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Visible-light Operated Biomass-oxygen Biofuel Cell

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The visible light-operated starch-O_2 biofuel cell consisting of chlorophyll derivative, chlorin-e_6 (Chl-e_6) adsorbed on nanocrystalline TiO_2 layer coated onto optical transparent conductive glass electrode (OTE) as an anode, billirubin oxidase (BOD) immobilized OTE as a cathode, and the fuel solution containing starch as a polysaccharide biomass, glucoamylase, glucose dehydrogenase (GDH) and NAD^+ is studied as a new type of biofuel cell. The short-circuit photocurrent (I_{SC}) and the open-circuit photovoltage (V_{OC}) of this cell are 6.0 μA cm^{-2} and 530 mV, respectively. The fill factor of this cell is estimated to be 35 %. The maximum power output is calculated to be 1.6 μWcm^{-2}. Thus, a new type of visible light-operated starch -O_2 biofuel cell with the visible photosensitization of Chl-e_6 molecules on nanocrystalline TiO_2 film electrode and BOD immobilized OTE is accomplished. The advantage of this biofuel cell is to use BOD immobilized OTE instead of the platinum electrode. We opened a new avenue in the development of the biofuel cell that did not depend on platinum.

1 Introduction

Energy utilization of the biomass resources is important in the environmental science and the development of energy source research fields [1]. Biofuel cells using biomass have been attracted much attention in recent years. By developing these photoinduced hydrogen production systems in a photoelectrochemical conversion system, a new type of photo-operated saccharide-O_2 biofuel cell can be developed. We previously reported the photo-operated biofuel cell using chlorophyll derivative adsorbed on nanocrystalline TiO_2 layer coated onto optical transparent conductive glass electrode (OTE) as an anode, platinum-coated OTE as a cathode, and the solution containing glucose, glucose dehydrogenase (GDH) and NAD^+ as a fuel [2-5]. In the view point of biomass utilization, however, the development of photo-operated biofuel cell using oligo- and polysaccaride is desirable.

In this paper, we describe the visible light-operated starch-O_2 biofuel cell consisting of chlorin-e_6 (Chl-e_6) adsorbed on nanocrystalline TiO_2 layer coated onto optical transparent conductive glass electrode (OTE) as an anode, billirubin oxidase (BOD) immobilized OTE as a cathode, and the solution containing polysaccaride starch, glucoamylase, glucose dehydrogenase (GDH) and NAD^+ as a fuel as shown in Figure 1.

2 Experimental Section

The nanocrystalline TiO_2 film is prepared by a similar procedure to that described in the literature [6]. TiO_2 powder is dispersed by grinding water and HNO_3 aqueous solution. The viscous suspension is spread onto optical transparent conductive glass plate (OTE) (1 x 5 cm) at room temperature using scotch tape as a spacer. A thin film is obtained by raking off the excess of suspension with a glass rod. After the tape is removed and the plate is dried using hot plate at 80 °C for 30 min, this plate is annealed at 450 °C for 30 min under ambient

condition to form a nanocrystalline TiO_2 film electrode. The thickness of the film, determined by using a micron-sensitive calliper, is about 10 μm.

