

# Biophotofuel cell (BPFC) generating electrical power directly from aqueous solutions of biomass and its related compounds while photodecomposing and cleaning

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Received: 20 November 2006 / Revised: 4 June 2007 / Accepted: 10 June 2007 / Published online: 3 July 2007  
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**Abstract** A biophotofuel cell (BPFC) generating electrical power directly from aqueous solutions of biomass and its related compounds with simultaneous photodecomposition and cleaning was investigated. The BPFC had a nanoporous TiO<sub>2</sub> photoanode and an O<sub>2</sub>-reducing cathode. As long as the compounds were either liquid or water-soluble they were photodecomposed and generated electrical power simultaneously. Various biomasses and related compounds such as glucose, amino acids, polysaccharides, proteins, lignin derivatives, cellulose derivatives and some polymers were investigated in the BPFC. Glucose was photodecomposed almost completely into CO<sub>2</sub> under O<sub>2</sub> within 20 h while generating electrical power. The incident photon-to-current conversion efficiency (IPCE) value of a 0.5 M glucose solution in the BPFC under O<sub>2</sub> was 29% based on the incident monochromatic light at 350 nm (intensity 3.6 mW cm<sup>-2</sup>). A glycine aqueous solution could be decomposed photochemically into CO<sub>2</sub>/N<sub>2</sub> in a nearly stoichiometric 4:1 (CO<sub>2</sub>:N<sub>2</sub>) molar ratio. The photodecomposition yield of 0.01 wt% lignosulfonic acid sodium salt was 86.5% in 24 h as estimated from the CO<sub>2</sub> evolved. The cellulose (sulfate) gave similar BPFC characteristics under air as under 1 atm O<sub>2</sub>. Among the compounds the highest V<sub>oc</sub> (open circuit voltage) value was 0.90 V for glutamic acid and phenylalanine.

**Keywords** Nanoporous titanium dioxide film · Biophotofuel cell (BPFC) · Biomass · Biomass related compound · Photoelectrochemical decomposition

## 1 Introduction

Biofuels that can be produced from biomass such as cornstarch, bagasse and lignocellulose derived from woods are attracting a great deal of attention as alternative fuels [1, 2]. However, the production of biofuels is an energy-consuming process so that the net energy acquired by the biofuels is not large enough to reduce CO<sub>2</sub> emission [3]. In addition to this, the environmental pollution by many biowastes such as livestock and human wastes, wastes from agriculture, industries, etc. is a big issue, which requires urgent solution. Since these biowastes are energy-rich (total biowastes in the world (ca. 130 EJ y<sup>-1</sup>) corresponding to 1/3 of the world energy demand (400 EJ y<sup>-1</sup>), the energy should be recovered and used simultaneously while decomposing and cleaning them. From these points of view, the present authors are interested in direct photoelectrochemical decomposition and energy conversion of biomass and its related compounds generating electrical energy, as one of the most feasible candidates for simultaneous environmental cleaning and energy conversion systems.

Photoelectrochemical reactions using semiconductor electrodes have been investigated since the work of Gerischer [4] and other groups. The photoelectrochemical reaction at a crystalline *n*-TiO<sub>2</sub> photoanode photodecomposed water by UV light under potential-controlled conditions [5]. Since then, crystalline *n*-TiO<sub>2</sub> photoanodes have been used to decompose many organic compounds [6–9]. At the TiO<sub>2</sub> surface, the holes produced by

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irradiation oxidize water or organic compounds, and simultaneously the photogenerated electrons reduce  $H^+$  to produce  $H_2$  at a counter electrode. A dye-sensitized solar cell (DSSC) was developed in the early 1990s. The cell is composed of a nanoporous  $TiO_2$  film sensitized with ruthenium bipyridyl dyes and redox electrolytes ( $I^-/I_3^-$  solution). The  $TiO_2$  film photoanode works not only as an acceptor for the photoexcited dye, but also as an electron conducting material [10–20]. We have proposed a biophotofuel cell (BPFC) that can generate electrical power by using a nanoporous  $TiO_2$  photoanode and an  $O_2$ -reducing cathode [21]. Although the BPFC can utilize only UV light, which is a minor fraction of solar irradiation, the cell can be utilized to photodecompose and clean various biomasses while recovering electrical energy from such wastes. A photoelectrochemical biofuel cell composed of a porphyrin-sensitized nanoparticulate  $TiO_2$  (or  $SnO_2$ ) film on a conducting glass (photoanode), NADH/NAD redox pair, an enzyme, an ion-permeable membrane and a counter electrode soaked in a glucose (ethanol or methanol) aqueous solution (fuel), was reported previously [22, 23]. However, in these reports  $O_2$  could not be used as electron acceptor at the cathode so that the system is not defined as a fuel cell.

In the present paper we investigated BPFC by using various biomass models and their related compounds derived from biomass resources such as polysaccharides, amino acids, polypeptides, cellulose paper, and synthetic polymers, and report cyclic voltammograms (CV) and BPFC characteristics of these compounds.

