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Photoelectrochemical reaction of biomass and bio-related compounds with nanoporous TiO_2 film photoanode and O_2-reducing cathode

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Abstract

Photoelectrochemical decomposition of many biomass and related compounds with a nanoporous TiO_2 film photoanode and an O_2-reducing cathode was successfully achieved to generate photocurrents. As long as the compound is either liquid or soluble (or solubilized) in water, it was able to be photodecomposed including even polymeric compound to produce electricity. Not only biomass (such as polysaccharides, proteins, cellulose, lignin, etc.) and bio-related materials (methanol, ethanol, glucose, amino acids, ammonia, urea, etc.), but also other electron-donating compounds, even synthetic polymers, could be photodecomposed generating electricity. The compounds underwent almost complete mineralization, i.e., they decomposed almost completely to produce either CO_2 from carbon compounds or dinitrogen (N_2) from nitrogen compounds such as ammonia. It was estimated that about 78% energy of the compound is converted to electrical energy in a maximum case. A photofuel cell (PFC) was proposed and thus proved that can use varieties of biomass and bio-related compounds including other organic compounds as a direct fuel to generate electricity by using photocatalytic oxidation at a nanoporous TiO_2 film photoanode and an O_2-reducing cathode.

Keywords: Nanoporous titanium dioxide film; Biomass; Bio-related compounds; Photofuel cell; Organic compounds

1. Introduction

Photoelectrochemical reactions at semiconductor electrodes was investigated from 1960s [1], and the famous work on a crystalline n-TiO_2 photoanode to photodecompose water by UV light evoked great attention in the related area [2]. Some organic compounds have also been photodecomposed by using crystalline TiO_2 photoanodes [3,4]. For these crystalline n-TiO_2 photoanode the semiconductor forms a kind of Schottky junction (called a liquid junction) at the TiO_2/aqueous electrolyte interface, the photogenerated holes oxidize water or organic compound on the TiO_2 surface, and the photogenerated electrons reduce protons to produce H_2 at a counter electrode (often Pt). In the beginning of 1990's, a nanoporous TiO_2 thin film was successfully applied to fabricate a dye-sensitized solar cell (DSSC) [5], and the cell is now investigated in many countries towards commercialization. In this DSSC, the TiO_2 film works as an electron acceptor for the photoexcited dye compound and at the same time as an electron-conducting material, rather than working as a liquid junction device. The photoreactivity of a nanoporous TiO_2 film itself besides the dye-sensitized system is an interesting and important issue towards future applications, but this subject is open to further investigation.

Biomass and bio-related compounds are attracting a great deal of attention to use as a renewable energy resource for reducing carbon dioxide (CO_2) emission, but their energy conversion into practical energy requires still elegant design

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and investigations. As one of the candidates for such energy conversion, the present authors are interested in direct photoelectrochemical energy conversion of biomass and bio-related compounds into electrical energy by utilizing its oxidation by O_2 which is an exo-energetic process. For this purpose, it is important not only to photodecompose the compounds at a semiconductor photoanode surface, but also to reduce O_2 at a counter cathode electrode to generate electricity instead of reducing protons into H_2 there.

In the present communication, it will be reported that many biomass and bio-related compounds including polymeric compounds such as polysaccharides, proteins, cellulose, lignin, saccharides, amino acids, alcohols, ammonia, urea, etc. can be decomposed photoelectrochemically to generate electricity by using a simple system composed of nanoporous TiO_2 film photoanode and an O_2-reducing cathode as long as the compounds are either liquid or prepared as an aqueous solution. Such a photoelectrochemical cell generating photocurrents could be called a photofuel cell (PFC) whose characteristics for these compounds will also be reported.

2. Experimental

2.1. Materials

A nanoporous TiO_2 film was prepared as follows. 12 g TiO_2 (P-25, received from Japan Aerosil Co. Ltd.) and acetylacetone (0.4 ml) were mixed well in a mortar while adding 4 ml water slowly during 2 h. Triton X-100 (0.2 ml) detergent was added and further mixed well with the TiO_2 slurry, and then the mixture was sonicated. This mixture was spin-coated (2000 rpm) on a FTO (fluorine-doped conducting glass) electrode (2 cm × 1 cm) for about 10 s to obtain 1 cm × 1 cm area of a nanoporous TiO_2 film, and the film was dried at 100 °C for 30 min. This procedure was repeated until the film thickness becomes 10 μm, and then the film was calcinated at 450 °C for 30 min.

