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Separate-type Pt-free photofuel cell based on a visible light-responsive TiO_2 photoanode: Effect of hydrofluoric acid treatment of the photoanode

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ABSTRACT

The present study deals with the effect of a hydrofluoric acid (HF) treatment of visible light-responsive TiO_2 (Vis-TiO_2) thin film photocatalysts on their photoelectrochemical performances. The Vis-TiO_2 thin film photocatalysts have been prepared on Ti metal substrates by a magnetron sputtering deposition method and then treated by an HF solution. The HF treatment of Vis-TiO_2 thin film photocatalysts leads to the dramatic enhancement of their photoelectrochemical performances under UV light and visible light irradiation. Moreover, separate-type Pt-free photofuel cells (SPFCs) constructed using the Vis-TiO_2 thin films as photoanodes can generate electricity under light irradiation and simultaneously decompose methanol. The SPFC based on the Vis-TiO_2 thin film photoanode etched by HF solution shows the enhanced cell performances with two times higher short-circuit current density and higher energy conversion efficiency than that based on the untreated Vis-TiO_2 thin film photoanode. In addition to the increase of surface area and surface roughness, the enhanced conductivity by HF treatment, which is confirmed by Mott–Schottky analyses, is found to be responsible for improvement of cell performances of the SPFC.

1. Introduction

The depletion of fossil fuels and the environmental pollution have stimulated the research on the development of new energy production technologies from clean and renewable resources. The utilization of biomass as a carbon-neutral feedstock is one of the most promising methodologies and has rapidly expanded all over the world. In 2008, a total quantity of biomass produced in entire world accounted for 9.7% of global primary energy supply [1]. However, other economic and environmental problems, such as food price rises and deforestation, are caused by the fact that most of the currently-used biomass fuels are made from foods as typified by sugar cane and corn. In this context, strongly desired is the utilization of biomass derived from wastes.

The photofuel cell (PFC) that can photodecompose various water-soluble organic compounds and simultaneously generate electricity, reported by Kaneko et al. [2,3], will present a reasonable solution in the field of biomass utilization for energy production. This epoch-making device comprises a nanoporous TiO_2 thin film photoanode and a Pt cathode for O_2 reduction and operates by merely irradiating with UV light in the presence of biomass derivatives as fuels. Although this device has these favorable characteristics, there are still areas that need improvement: (i) the extension of usable light wavelengths in the TiO_2 photoanode, (ii) the development of new cathode electrodes alternative to expensive Pt and (iii) the decrease in the activation energy for the reduction reaction at the cathode.

In these lines, we have developed and reported a separate-type Pt-free photofuel cell (SPFC), in which two different electrolytes containing various biomass derivatives and an iodine redox solution are used in the respective separated anode and cathode compartments [4]. The iodine redox solution added into the cathode electrolyte promotes the reduction reaction at the cathode and enables us to use a carbon electrode as the cathode alternative to costly Pt due to the lower activation energy for the I_3^- reduction than that for O_2 reduction. Moreover, as for the photoanode in the SPFC, the use of a visible light-responsive TiO_2 (Vis-TiO_2) thin film photocatalyst that is prepared by a radio-frequency magnetron sputtering deposition (RF-MS) [5–7] allows for the efficient utilization of solar light.

For further improvement of photovoltaic performances of the SPFC, surface treatments of Vis-TiO_2 thin film photoanodes enabling to increase the surface area and surface roughness and to modify the surface characteristics are considered to be helpful techniques. Until now, various surface treatments of photocatalysts,

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including hydrothermal treatment [8–10], anodization [11,12] and chemical etching [13–16], have been attempted and proven to improve their photocatalytic activities. Among those, chemical etching employing hydrofluoric acid (HF) solution at room-temperature was reported to permit the fine tuning of surface morphology of TiO_2 particles through the selective dissolution of anatase TiO_2 moieties rather than rutile ones [14].

Herein, the effect of HF etching on photoelectrochemical performances of the Vis-TiO_2 thin film photoanode was investigated. The SPFC based on the Vis-TiO_2 thin film photoanode treated by HF solution was subsequently constructed, and its cell performance was evaluated in the presence of methanol fuel as a model organic compound. Furthermore, factors affecting the cell performances of SPFCs were revealed through Kr adsorption measurements, FE-SEM observations, XPS measurements and Mott–Schottky analyses.

2. Experimental

2.1. Synthesis of Vis-TiO_2 thin film

The Vis-TiO_2 thin film was prepared on a Ti foil substrate by an RF–MS method using O-NARU Tech N-SP-12 according to the working conditions described in our previous literature [5–7]. In the deposition, a TiO_2 plate (High Purity Chemicals Lab., Corp., Grade: 99.99%) and Ar gas (99.995%) were employed as the target material and sputtering gas, respectively. The substrate was placed parallel to the sputtering target with a substrate–target distance of 75 mm. The base pressure in the sputtering chamber was set at 6.0×10^{-4} Pa and the working pressure was 2.0 Pa. The deposition of the Vis-TiO_2 thin film was performed at a substrate temperature (T_s) of 873 K and an RF power of 300 W. The film thickness of Vis-TiO_2 was determined to be 3.0 μm using scanning electron microscopy.