## 2 Experimental

### 2.1 Materials

Titanium dioxide (P-25, particle size, ca. 21 nm; specific surface area,  $50 \pm 15 \text{ m}^2 \text{ g}^{-1}$ ) was received from Japan Aerosil Co. Ltd, and titanium dioxide (F-5, particle size 20 nm; specific surface area,  $60\text{--}85 \text{ m}^2 \text{ g}^{-1}$ ) from Showa Denko Co. Ltd. Sodium sulfate, phosphoric acid, glutamic acid, glucose and platinum black were purchased from Kanto Kagaku Co. Ltd and glycine from Junsei Chemical Co. Ltd. Tyrosine, cysteine and phenylalanine were purchased from Tokyo Chemical Industry Co. Ltd, agarose from Acros and gelatin from Sigma. Curdlan and polyethylenglycol (PEG) were from Wako Pure Chemical Co. Ltd, Triton X-100, polyacrylamide (PMA) and hexachloroplatinate from Kishida Chemical Co. Ltd and amylopectin from Fluka. Cellulose sulfate was purchased from Scientific Polymer Products, Inc, lignosulfonic acid sodium salt from Aldrich Co. Ltd, and collagen from Nitta Gelatin, Inc. Ar gas (purity > 99%) was obtained from Nippon Sanso Corp. These chemicals were of the purest grade

available and used as received. F-doped  $SnO_2$  conductive glass (FTO, surface resistance,  $10 \Omega/\text{sq}$ ) was received from Asahi Glass Co. Ltd.

### 2.2 Preparation of nanoparticulate $TiO_2$ films

A conventional  $TiO_2$  film was prepared with P-25 or F-5 as follows: 12 g  $TiO_2$  (P-25 or F-5) and acetylacetone (0.4 mL) were mixed well while adding 4 mL water slowly for 2 h. Triton X-100 detergent (0.2 mL) was added and further mixed well with the  $TiO_2$  slurry followed by sonication. This mixture was spin-coated at 2,000 rpm on an FTO electrode ( $2 \text{ cm} \times 1 \text{ cm}$ ) for about 10 s to obtain  $1 \text{ cm} \times 1 \text{ cm}$  area of a nanoporous  $TiO_2$  film, and the film was dried at  $100 \text{ }^\circ\text{C}$  for 30 min. This procedure was repeated until the film thickness became  $10 \mu\text{m}$ , and then the film was finally calcinated at  $450 \text{ }^\circ\text{C}$  for 30 min.

### 2.3 Measurements

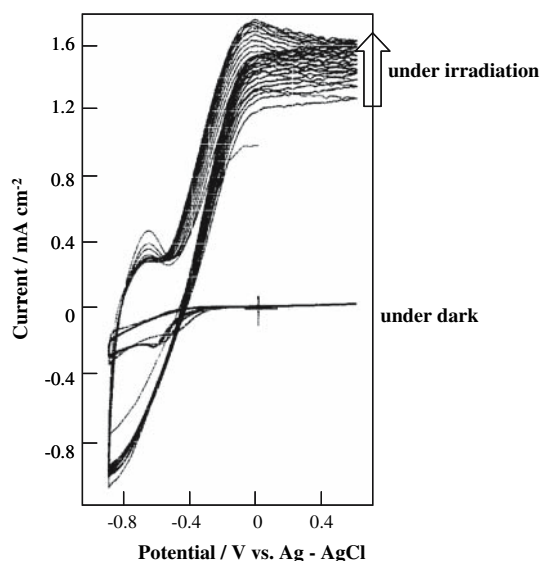
As an example glucose was used as the compound photodecomposed by a nanoporous  $TiO_2$  film photoanode. The cyclic voltammogram (CV) was measured as follows. The  $TiO_2$  film electrode ( $1 \text{ cm} \times 1 \text{ cm}$ ), a Pt-black coated Pt plate cathode (Pt-black/Pt) ( $1 \text{ cm} \times 1 \text{ cm}$ ), and a Ag-AgCl reference electrode were soaked in a 5 mL of glucose aqueous solution (from 1 mM to 0.63 M, pH 5 or 12) in a 10 mL cylindrical cell made of Pyrex glass containing 0.1 M  $Na_2SO_4$  electrolyte.  $O_2$  gas was bubbled into the solution for 30 min and the  $TiO_2$  film was irradiated from the FTO side with a 500 W xenon lamp with a light intensity of  $450 \text{ mW cm}^{-2}$ . A solar simulator (Pecell Technologies Co. Ltd.) was also used under AM 1.5 and  $100 \text{ mW cm}^{-2}$  irradiation conditions. A cylindrical reactor (Pyrex glass cell) was sealed with a rubber septum, through which the gas phase was sampled by a syringe. A sample aliquot of  $100 \mu\text{L}$  gas was taken for analysis. The  $N_2$  gas evolved was analyzed by gas chromatography (Shimadzu, GC2014) with a 5A molecular sieve column at  $40 \text{ }^\circ\text{C}$  under Ar carrier gas.  $CO_2$  was analyzed with a silica gel column. All the photoelectrochemical measurements and reactions were performed at  $25 \text{ }^\circ\text{C}$ .