2.2. Measurements

As an example ammonia was used as the compound photodecomposed by a nanoporous TiO_2 film photoanode. Cyclic voltammogram (CV) was measured as follows. The TiO_2 film electrode (1 cm × 1 cm), a Pt-black coated Pt plate cathode (1 cm × 1 cm), and a Ag–AgCl reference electrode were soaked in a 5 ml of 10 M NH_3 aqueous solution (pH 12) in a 10 ml cylindrical cell containing also 0.1 M Na_2SO_4 electrolyte. O_2 gas was bubbled into the water for 30 min to substitute the air with O_2. The TiO_2 film was irradiated with a 500 W xenon lamp through an IR-cutoff filter (IRA-25S) (light intensity 503 mW cm^{-2}). The gases (N_2, H_2 and O_2) evolved were analyzed by a gas chromatograph (Shimadzu, GC2014) with a 5A molecular sieve column at 40 °C using argon carrier gas. CO_2 was analyzed with a silica gel column. All the photoelectrochemical reactions were performed at 25 °C.

The *I–V* characteristics of the photofuel cell (PFC) were measured by a two electrodes system, i.e., with a nanoporous TiO_2 photoanode and a Pt plate cathode soaked in an aqueous solution of the fuel compound at 25 °C.

3. Results and discussion

A direct ammonia fuel cell is now attracting attention to use as a mediator for a fuel cell, but the currents produced by a direct ammonia fuel cell (under room temperature) have been in a low level of around 30 μA cm^{-2} [6a]. Recently, high current density was achieved by a direct ammonia fuel cell using ammonia gas and proton conducting $BaCeO_3$ solid electrolyte doped with gadolinium and praseodymium, but under high temperature (700 °C). It will at first be shown that an ammonia (NH_3) aqueous solution can be photodecomposed under room temperature by the nanoporous TiO_2 film photoanode in combination with an O_2-reducing Pt cathode to generate electricity.

The cyclic voltammogram (CV) at a fluorine-doped conducting glass electrode (FTO)/nanoporous TiO_2 film photoanode in a 10 M NH_3 aqueous solution (pH 12) in the dark and under irradiation under 1 atm O_2 atmosphere at 25 °C are shown in Fig. 1(a). Although the CV curves both under dark and illumination changed gradually with time, they tended to reach a constant value, and the CV under illumination exhibited clear photoanodic currents. The CV curves showed some hysteresis, i.e., the magnitude of the photocurrents in the anodic and cathodic scans are different, which could be ascribed to some slow step among the photoelectrochemical processes probably due to a multi-electron nature either of the decomposition of ammonia to N_2 (Eq. (1)) or O_2 reduction.

$$2NH_3 \rightarrow N_2 + 6H^+ + 6e^- \quad (1)$$

The characteristics of an ammonia direct PFC (APFC) with this FTO/TiO_2 photoanode and Pt-black/Pt cathode under 1 atm O_2 atmosphere is shown in Fig. 1(b), giving under the present non-optimized cell conditions open circuit photovoltage (V_{oc}) 0.84 V, short circuit photocurrent density (J_{sc}) 0.53 mA cm^{-2}, fill factor (FF) 0.63, where FF is the ratio of a real maximum electric power output per theoretical maximum power output ($= V_{ox} \times J_{sc}$) estimated from the *J–V* curve (Fig. 1(b)) under irradiation. Under the present non-optimized conditions, the incident photon-to-current conversion efficiency (IPCE) of the APFC (Fig. 1(b)) was 19% based on the incident monochromatic light at 340 nm (intensity, 1.47 mW cm^{-2}). It should be noted here that the characteristics of the N_2/H_2 producing system reported earlier by our group [7] as a photoelectrochemical cell operated under Ar atmosphere was very poor as a photocell in comparison to the present PFC operated under O_2 atmosphere since the theoretical maximum cell voltage is only 0.06 V for the N_2/H_2 producing system calculated based on the conduction band edge (E_{CB}) of the TiO_2 (−0.77 V vs. SHE at pH 12, as estimated