



Research paper

Influence of allophane distribution on photocatalytic activity of allophane–titania composite films



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ABSTRACT

Allophane–titania composite films were prepared from titanium alkoxide sols dispersing the natural clay mineral allophane as a nano-sized adsorbent. The composites of the titania dispersing the allophane particles in the whole film efficiently degraded trichloroethylene and acetaldehyde better than the normal titania and the titania dispersing the allophane only on the film surface. The titania dispersing the allophane particles in the whole film produced lower amounts of the intermediate products in certain stages than the titania. These results are due to the effective reactant transport from the allophane to titania. Photocatalytic degradation of glucose and photoelectrochemical measurements using an electrolyte solution containing glucose indicated that oxidative degradation of the glucose enhanced the generation of electricity during UV irradiation. A higher short circuit current was observed using the film dispersing the allophane on the surface layer with an ca. 50-nm thickness than the titania and those dispersing the allophane only on the film surface. Allophane effectively adsorbed the glucose molecules and transported them to the titania, then the products were desorbed into the liquid phase. Therefore, the holes were efficiently transported and consumed by the glucose oxidation.

1. Introduction

Glasses and ceramics, especially nanocomposites of some inorganic materials, can be prepared from not only homogeneous solutions, but also from heterogeneous systems by the sol-gel method (Brinker and Scherer, 1990). Nanoparticles are hybridized with some host matrices by dispersing them in the starting solutions containing the main materials. The nanocomposites consisting of titania and a natural clay mineral, allophane, were prepared from the titanium alkoxide sols dispersing the allophane nanoparticles (Nishikiori et al., 2011a, 2012b, 2014, 2015a,b). Allophane is a hydrated aluminosilicate ($1-2\text{SiO}_2\cdot\text{Al}_2\text{O}_3\cdot 5-6\text{H}_2\text{O}$) having a 3.5–5.0 nm-sized hollow spherical structure with 0.3–0.5 nm-sized defects on its surface (Hall et al., 1985; Henmi and Wada, 1976; Kitagawa, 1971; van der Gaast et al., 1985; Wada and Wada, 1977). The walls of the hollow spheres consist of inner silica and outer alumina layers with a hydroxylated or hydrated surface. Some studies suggest that these surfaces have a significant ability to adsorb ionic or polar pollutants due to their amphoteric ion-exchange activity and high surface area (Hall et al., 1985; Kitagawa, 1971;

Hanudin et al., 1999). Allophane is convenient for dispersing in some host materials because it consists of the smallest structural units of all the clay minerals. There is a possibility that the high dispersion of allophane nanoparticles on a photocatalyst surface allows retention of the semiconductivity and activity.

In our previous study, the allophane–titania nanocomposites were prepared as effective photocatalysts because the allophane can efficiently adsorb the polar organic molecules on the nanoparticle surface (Nishikiori et al., 2011a, 2012b, 2014, 2015b). The nanocomposites can be effective in degrading organic compounds if the adsorbed molecules are quickly brought to the titania surface. During the photocatalytic degradation of trichloroethylene (TCE) using the allophane-titania nanocomposite, emission of the intermediate product, phosgene, was drastically inhibited (Nishikiori et al., 2011a, 2015b). The allophane–titania nanocomposite electrodes for photofuel cells were also prepared (Nishikiori et al., 2012b, 2014). Photofuel cells, which are based on the mechanism of a photoelectrochemical cell, generate electricity assisted by oxidizing the fuel during UV irradiation (Antoniadou and Lianos, 2010; Antoniadou et al., 2010; Kaneko et al., 2006; Ueno et al., 2009).

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The photofuel cell electrodes generally act in the liquid phase containing the fuel. In such systems, the concentration of the fuel on the photocatalyst surface is one of the important parameters for improving the energy conversion efficiency (Nishikiori et al., 2011b, 2012a). The electrochemical measurements indicated that the oxidative degradation of glucose and starch in the solutions or dispersions enhanced the generation of electricity during UV irradiation. A higher photocurrent was observed using the allophane–titania nanocomposite electrode adsorbing a higher amount of the molecules.

The distribution of the allophane particles into the composite film is important for the accessibility and photocatalytic performance. When the allophane particles are dispersed in the whole film, a significant amount of the reactant molecules can be adsorbed, but this inhibits the photocatalytic activity. One of the reactants, oxygen, should also easily diffuse deep inside the film. The allophane particles should be dispersed only in the layer near the surface.

In this study, we investigated the influence of the allophane distribution in the allophane–titania composite film on its photocatalytic activity. The accessibility and activity of the porous composite for the organic molecules was discussed.