The J–V characteristics of the photofuel cell (PFC) were measured by a two electrode system, i.e., with a nanoporous  $TiO_2$  photoanode and a Pt plate cathode soaked in an aqueous solution of the fuel compound at  $25 \text{ }^\circ\text{C}$ .

## 3 Results and discussion

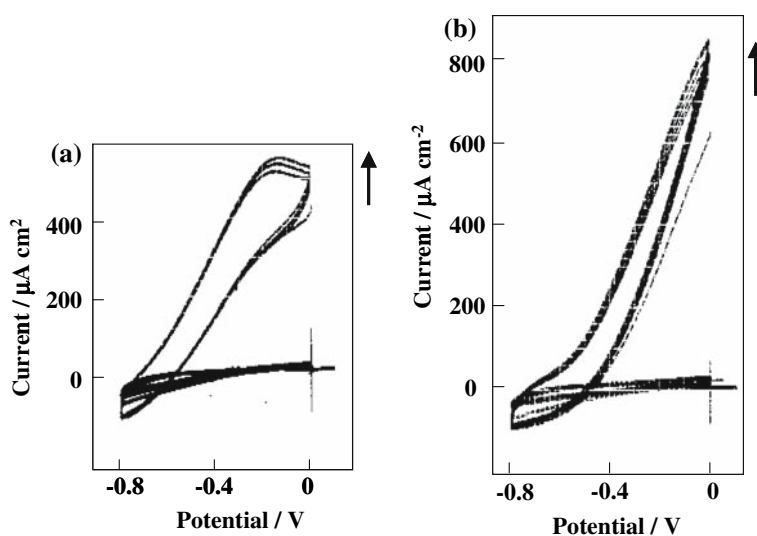
The CV under 1 atm  $O_2$  atmosphere at an FTO/nanoporous  $TiO_2$  (P-25) film photoanode soaked in a 0.63 M glucose aqueous solution (pH 12) in the dark and under irradiation

at 25 °C is shown in Fig. 1. After the CV curve under irradiation increased gradually with time, it tended to reach a constant value, showing that a steady state photoanodic current was generated. The CV under irradiation exhibited some hysteresis indicating that a slow electrochemical step is involved, most probably of a multi-electron nature either in glucose oxidation or O<sub>2</sub> reduction. Figures 2(a) and (b) show the typical characteristics of PFC in 0.5 M and 0.05 M glucose solutions at pH 5, respectively, with the FTO/TiO<sub>2</sub> (P-25) film photoanode and a Pt-black/Pt cathode under 1 atm O<sub>2</sub> atmosphere at 25 °C, and the results are summarized in Table 1 giving V<sub>oc</sub> (open circuit volt-



**Fig. 1** Cyclic voltammograms of glucose (0.56 M) in an aqueous solution (pH12) containing Na<sub>2</sub>SO<sub>4</sub> (0.1 M) under O<sub>2</sub> by using FTO/TiO<sub>2</sub>(P-25) photoanode, Pt/Pt black cathode and Ag/AgCl reference electrode. Light source, Xe lamp (450 mW cm<sup>-2</sup>); sweep direction, 0 → -0.9 → 0.6 → 0; scan rate, 10 mV s<sup>-1</sup>

**Fig. 2** PFC characteristics of glucose in an aqueous solution containing Na<sub>2</sub>SO<sub>4</sub> (0.1 M) by using FTO/TiO<sub>2</sub>(P-25) photoanode, Pt/Pt black cathode under O<sub>2</sub>: (a) Glucose, 0.5 M; (b) Glucose, 0.05 M. Light source, Xe lamp (450 mW cm<sup>-2</sup>); sweep direction, 0 → -0.8 → 0; scan rate, 20 mV s<sup>-1</sup>

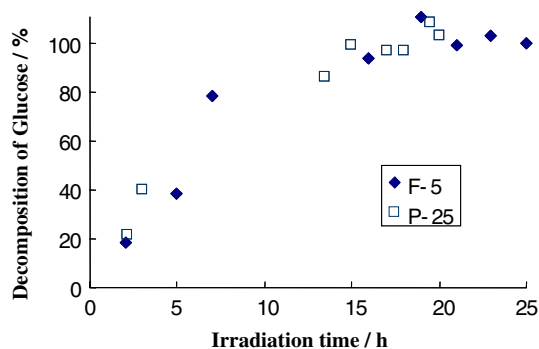


**Table 1** Photofuel cell (PFC) characteristics of glucose solutions (pH 5.0) under O<sub>2</sub> atmosphere, irradiated by Xe lamp (450 mW cm<sup>-2</sup>)

Glucose (conc./M)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF
0.50	0.64	0.50	0.32
0.05	0.60	0.80	0.20

age), J<sub>sc</sub> (short circuit current density) and FF (fill factor). The FF means the ratio of a real maximum electrical power output per theoretical maximum output (= V<sub>oc</sub> × J<sub>sc</sub>) estimated from the J–V curve (Figs. 2(a) and (b)) under irradiation. For the estimation of the V<sub>oc</sub> and FF values, the average of the anodic and the cathodic scans was adopted. V<sub>oc</sub> was little dependent on glucose concentration, but the J<sub>sc</sub> was higher when the glucose concentration was lower. Since V<sub>oc</sub> is determined by the conduction band energy level (E<sub>cb</sub>) and the O<sub>2</sub> reduction potential, it is reasonable that V<sub>oc</sub> is almost independent of the fuel concentration. That higher glucose concentration induced lower photocurrent may be ascribed to the higher viscosity of the solution and therefore slower diffusion of the fuel molecules in the nanopores of the TiO<sub>2</sub>.

