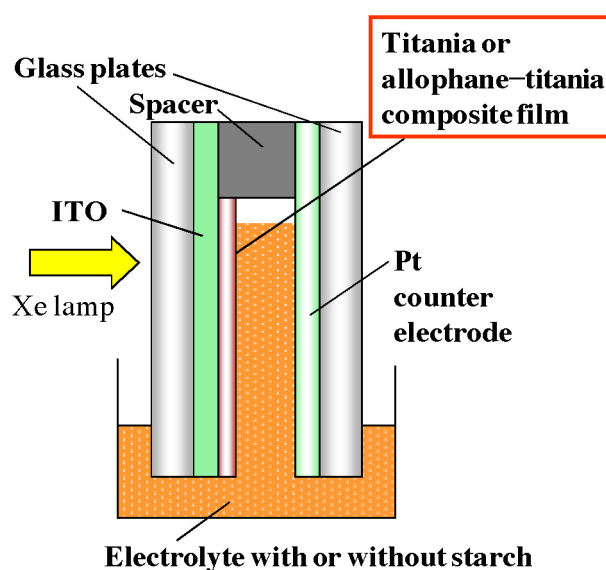
The sol–gel reaction system was prepared by mixing 5.0 cm^3 of titanium tetraisopropoxide, 25.0 cm^3 of ethanol, 0.21 cm^3 of water, and 0.21 cm^3 of concentrated nitric acid as the catalyst for the sol–gel reaction. The allophane was dispersed in the sol–gel systems of titanium tetraisopropoxide in 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. The 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.

The electrolyte solutions or suspensions for the photofuel cell reaction were prepared at 50°C by mixing 0.20 mol dm^{-3} of an aqueous $NaOH$ solution with 0, 0.14, 0.28, 0.42, or 0.56 mol dm^{-3} of starch.

2.3. Measurements

The surface morphology of the electrode samples was observed, and their layer thickness was estimated from their cross section 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 specific surface areas of the flakes of the electrode samples were estimated by the BET (Brunauer–Emmett–Teller) method from the adsorption isotherms of nitrogen gas using a volumetric gas adsorption instrument (BEL Japan, BELSORP-mini). Each flake sample of 5.0 mg was added to 50 cm^3 of an MB aqueous solution ($1.0 \times 10^{-5}\text{ mol dm}^{-3}$) and agitated in the dark for 12 h. It was confirmed that the adsorption of MB was equilibrated. The amount of the MB adsorbed on each sample was estimated from the equilibrium concentration in the MB aqueous solution.

The present photofuel cells consisted of two electrodes and electrolyte as shown in Scheme 1. The electrolyte solutions were



Scheme 1. Structure of the photofuel cell.

allowed to soak into the space between the electrode sample and the counter Pt electrode ($60\text{ mm} \times 25\text{ mm}$). The distance between the two electrodes was adjusted to ca. 1.0 mm using a spacer. The FTIR spectra of the electrolyte solution containing 0.28 mol dm^{-3} of starch were observed as a function of the UV irradiation time using an FTIR spectrophotometer (Shimadzu IRPrestige-21) with an attenuated total reflection (ATR) accessory and a ZnSe prism in order to evaluate the changes in concentrations of the starch and the products. The UV light ($\lambda > 240\text{ nm}$) was obtained from a 150 W Xe short arc lamp (Ushio UXL-155). The area of the irradiated electrode was 10 cm^2 . The produced CO_2 was dissolved as CO_3^{2-} in the present basic solutions. The concentrations of starch and CO_3^{2-} estimated from the absorbance at 1003 and 1418 cm^{-1} of their main bands, which were calibrated using 0.20 mol dm^{-3} of an aqueous $NaOH$ solution with starch and sodium carbonate, respectively.

Monochromatic lights obtained from a fluorescence spectrophotometer (Shimadzu RF-5300) with a 150 W Xe short arc lamp (Ushio UXL-155) were irradiated on the electrodes for the spectroscopic measurements. During light irradiation, the short circuit currents of the electrodes were measured in the electrolyte solutions with and without 0.28 mol dm^{-3} of starch by a digital multimeter (ADCMT 7461A). The I – V curves of the electrodes were measured in the electrolyte solutions with 0 – 0.56 mol dm^{-3} of starch by a potentiostat (Hokuto Denko HSV-100) during irradiation by the 150 W Xe short arc lamp. The area of the irradiated electrode was 0.4 cm^2 . The intensity at each wavelength of the light source was obtained using a power meter (Molelectron PM500A) in order to estimate the energy conversion efficiency in the electrode samples.

The DC electrical resistance of the ITO electrode was measured using the digital multimeter (ADCMT 7461A). The resistivity values for the ITO electrodes unheated and heated at 500°C for 30 min were 2.0×10^{-4} and $4.9 \times 10^{-4}\ \Omega\text{ cm}$, respectively. The resistivity of the heated ITO was low enough to determine the electric properties of the electrode samples.

3. Results and discussion

3.1. Characterization of the electrodes

Fig. S1 shows the SEM images of the surface and cross section of the 1.0% allophane–titania composite film. This film consisted

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