2. Experimental

2.1. Materials

Ethanol ($\text{C}_2\text{H}_5\text{OH}$), titanium tetraisopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$), nitric acid (HNO_3), hydrochloric acid (HCl), sodium hydroxide (NaOH), TCE (CHClCCl_2), acetaldehyde (CH_3CHO), and glucose ($\text{C}_6\text{H}_{10}\text{O}_6$) (Wako, S or reagent grade) were used without further purification. The water was deionized and distilled. Macroporous Si/SiC filter blocks (Tani, 2005) (1.5 g, 30 mm \times 3.0 mm \times 1.5 mm) (Nippon Pillar Packing) and glass plates coated with the ITO transparent electrode (60 mm \times 25 mm) (AGC Fabritec) were soaked in hydrochloric acid (1.0 mol dm^{-3}) for 1 h, then rinsed with water. The allophane ($1.6\text{SiO}_2\cdot\text{Al}_2\text{O}_3\cdot 5\text{--}6\text{H}_2\text{O}$) was extracted by elutriation of Kanuma soil from Tochigi, Japan, as previously described (Nishikiori et al., 2009, 2010). The specific surface area, total pore volume, and average pore diameter of the allophane were determined to be $320 \text{ m}^2 \text{ g}^{-1}$, $0.34 \text{ cm}^3 \text{ g}^{-1}$, and 4.2 nm using a volumetric adsorption measurement instrument (BEL Japan, BELSORP-mini), respectively.

2.2. Sample preparation

The sol–gel reaction system A0-1 was prepared by mixing 5.1 cm^3 of titanium tetraisopropoxide, 30.0 cm^3 of ethanol, and 0.15 cm^3 of concentrated nitric acid as the catalyst for the sol–gel reaction. The allophane was dispersed in the sol – gel systems A0 in which the Al/(Al + Ti) ratios were 1/1000. The sol–gel system with the allophane was labeled A01-1. The systems A0-1 and A01-1 were agitated and allowed to react during ultrasonication for 24 h, in which the macroporous Si/SiC filter blocks were immersed. The filter blocks were withdrawn, then heated at 500°C for 3 h in order to prepare the titania-coated sample (Block A0) and 0.10% allophane–titania composite-coated sample (Block A01).

The allophane powder, 15 mg, was dispersed in 35.3 cm^3 of water during ultrasonication for 24 h. The block coated with the system A0 as already described was immersed in an aqueous dispersion containing the allophane, withdrawn, then heated at 500°C for 3 h in order to prepare the titania-coated sample supporting the allophane particles on the surface (Block A01s). The net weight of the titania and allophane–titania composites were $75 \pm 5 \text{ mg}$.

The sol–gel reaction system A0-2 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 system A0-2 in which the Al/(Al + Ti) ratio was 1/1000. The sol–gel system with

allophane was labeled A01-2. The systems A0-2 and A01-2 were agitated and allowed to react during ultrasonication for 24 h. The glass plates with the ITO transparent electrode were dip-coated six times with the system A0-2, then heated at 500°C for 30 min in order to prepare the titania electrode (Electrode T6). The ITO electrodes were also coated with the system A0-2 three, four, and five times, then with the system A01-2 three, two, and one times, which were labeled Electrodes T3-A3, T4-A2, T5-A1, respectively.

Electrode T6 was immersed in the aqueous dispersion containing the allophane, withdrawn, then heated at 500°C for 30 min in order to prepare the titania-coated electrode supporting the allophane particles on the surface (Electrode T6-A).

The electrolyte solutions for the photofuel cell reaction were prepared by mixing 0.20 mol dm^{-3} of an aqueous NaOH solution with and without 0.28 mol dm^{-3} of glucose.

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 SU8000). The crystalline phase was determined by an X-ray diffractometer (Rigaku SmartLab) during $\text{CuK}\alpha$ irradiation.

The elemental ratios of Al and Ti to the whole samples were obtained by inductively coupled plasma emission analysis of their solutions prepared with hydrofluoric acid, nitric acid, and sulfuric acid using an ICP emission spectrometer (Shimadzu ICPS-8000).

The samples were placed in an infrared cell made of Pyrex glass with KBr single crystals. The TCE and acetaldehyde gases diluted with dry air were injected into the infrared cell in which its concentration was 2.0×10^{-4} and $2.8 \times 10^{-4} \text{ mol dm}^{-3}$, respectively. The cell was maintained at ambient temperature until the adsorption of TCE was equilibrated for 600 min. The degradation reaction of the TCE was carried out in the cell by near-UV light irradiation using two 4-W black light bulbs (Toshiba FL4BLB) and two 10-W black light bulbs (NEC FL10BL-B) at ambient temperature. The FTIR spectra of the gas phase were observed as a function of the UV irradiation time using an FTIR spectrophotometer (Shimadzu IRPrestige-21) in order to examine the changes in the concentrations of the TCE and products (Nishikiori et al., 2011a).

The present photofuel cells consisted of two electrodes and electrolyte. The electrolyte solutions were allowed to soak into the space between the electrode sample and the counter Pt electrode (60 mm \times 25 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} glucose 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 the concentrations of the glucose 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 .

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} glucose by a digital multimeter (ADCMT 7461A). 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.

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