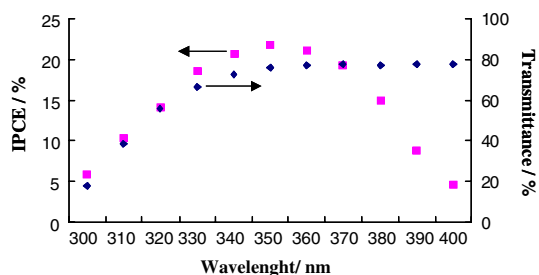
CO<sub>2</sub> gas was evolved during the photoelectrochemical process due to the decomposition of glucose with simultaneous consumption of O<sub>2</sub> in the glucose PFC. To compare the difference in the kind of TiO<sub>2</sub> particles, two TiO<sub>2</sub> particles, P-25 (particle size: ca. 21 nm; specific surface area: 50 ± 15 m<sup>2</sup> g<sup>-1</sup>) and F-5 (particle size 20 nm; specific surface area: 60–85 m<sup>2</sup> g<sup>-1</sup>), were used. The decomposition rates of a 1 mM glucose solution in the PFC using these two TiO<sub>2</sub> particles are shown in Fig. 3. The figure shows that both the TiO<sub>2</sub> exhibit a similar trend within the data scattering, suggesting that the specific surface area did not influence the photodecomposition rate at the 1 mM



**Fig. 3** Decomposition rate of a 1 mM glucose aqueous solution in PFC using FTO/TiO<sub>2</sub>(P-25) photoanode, Pt/Pt black cathode under O<sub>2</sub>, irradiated by Xe lamp (450 mW cm<sup>-2</sup>)

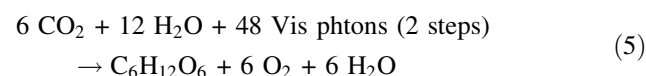
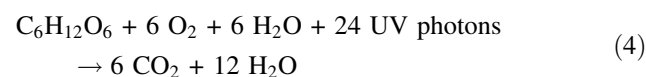
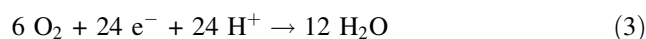
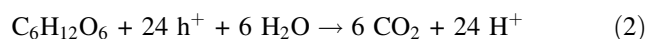
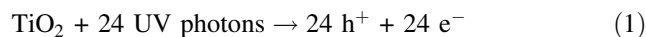
concentration level. Within 20 h irradiation the glucose was almost completely decomposed in both cases.

The incident photon (on the cell glass)-to-current conversion efficiency (IPCE) of a 0.5 M glucose solution in the PFC under O<sub>2</sub> was investigated and the result is shown in Fig. 4. The transmittance of the cell glass is also shown in Fig. 4. Unlike a quartz cell (transparent over 200 nm), the present Pyrex glass cell does not transmit the light below a wavelength of 300 nm as shown in Fig. 4. The IPCE curve showed a maximum around 350 nm. The decrease in the IPCE values below the wavelength of 350 nm is ascribable to the decrease in the photon number transmitted by the cell glass as shown in the transmittance curve. In contrast, the decrease in IPCE over the wavelength of 350 nm is due to the absorption of photons by the TiO<sub>2</sub> film since the band gap of TiO<sub>2</sub> is ca. 3.1 eV (about 400 nm) meaning that the absorption edge of the photon by the TiO<sub>2</sub> is at 400 nm so that absorption by the TiO<sub>2</sub> increases when the wavelength is below 400 nm. The IPCE value at the peak was corrected by the transmittance of the cell glass (76%), giving an IPCE (29%) based on the transmitted monochromatic light at 350 nm (intensity 3.6 mW cm<sup>-2</sup>). The IPCE value for glucose was much higher than that (19%) for the ammonia PFC (APFC) reported previously [21].



