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Research paper

Photoelectrochemical properties of dye-dispersing allophane–titania composite electrodes

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ABSTRACT

Dye-dispersing allophane–titania composite electrodes were prepared from titanium alkoxide sols containing dye and allophane. The photoelectric conversion properties of the electrodes were investigated by photoelectrochemical measurements. The photocurrent values in the UV range decreased with an increase in the allophane content, whereas those in the visible range were increased by adding 1.0% (Al/Ti ratio) allophane. As a small amount of allophane nanoparticles were highly dispersed in the titania electrodes, the dye molecules were dispersed in the electrodes without decreasing the efficiency of the electron injection from the dye to the titania conduction band. The dye molecules dispersed on the titania nanoparticle surface were capped with allophane nanoparticles which prevented desorption. The dye molecules strongly interacted with the titania nanoparticle surface and efficiently injected the excited electrons into the titania conduction band.

1. Introduction

Adsorption is important for a photocatalytic reaction process involving direct oxidation and reduction by the photogenerated holes and electrons. Natural clay minerals have attracted considerable attention as unique and functional adsorbents (Xu et al., 1998; Bergaya et al., 2006; Cea et al., 2007). The clay−titania composites were studied for the effective adsorption and degradation of organic compounds (Yoneyama et al., 1989; Kitayama et al., 1998; Tao et al., 1999; Suárez et al., 2008; Hewer et al., 2009). Allophane, a natural clay mineral distributed throughout the world, is a hydrated aluminosilicate ($1-2SiO_2 \cdot Al_2O_3 \cdot 5-6H_2O$) having a 3.5−5.0 nm-sized hollow spherical structure with 0.3−0.5 nm-sized defects on its surface (Kitagawa, 1971; Henmi and Wada, 1976; Wada and Wada, 1977; Hall et al., 1985; van der Gaast et al., 1985). 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 (Kitagawa, 1971; Hall et al., 1985; Hanudin et al., 1999). Allophane consists of the smallest structural units of all the clay minerals. The clay–titania composites can be effective in degrading organic compounds if the adsorbed molecules are quickly brought to the titania surface. However, hybridization of the 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.

In our previous study, a highly adsorptive allophane−titania nanocomposite photocatalyst was prepared by dispersing allophane nanoparticles into the titania by the sol–gel method (Nishikiori et al., 2011a). During the photocatalytic degradation of trichloroethylene using the allophane−titania nanocomposite, emission of the intermediate product, phosgene, was drastically inhibited. These compounds were rapidly adsorbed on the allophane, then gradually degraded after diffusing to the titania.

The electronic application of photocatalysts is being developed 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 (Grätzel, 2003). They are also useful as photofuel cell electrodes to generate electricity assisted by oxidizing the fuel materials during UV irradiation (Kaneko et al., 2006; Ueno et al., 2009; Antoniadou and Lianos, 2010; Antoniadou et al., 2010). The organic compounds added to the electrolyte solutions prevent the backward processes due to efficient consumption of the electrons and holes. In such systems, the concentration of the fuel material on the photocatalyst surface is one of the variables for improving the energy conversion efficiency (Nishikiori et al., 2011b, 2012a). A method to increase the concentration is the use of the appropriate adsorbents. Actually, a higher short circuit current was observed in a photofuel cell using the 0.10% allophane-containing titania electrode than that with the normal titania electrode (Nishikiori et al., 2012b, 2014a). Allophane effectively adsorbed the

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glucose and starch molecules and then brought them close to the titania nanoparticles, on which their oxidation induced the electrogeneration.

The sol–gel reaction using a titanium alkoxide sol containing the dye molecules without heating easily allows the formation of the dye-dispersing titania films, which are amorphous or nanocrystalline (Dislich, 1971; Dislich, 1983; Brinker and Scherer, 1990; Brinker et al., 1991a, 1991b). In such systems, the dye molecules can be highly dispersed on the surface of the individual titania nanoparticles without their aggregation. The dye–titania electronic interaction is very important for the electron injection process in the photovoltaic materials such as the dye-sensitized solar cells (Grätzel, 2003; El Mekkawi and Abdel-Mottaleb, 2005; Sharma et al., 2009). The functional groups were induced in the sensitized dye molecules in order to form a strong bond between the dye chromophore and the titania surface (Hilgendorff and Sundström, 1998; Ramakrishna and Ghosh, 2001; El Mekkawi and Abdel-Mottaleb, 2005). Each molecule prefers to be strongly bonded to the titania surface for an efficient electron injection and reducing the energy transfer between the molecules which form the aggregates.

In such systems, a significant number of dye molecules prefer to be highly dispersed on the individual titania nanoparticles. Allophane is expected to increase the number of dye molecules due to its high adsorption ability. In this study, the dye-dispersing allophane–titania composite electrodes were prepared from titanium alkoxide sols containing the dye and allophane. A fluorescein dye, which has been used in our systematic study of dye-dispersing titania electrodes, was used as a sensitizer. The dye–titania interaction and photoinduced electron transfer can be evaluated by photocurrent measurements as previously reported (Nishikiori et al., 2011c, 2012c, 2014b; Setiawan et al., 2013). The spectroscopic and photoelectric conversion properties of the dye-dispersing allophane–titania composite electrodes were investigated in order to clarify the influences of the dye and allophane dispersion on the electron transfer properties.