2.2. HF treatment of Vis-TiO_2 thin film

The prepared Vis-TiO_2 thin film was then subject to an HF treatment. The thin-film sample was immersed into a 0.045% HF aqueous solution at room-temperature. The HF treatment time was varied from 15 to 180 min. After HF treatment, the samples were washed with deionized water and dried at 373 K for 1 h. Herein, the thus-obtained Vis-TiO_2 thin films are referred to as HF(X)-Vis-TiO_2 (X = HF treatment time).

2.3. General methods

UV–vis absorption spectra were recorded with a Shimadzu UV–vis recording spectrophotometer 2200A in a transmission mode. X-ray diffraction (XRD) data were obtained by a Shimadzu X-ray diffractmeter XRD-6100 using Cu Kα radiation (λ = 1.5406 Å). Kr adsorption measurements were performed using BELSORP TCV (BEL Japan, Inc.) at 77 K. The samples (5 mm × 20 mm) were degassed under vacuum at 373 K for 12 h prior to data collection. The BET (Brunauer–Emmett–Teller) method was applied to determine the surface areas. Field emission scanning electron microscopy (FE-SEM) images were obtained by a Hitachi S-4500. X-ray photoelectron spectroscopy (XPS) data were recorded on a Shimadzu ESCA-3200.

2.4. Photoelectrochemical and electrochemical measurements

The photoelectrochemical properties were investigated by an HZ3000 potentiostat (Hokuto Denko Corp.) equipped with a three-electrode cell that consists of a TiO_2 thin film electrode (Vis-TiO_2 thin film or HF(X)-Vis-TiO_2 thin film deposited on a Ti foil substrate), a Pt electrode and a saturated calomel electrode (SCE) as the working, counter and reference electrodes, respectively. The electrolyte was a 0.1 M $HClO_4$ aq. with or without various concentrations of methanol. The electrolyte solution was mechanically stirred and degassed by purging with 99.99% pure Ar gas before and during the experiment. The light irradiation was carried out with a 500 W Xe arc lamp (Ushio Inc.) equipped with an appropriate cutoff filter. The working electrode area was fixed at 2.0 cm^2.

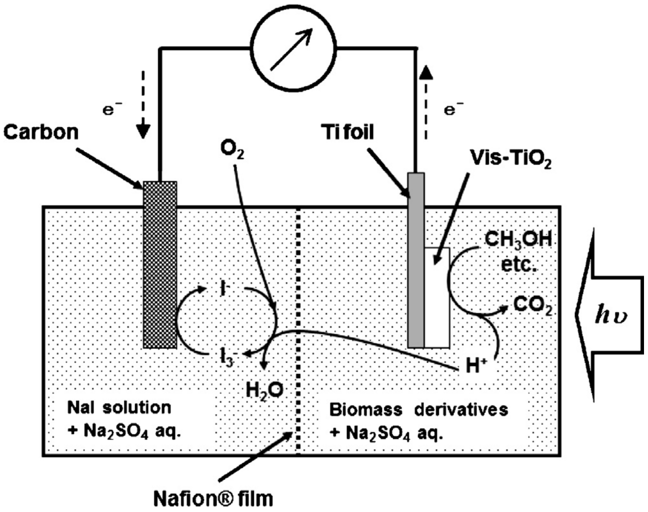

Fig. 1. A scheme of electric power generation by using a separate type photofuel cell (SPFC).

The electrochemical experiments were carried out by using the above-mentioned three-electrode system at room-temperature in the dark. The employed electrolyte was 0.25 M K_2SO_4 aq. (pH 6.7). To investigate the change of the surface charge distribution of thin films before and after the HF treatment, chronoamperometry was measured [17]. Firstly, thin-film samples were polarized at +1.0 V vs SCE for 5 min, and subsequently, the potential was shifted to the prescribed value (−0.4 to +0.4 V vs SCE).

2.5. Evaluation of photovoltaic performances of SPFCs

The photovoltaic performances of SPFCs were evaluated under light irradiation from a 500 W Xe arc lamp. The configuration diagram of SPFCs is shown in Fig. 1. A Pyrex glass container (L 35 mm × W 70 mm × H 60 mm) was divided by a proton exchange membrane (Nafion® film) into two compartments for anode and cathode reactions. The HF(60)-Vis-TiO_2 thin film or Vis-TiO_2 thin film deposited on a Ti foil substrate as the anode electrode was immersed into 0.50 M Na_2SO_4 aq. containing methanol as fuel. These thin films were insulated by epoxy resin except for the reaction area (1.0 cm^2). The carbon as the cathode electrode was immersed into 0.50 M Na_2SO_4 aq. containing 0.50 M NaI aqueous solution or containing 0.50 M NaI and 0.025 M I_2 aqueous solution. The pH of anode and cathode electrolytes was adjusted to 2 by adding 1.0 M H_2SO_4 aq. The photocurrent–voltage (I–V) curves for the constructed SPFCs were recorded with an HZ3000 potentiostat under gentle stirring. The light irradiation was carried out with a 500 W Xe arc lamp adjusted to the light intensity of about 100 mW cm^{-2} through a water filter. The anode electrolyte was degassed by purging with 99.99% pure Ar gas before and during the experiment.

3. Results and discussion

3.1. Effect of HF treatment of Vis-TiO_2 thin film

The effect of the treatment time in HF solution on the photocurrent for the Vis-TiO_2 thin film was investigated by