**Fig. 4** IPCE of 0.5 M glucose in PFC using FTO/TiO<sub>2</sub>(P-25) photoanode and Pt/Pt black cathode under O<sub>2</sub>, and transmittance of the cell glass

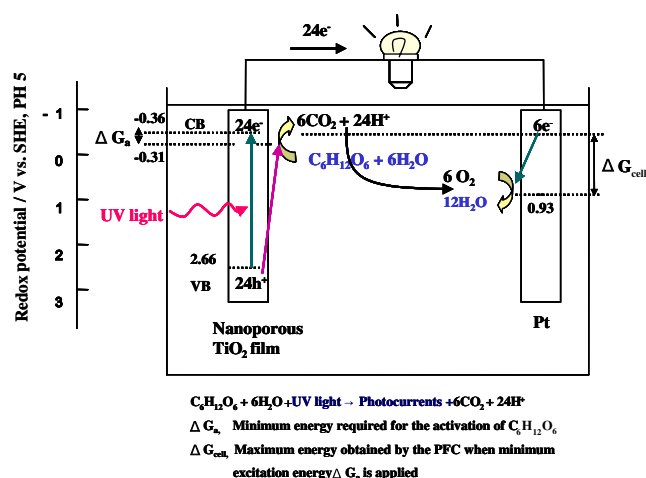
The mechanism of glucose photodecomposition by irradiation on a TiO<sub>2</sub> photoanode and the energy diagram of the glucose PFC can be represented by Fig. 5. In the TiO<sub>2</sub> the photoinduced charge separation produces an electron (e<sup>-</sup>) in the conduction band and a hole (h<sup>+</sup>) in the valence band (Eq. (1)); the glucose molecule then reacts with h<sup>+</sup> on the TiO<sub>2</sub> to finally produce CO<sub>2</sub> and protons (H<sup>+</sup>) (Eq. (2)). The electrons are transported to the Pt-black/Pt cathode via the outer circuit, and then O<sub>2</sub> is reduced there to produce H<sub>2</sub>O (Eq. (3)). Thus the total reaction is represented by Eq. (4).



The photosynthesis reaction is represented by Eq. (5), demonstrating that the present PFC reaction is the reverse of the photosynthesis. Under O<sub>2</sub> atmosphere the theoretical maximum cell voltage of the present glucose PFC is 1.29 V according to the calculated value based on the conduction band edge (E<sub>cb</sub>) of TiO<sub>2</sub> (-0.36 V vs. SHE at pH 5, estimated from the value of E° = -0.06 V vs. SHE at pH 0 [11] and the redox potential for O<sub>2</sub>/H<sub>2</sub>O (0.93 V vs. SHE at pH 5, estimated from the value of E° = 1.23 V vs. SHE at pH 0). Since the redox potential of glucose is low (E° = -0.014 V vs. SHE at pH 0, calculated from thermodynamic data), which is close to the E<sub>cb</sub> of TiO<sub>2</sub> (E° = -0.06 V vs. SHE), the minimum energy required for photoactivation is actually very small (0.05 eV). In the future an appropriate photoanode material capable of utilizing at least visible light with a high photon flux number should be investigated in order that a more efficient glucose PFC is realized.

According to whether the compounds are either liquid or water-soluble, they can be photodecomposed by the PFC while generating electrical power. Various biomasses and their related compounds such as amino acids, polysaccharides, proteins, lignin derivatives, cellulose derivatives and some polymers were investigated in the PFC. The PFC characteristics under 1 atm O<sub>2</sub> in a 0.5 M glycine and a 0.5 M glutamic acid aqueous solution (pH 5) in the dark

**Fig. 5** Energy diagram of glucose PFC (at pH 5.0) using nanoporous TiO<sub>2</sub> film photoanode and Pt/Pt black cathode soaked in a glucose aqueous solution under O<sub>2</sub>

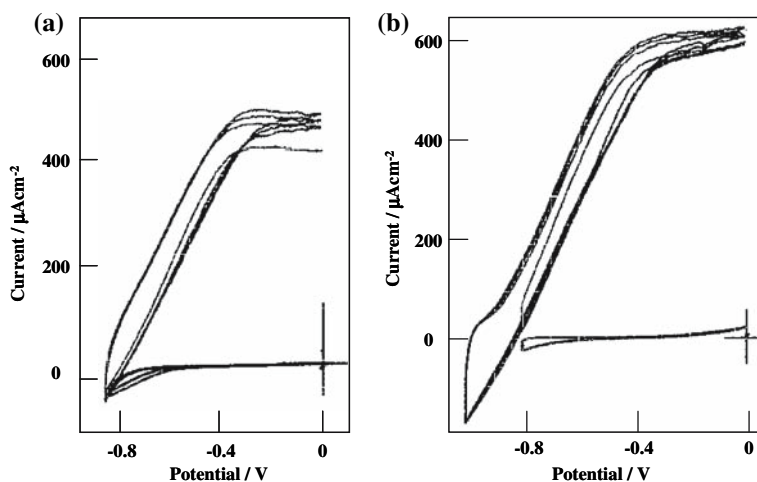


and under irradiation at 25 °C is shown in Figs. 6(a) and (b), respectively. Both compounds gave clear PFC characteristics. CO<sub>2</sub> and N<sub>2</sub> gas evolution rate and the decomposition rate of a 0.5 M glycine aqueous solution in the PFC are shown in Figs. 7(a) and (b), respectively. The volume of CO<sub>2</sub> and N<sub>2</sub> gas measured by a gas chromatograph was corrected based on the solubility of both gases in water. The glycine aqueous solution can be converted photochemically into CO<sub>2</sub>/N<sub>2</sub> in a nearly stoichiometric 4:1 (CO<sub>2</sub>:N<sub>2</sub>) molar ratio as shown in Fig. 7(a). Over 48 h, the values for the decomposition rate based on N<sub>2</sub> and CO<sub>2</sub> evolved were 62.1% and 62.2%, respectively (Fig. 7(b)).