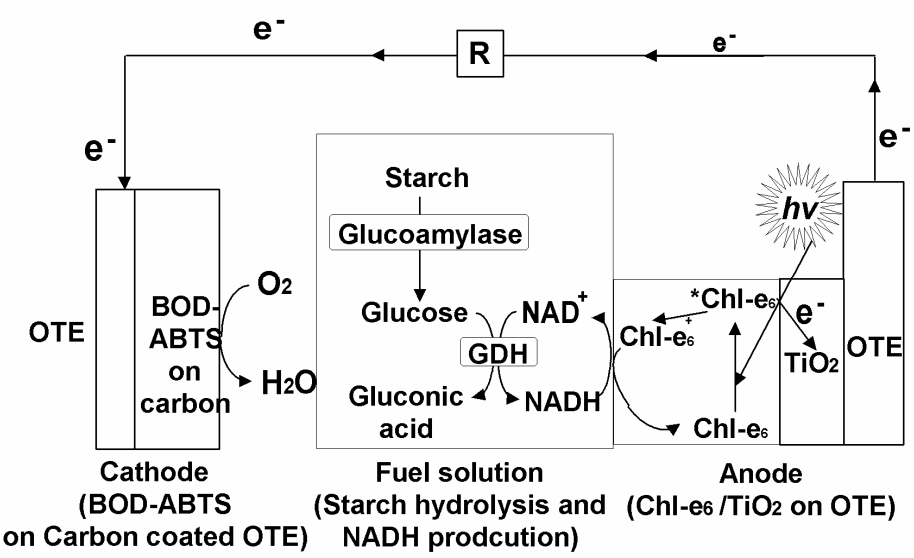

Figure 1: Visible light-operated starch-O_2 biofuel cell based on the combination of NAD^+ reduction with enzymatic starch hydrolysis photosensitization of Chl-e_6 on nanocrystalline TiO_2 layer coated OTE (anode) and the electrochemical reduction to the water of oxygen on to the BOD immobilized OTE (cathode).

Chl-e_6 adsorbed nanocrystalline TiO_2 electrode is prepared as follows. An OTE glass plate with a nanocrystalline TiO_2 film is dipped into 0.2 mmol dm^{-3} Chl-e_6 in methanol solution at room temperature for 6 h. After dipping, the plate is washed with methanol several times and then the plate is dried under vacuum overnight.

The BOD immobilized carbon-coated OTE electrode is prepared as following method. An OTE glass plate is dipped into BOD and 2,2'-Azino-bis((3-ethylbenzo-)thiazoline-6-sulfonic acid (ABTS) in Tris-HCl buffer solution at room temperature for 30 min. After dipping, the plate is dried at room temperature for 30 min under ambient condition. The active area of electrode is 1.0 cm^2.

Photocurrent-photovoltage characteristic of the Chl-e_6 adsorbed on TiO_2 electrode is measured with a sandwich type cell. The working electrode with the Chl-e_6 adsorbed on TiO_2 film is gently squeezed together with a BOD immobilized carbon-coated OTE glass electrode (counter electrode) using spring and irradiated from the substrate side of working electrode. The anodic solution is consisted of 0.1 mol dm^{-3} starch, 5 units glucoamylase, 3.5 mmol dm^{-3} NAD^+, 5 units GDH and 0.1 mol dm^{-3} KCl in 50 mmol dm^{-3} in 50 μl of 10 mmol dm^{-3} potassium phosphate buffer (pH 7.0). The dissolved oxygen in anodic solution is used as cathodic reaction of oxygen to water. A solar simulator (YSS-40, Yamashita Denso) is used as a light source (A.M. 1.5 100 mW cm^{-2}) for the photocurrent and photovoltage characteristics with the two digital multimeter with model 2000-J (Keithley) as a current meter and model 34401A (Agilent) as a voltage meter, respectively.

3 Results and Discussion

The photocurrent responses of photoinduced starch-O_2 biofuel cell were measured under 100 mWcm^{-2} irradiation. Figure 2 shows the photocurrent responses of starch-O_2 biofuel cell with 100 mWcm^{-2} irradiation. From Figure 2, the generated photocurrent increased with irradiation ("ON" in Figure 2). The photocurrent was estimated to be 6.0 μA cm^{-2}. In contrast, no current generation was observed under dark condition ("OFF" in Figure 2). The current changes also were fully reversible and hysterisis was not observed during the measurements.