2. Experimental

2.1. Materials

Fluorescein, ethanol, titanium tetraisopropoxide, nitric acid, hydrochloric acid, diethylene glycol, iodine, and lithium iodide (Wako, S or reagent grade) were used without further purification. The water was deionized and distilled. Glass plates coated with the indium tin oxide (ITO) transparent electrode (60 mm × 25 mm) (AGC Fabritec) were soaked in hydrochloric acid (1.0 mol dm^{-3}) for 1 h, then rinsed with water. The electrolyte for the photoelectric measurement consisted of a diethylene glycol solution of iodine (5.0×10^{-2} mol dm^{-3}) and lithium iodide (0.50 mol dm^{-3}). 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 previously described (Nishikiori et al., 2009, 2010).

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 and labeled S0. The concentration of nitric acid was 7.5×10^{-2} mol dm^{-3} in the S0. Fluorescein was dissolved in the S0 at a concentration of 1.0×10^{-2} mol dm^{-3}, which was labeled S0-f. The allophane was dispersed in the S0 and S0-f in which the Al/(Al + Ti) ratios were 0 (0% allophane), 1/1000 (0.10% allophane), 1/100 (1.0% allophane), and 1/10 (10% allophane). The sol–gel systems with and without fluorescein and/or allophane were agitated and allowed to react during ultrasonication for 1 day. The glass plates with the ITO transparent electrode were dip-coated 3 times with the S0 and then heated at 500 °C for 30 min in order to prepare the anatase-type titania electrodes. This layer plays the role as a blocking layer in order to suppress the charge recombination at the interface between the upper layer and the ITO layer (Cameron and Peter, 2003; Hart et al., 2006; Patrocinio et al., 2009). These electrodes were dip-coated 5 times with the S0 containing 0%, 0.10%, 1.0%, and 10% allophane and then steam-treated at 100 °C for 120 min. The dye-free electrodes were immersed in fluorescein ethanol solution at a concentration of 1.0×10^{-3} mol dm^{-3} for 24 h in order to prepare the dye-adsorbing allophane–titania composite electrodes. On the other hand, the titania-based electrodes were dip-coated 5 times with the S0-f containing 0%, 0.10%, 1.0%, and 10% allophanes and then steam-treated at 100 °C for 120 min in order to prepare the dye-dispersing allophane–titania composite electrodes. The glass plates without the ITO were also coated with the sols in order to measure the XRD patterns.

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 crystalline phase was determined using an X-ray diffractometer (Rigaku RINT-2200 V). The flakes of the film and powder samples were pressed in KBr pellets and their IR spectra were obtained using an FTIR spectrophotometer (Shimadzu FTIR-8300).

The iodine-based electrolyte was allowed to soak into the space between the electrode sample and the Pt counter-electrode. Monochromatic light from a fluorescence spectrophotometer (Shimazdu RF-5300) with a 150 W Xe short arc lamp (Ushio UXL-155) was irradiated on the electrodes for the spectroscopic measurements. During the light irradiation, the short circuit currents of the electrodes were measured in the electrolyte solutions by a digital multimeter (ADCMT 7461A). The *J*–*V* curves of the electrodes were measured by a potentiostat (Hokuto Denko HSV-100) during the visible light (0.40 W cm^{-2}) irradiation at a wavelength longer than 400 nm emitted by the 150 W Xe short arc lamp using a sharp cutoff filter. The intensity at each wavelength of the light source was obtained using a power meter (Molectron PM500A) in order to estimate the incident photon-to-current conversion efficiency (IPCE) and quantum efficiency for the photocurrent from the excited ligands, i.e., absorbed photon-to-current quantum efficiency (APCE), in the electrode samples. The visible absorbance of the present electrode samples was lower than 1.0 which was sufficient to measure the number of absorbed photons in order to calculate the quantum efficiency.

3. Results and discussion

3.1. Characterization of the electrodes

Fig. 1 shows the SEM images of the surface of the dye-dispersing titania and allophane–titania composite electrodes. The films consist of 10–30-nm-sized particles regardless of the allophane content and cannot be distinguished because the allophane particles are very small (Nishikiori et al., 2011a). The thickness of the titania layer was ca. 400 nm as previously reported. The TEM image of the 1.0% allophane–titania composite powder was previously reported (Nishikiori et al., 2012b, 2014a). 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 amorphous particles of allophane were dispersed on the titania particle surface. The allophane particles were tightly attached to the titania surface.

Fig. 2 shows the XRD patterns of the dye-dispersing titania and allophane–titania composite films. The peaks at around 25.3°, 37.8°, and 48.1° are assigned to the (101), (004), and (200) planes of the anatase-type titania in all the films, respectively. Their crystallite size was estimated from the full-width at half-maximum of the 25.3° peak using Sherrer's equation to be 8.2 nm for the titania, 8.1 nm for the