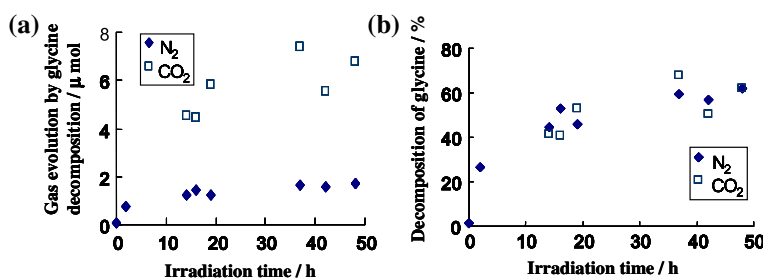
These results indicate that glycine can be photodecomposed almost completely into CO<sub>2</sub> and N<sub>2</sub> while generating electrical power. The PFC characteristics of various kinds of amino acid are summarized in Table 2. Various kinds of amino acids can be photodecomposed and at the same time utilized as fuels for the PFC. The difference in the values is ascribable to the ability as donors as well as their binding ability onto the TiO<sub>2</sub>.

As examples of naturally occurring polymers, the PFC characteristics of amylopectin and gelatin were investigated and the results are shown in Figs. 8 (a) and (b). The PFC characteristics of various kinds of polysaccharides and

**Fig. 6** PFC characteristics of amino acid in an aqueous solution containing Na<sub>2</sub>SO<sub>4</sub> (0.1 M) by using FTO/TiO<sub>2</sub>(P-25) photoanode and Pt/Pt black cathode under O<sub>2</sub>: (a) Glycine, 0.5 M; (b) Glutamic acid, 0.5 M. Light source, Xe lamp (450 mW cm<sup>-2</sup>); sweep direction, 0 → -0.8 → 0; scan rate, 20 mV s<sup>-1</sup>



**Fig. 7** (a) Gas evolution and (b) decomposition rate calculated based on the evolved N<sub>2</sub> and CO<sub>2</sub> of 1 mM glycine in PFC using FTO/TiO<sub>2</sub>(F-5) photoanode and Pt/Pt black cathode under O<sub>2</sub>, irradiated by Xe lamp (450 mW cm<sup>-2</sup>)



**Table 2** Photofuel cell (PFC) characteristics of various amino acids aqueous solutions, irradiated by Xe lamp ( $450 \text{ mW cm}^{-2}$ )

Fuel (conc./M)	pH	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF
Glycine (0.5)	5	0.76	0.45	0.51
Glutamic acid (0.5)	1	0.90	0.64	0.42
Tyrosine (0.5)	13	0.86	0.43	0.36
Phenylalanine (0.5)	13	0.90	0.61	0.53

polypeptides are summarized in Table 3. In both cases the  $V_{oc}$  values are almost similar (0.6 V) and the  $J_{sc}$  values are between 0.19 and  $0.42 \text{ mA cm}^{-2}$ . It is of importance that not only low molecular compounds such as amino acids and glucose, but also naturally occurring polymers can be photodecomposed and at the same time generate electrical power.

Recently, the decomposition of biomasses including lignocellulose and lignin has attracted a great deal of attention in order to clean them [1, 24]. As for the derivatives of cellulose and lignin, the PFC characteristics of cellulose sulfate and liginosulfonic acid sodium salt were investigated and the results are shown in Figs. 9 (a) and (b), respectively. It should be noted that even a lignin derivative is capable of being photodecomposed simultaneously generating electrical power; it is usually difficult to decompose lignin derivatives except by burning [25]. The  $V_{oc}$  values for both compounds were almost similar as the naturally occurring polymers mentioned above, but the  $J_{sc}$  value for liginosulfonic acid sodium salt was lower than that of the other compounds. Since the solution of the compound is brown colored, the lower value of  $J_{sc}$  might be partly ascribed to a filter effect. In other experiments the decomposition rate of 0.01 wt% liginosulfonic acid sodium salt reached 86.5% in 24 h based on the  $\text{CO}_2$  evolved; this value was corrected based on the solubility of  $\text{CO}_2$  gas in water (Fig. 10).