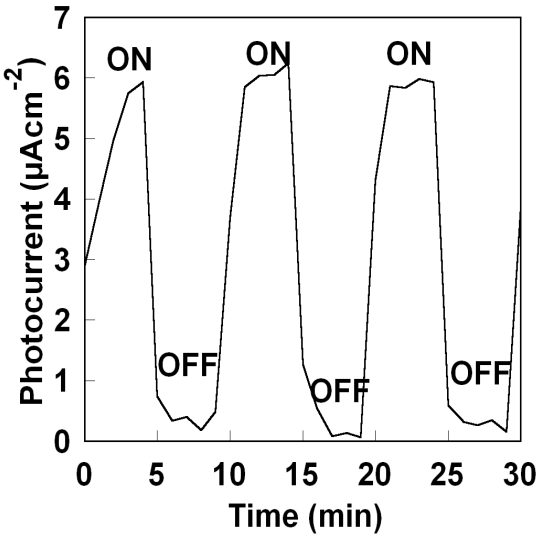

Figure 2: Photocurrent response of photo-operated starch fuel cell with 100 mWcm^{-2} irradiation.

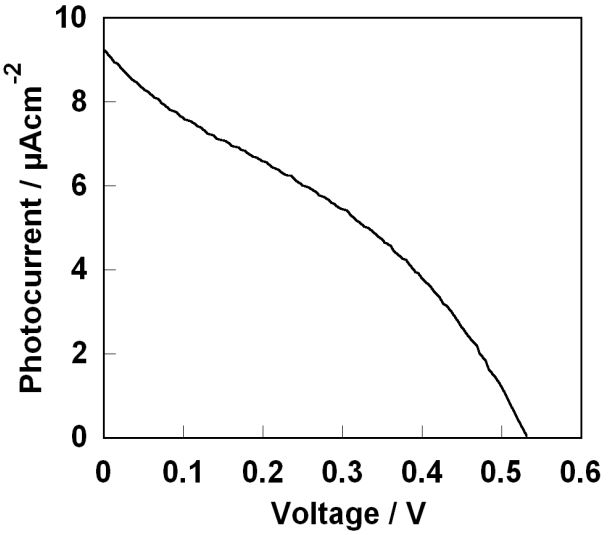

Figure 3: Photocurrent-photovoltage characteristic of photo-operated starch-O_2 biofuel cell under 100 mW cm^{-2} condition.

Figure 3 shows the photocurrent-photovoltage characteristics of photo-operated starch-O_2 biofuel cell irradiated with 100 mWcm^{-2}. The short-circuit photocurrent (I_{SC}) was 9.0 μA cm^{-2}, and the open-circuit photovoltage (V_{OC}) is 530 mV, respectively. The maximum power is estimated to be 1.6 μW cm^{-2}. In contrast, I_{SC} and V_{OC} under the dark condition are *c.a.* zero. Thus, this cell is operated with the visible-light photosensitization of TiO_2 film by Chl-e_6. These results show that photo-operated starch-O_2 biofuel cell based on the visible-light photosensitization of TiO_2 film by Chl-e_6 was developed.

Thus, a new type of visible light-operated starch- O_2 biofuel cell with the visible photosensitization of Chl-e_6 molecules on nanocrystalline TiO_2 film electrode and BOD immobilized carbon-coated OTE was accomplished.

4 Conclusion

In this work, visible light-operated starch-O_2 biofuel cell consisting of Chl-e_6 adsorbed on nanocrystalline TiO_2 layer coated onto optical transparent conductive glass electrode (OTE) as an anode, BOD immobilized carbon-coated OTE as a cathode, and the solution

containing starch, glucoamylase, glucose dehydrogenase (GDH) and NAD^+ as a fuel was studied. The I_{SC} and V_{OC} values of this cell are 9.0 μA cm^{-2} and 530 mV, respectively. As the conversion efficiency of photon-to-current and cell performance are still low, however, new type of starch-O_2 biofuel cell operated with photoenergy was developed by using the visible-light sensitization of Chl-e_6 on nanocrystalline TiO_2 film electrode and BOD immobilized electrode.

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