Synthetic polymers in addition to the naturally occurring polymers mentioned above can also be photodecomposed to generate electrical power. As an example of typical water-soluble polymers, the PFC characteristics of polyethyleneglycol (PEG) was investigated as shown in Fig. 11

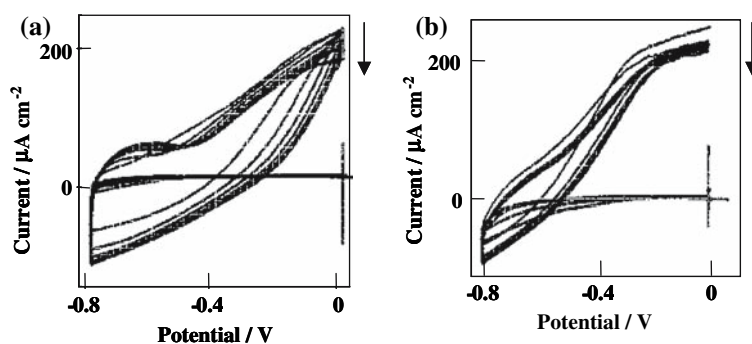
**Table 3** Photofuel cell (PFC) characteristics of various polysaccharides and polypeptides aqueous solutions, irradiated by Xe lamp ( $450 \text{ mW cm}^{-2}$ )

Fuel (wt%)	pH	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF
Agarose (2)	5	0.60	0.14	0.51
Amylopectin (2)	5	0.60	0.22	0.30
Curdlan (2)	5	0.56	0.19	0.28
Gellan Gum (2)	5	0.60	0.42	0.31
Gelatin (2)	5	0.60	0.28	0.27
Collagen (3 mg/L)	1	0.60	0.23	0.24

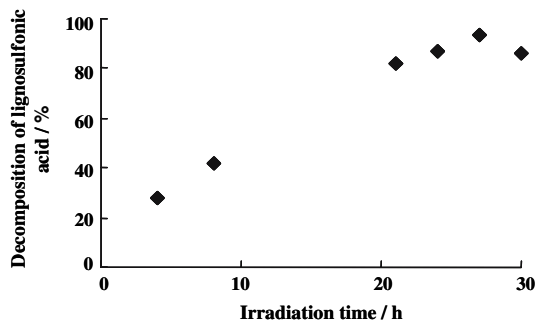
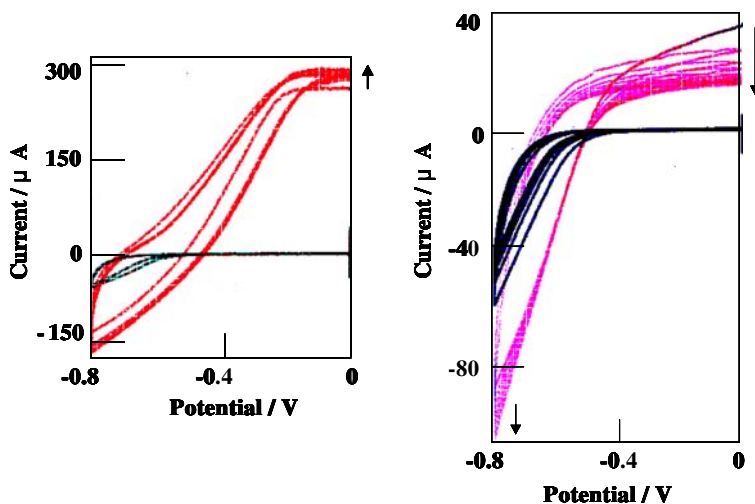
and the results are summarized in Table 4, including the results of polyacrylamide (PAAm) as another example of synthetic polymers. Both  $V_{oc}$  and  $J_{sc}$  values of these synthetic polymers are similar to those of the naturally occurring polymers mentioned above. The lower  $J_{sc}$  values are ascribed to the difficult penetration of the polymers into the nanopores of  $\text{TiO}_2$ .

Irradiation by a solar simulator at airmass (AM) 1.5 and  $100 \text{ mW cm}^{-2}$  is also effective for generating electrical power. A 0.5 M glucose and a 0.5 M glycine aqueous solution was investigated for the PFC and the results are shown in Table 5. These also exhibit the effectiveness of solar irradiation for generating electrical power. In the case of glucose the values for both  $V_{oc}$  and FF were similar (Table 1), but the  $J_{sc}$  value under solar simulator was depressed by 50% due to the lower light intensity than that of the xenon lamp. On the other hand, for a glycine aqueous solution, all values under the solar simulator were smaller than those by xenon lamp (compare Tables 2 and 5).

To investigate the effect of  $\text{O}_2$  partial pressure (1 atm  $\text{O}_2$  or air), the PFC characteristics of glucose and cellulose sulfate were studied and the results are shown in Table 6. The difference in the  $J_{sc}$  values between under  $\text{O}_2$  and air are clearly observed for glucose. In the case of cellulose sulfate the  $J_{sc}$  and  $V_{oc}$  values are almost similar under  $\text{O}_2$  and air. Although the PFC characteristics are in general worse under air than under  $\text{O}_2$ , it is of importance that the present PFC can, in principle, also work under air.

**Fig. 8** PFC characteristics of naturally occurring polymer in an aqueous solution containing  $\text{Na}_2\text{SO}_4$  (0.1 M) by using FTO/ $\text{TiO}_2$ (P-25) photoanode and Pt/Pt black cathode under  $\text{O}_2$ : (a) amylopectin, 2 wt%; (b) gelatin, 2 wt%. Light source, Xe lamp ( $450 \text{ mW cm}^{-2}$ ); sweep direction,  $0 \rightarrow -0.8 \rightarrow 0$ ; scan rate,  $20 \text{ mV s}^{-1}$ 

**Fig. 9** PFC characteristics of derivatives of cellulose and lignin in an aqueous solution containing Na<sub>2</sub>SO<sub>4</sub> (0.1 M) by using FTO/TiO<sub>2</sub>(F-5) photoanode and Pt/Pt black cathode under O<sub>2</sub>: (a) cellulose sulfate, 2 wt%; (b) lignosulfonic acid sodium salt, 0.5 wt%. Light source, Xe lamp (450 mW cm<sup>-2</sup>); sweep direction, 0 → -0.8 → 0; scan rate, 20 mV s<sup>-1</sup>



**Fig. 10** Decomposition rate of 0.01 wt% lignosulfonic acid sodium salt in PFC using FTO/TiO<sub>2</sub>(F-5) photoanode and Pt/Pt black cathode under O<sub>2</sub>, irradiated by Xe lamp (450 mW cm<sup>-2</sup>)

**Table 4** Photofuel cell (PFC) characteristics of polyethylene glycol (PEG) and polyacrylamide (PAAm) aqueous solutions (pH 5), irradiated by Xe lamp (450 mW cm<sup>-2</sup>)

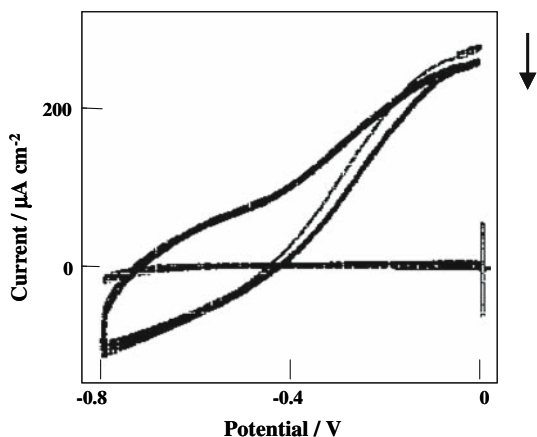
Fuel (wt%)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF
PEG (2)	0.60	0.28	0.27
PMA (2)	0.60	0.23	0.24

**Table 5** Photofuel cell (PFC) characteristics of glucose and glycine aqueous solutions (pH 5) under O<sub>2</sub> atmosphere, irradiated by solar simulator (100 mW cm<sup>-2</sup>)

Fuel (conc./M)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF
Glucose (0.5)	0.62	0.28	0.26
Glycine (0.5)	0.60	0.10	0.32

**Table 6** Photofuel cell (PFC) characteristics of glucose and glycine aqueous solutions (pH 5) under O<sub>2</sub> and air, irradiated by Xe lamp (450 mW cm<sup>-2</sup>)

Fuel	Atmosphere	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF
Glucose (0.5 M)	O <sub>2</sub>	0.64	0.50	0.32
	Air	0.32	0.24	0.26
Cellulose sulfate (2 wt%)	O <sub>2</sub>	0.56	0.29	0.34
	Air	0.56	0.26	0.21



**Fig. 11** PFC characteristics of 2 wt% polyethyleneglycol in an aqueous solution containing Na<sub>2</sub>SO<sub>4</sub> (0.1 M) by using FTO/TiO<sub>2</sub>(P-25) photoanode and Pt/Pt black cathode under O<sub>2</sub>. Light source, Xe lamp (450 mW cm<sup>-2</sup>); sweep direction, 0 → -0.8 → 0; scan rate, 20 mV s<sup>-1</sup>

In the PFC system, V<sub>oc</sub> is determined by the potential difference between the level of the E<sub>cb</sub> and the redox potential of O<sub>2</sub> reduction at the cathode. In Table 6 V<sub>oc</sub> under O<sub>2</sub> or air is about 1/2 or 1/4 of the theoretical V<sub>oc</sub> (1.29 V). It is most probable that the reaction involves a different mechanism in the first step of O<sub>2</sub> reduction. The first step of the reduction is either a 4-electron reduction of O<sub>2</sub> (E° = 1.23 V vs. SHE) or a two-electron reduction of O<sub>2</sub>

( $E^\circ = 0.68$  V vs. SHE). In the former case, the theoretical  $V_{oc}$  should be 1.29 V but in the latter case,  $V_{oc}$  should be 0.74 V, so that two-electron  $O_2$  reduction would be involved at the cathode.

#### 4 Conclusion

Various biomass resources and their related compounds including other synthetic polymers were successfully photodecomposed at a nanoporous  $TiO_2$  film photoanode with an  $O_2$ -reducing cathode while generating electrical power. Their BPFC characteristics were demonstrated. The results show that the BPFC can be fabricated using aqueous solutions of the compounds derived from biomass and biowastes. The present BPFC could utilize visible light instead of UV light in the near future by using appropriate small bandgap photoanode materials to generate electrical power from biomass and biowastes with solar irradiation.

**Acknowledgement** This work was supported by a Grant-in-Aid for Scientific Research (18550164) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

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