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Biophotochemical cell (BPCC) to photodecompose biomass and bio-related compounds by UV irradiation with simultaneous electrical power generation

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ABSTRACT

UV-light decomposition and simultaneous electrical power generation from urea, a urine model, with a biophotochemical cell (BPCC) comprising a nanoporous TiO_2 photoanode and an O_2-reducing cathode showed that urea can be photodecomposed to CO_2 and N_2 at the theoretical 1/1 molar ratio while donating electrical charges into the outer circuit at a high efficiency of more than 90%. Photodecomposition of ammonia, product from urine catalyzed by urease present abundant in nature, was also investigated by a thin layer cell to prove that urine can be photo (UV) decomposed and cleaned with simultaneous electrical power generation. The effect of air bubbling on the thin layer cell performance was studied by using a glycine aqueous solution. It was demonstrated that the I–V characteristics of a thin layer cell degraded rapidly without air bubbling, but are maintained nearly constant under air bubbling. It was demonstrated that the energy conversion efficiency from glycine to electrical power can reach 50%. In order to fabricate a submodule for the future module fabrication, thin layer cells with different sizes from $2\,cm \times 2\,cm$ to $20\,cm \times 20\,cm$ were fabricated, and the I–V characteristics of a glycine aqueous solution were investigated in these cells. It was found that enlargement of the cell is in principle no problem to obtain conversion efficiency similar to a small size cell. It was found that MnO_2 is as efficient as a Pt- based catalyst for the O_2-reducing cathode. It was shown that tris(2,2′-bipyridine)ruthenium(II) complex can in principle work as a sensitizer for a visible light-driven BPCC.

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1. Introduction

Biomass wastes are serious pollutants in our environment [1], so that it is an urgent issue to clean such environmental pollutants. It is important that such biomass wastes contain tremendous energy, amounting to 130 EJ/year in the world [2], which corresponds to nearly one third of the world's energy demand (450 EJ/year). Photoelectrochemical decomposition of organic compounds at semiconductor photoanode has been studied from the middle of the last century [3]. It has been reported that a crystalline TiO_2 photoanode can photodecompose water [4] and other organic compounds under solar (UV) irradiation, but this electrode system usually needed artificial applied potential, so that without bias potential the activity was not high enough to photodecompose high concentrations of organic compounds or biomass. Afterwards fine powders and thin films of TiO_2 have been applied to clean mainly a low concentration of organic compounds; they are now known as photocatalysts and applied to various practical uses [5]. Later a dye-sensitized nanoporous TiO_2 film photoanode was used for a

dye-sensitized solar cell (DSSC) [6], for which a porous TiO_2 was utilized as an electron acceptor but not as a kind of Schottky-junction semiconductor. Recently, the present authors succeeded by using both a highly porous TiO_2 photoanode and an O_2-reducing cathode [7–9] in fabricating a biophotochemical cell (BPCC) that can photodecompose and clean high concentrations of various organic compounds and biomass to CO_2 and N_2 under UV-light irradiation without any applied potential, generating simultaneously electrical power.

In order to practically use this BPCC, further development was needed such as maintaining the cell performance against rapid O_2 consumption, larger size cell fabrication, utilization of active O_2-reducttion catalyst instead of precious Pt, etc. These important issues have successfully been solved in further investigations, and will be reported in the present paper.

2. Experimental

2.1. Materials

TiO_2 (P-25) was received from Japan Aerosil Co. Ltd. (particle size ca. 20 nm). Ti-nanoxide T/SP paste was purchased from Solaronics Co. Ltd. F-doped SnO_2 conductive glass (FTO, surface resistance

$10\,\Omega/\square$) was purchased from AGC Fabritec Co. Ltd. MnO_2 was of the purest grade from Wako Chemicals Co. Ltd. and used without further purification.

2.2. Electrodes

A nanoporous TiO_2 film was prepared as follows. 12 g TiO_2 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 an FTO (fluorine-doped conducting glass) electrode ($2\,cm \times 1\,cm$) during about 10 s to obtain $1\,cm \times 1\,cm$ 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 became $10\,\mu m$, and then the film was finally calcined at $450\,°C$ for 30 min. In another case commercially available Ti-nanoxide T/SP paste was coated on an FTO by a squeeze coating method. For this process, an adhesive tape (thickness about $70\,\mu m$) was used as a spacer to adjust the TiO_2 film thickness to around $10\,\mu m$. The deposited TiO_2 film was dried at room temperature, and then calcined at $450\,°C$ for 30 min.

Pt was coated on an FTO electrode by reductive electrodeposition in a $H_2[PtCl_6]$ aqueous solution. MnO_2 cathode was prepared as follows. 0.3 g MnO_2 and 0.3 g active carbon were mixed well in a mortar, suspended in a 5 wt% Nafion solution (20 μL alcoholic solution), and then the mixture was cast on a $1\,cm^2$ carbon paper (from Toray Co. Ltd.). This carbon paper was then treated in a 30 wt% NaOH aqueous solution at $40\,°C$ for 17 h. A Cu wire was attached by a conductive Ag epoxy resin on this $C/MnO_2/Nafion$ carbon paper followed by coating with an insulating epoxy resin. In order to make another side of a Pt cathode contact with air, a membrane electrode assembly (MEA) purchased from FC Co. Ltd. was used that is composed of carbon paper/Pt-carbon catalyst/Nafion 117 membrane/Pt-carbon catalyst/carbon paper.

2.3. Cells

A liquid sample was used without any pretreatment. Cyclic voltammogram (CV) was measured as follows. A TiO_2 film electrode (effective area of $1\,cm \times 1\,cm$), a Pt-black coated Pt plate cathode ($1\,cm \times 1\,cm$), and a Ag-AgCl reference electrode were soaked in a 5 mL sample aqueous solution (containing 0.1 M Na_2SO_4 electrolytes) in a 10 mL cylindrical cell (Cell 1). The cylindrical cell was

sealed airtight with a rubber septum, through which the gas phase sample was taken out by a syringe. Before starting the photoirradiation, O_2 gas was introduced into the water during 30 min to substitute the air by O_2. A $5\,cm \times 5\,cm$ sandwich type thin layer cell (Cell 2; Fig. 1, effective electrode area is $4\,cm \times 4\,cm$) was fabricated using a $4\,cm \times 4\,cm$ nanoporous TiO_2 thin film photoanode coated on an FTO ($5\,cm \times 5\,cm$) and a $4\,cm \times 4\,cm$ Pt-black cathode coated on a $5\,cm \times 5\,cm$ ITO (indium tinoxide) conductive glass. A 5 mm thick spacer made of neoprene rubber was put between the TiO_2/FTO photoanode and the Pt-black/ITO cathode to fabricate a thin layer type cell. In order to collect charges from the anode and the cathode to the outer circuit, 5 mm wide Cu or stainless steel charge collectors were put on the three edges of both the working and the counter electrodes. A plastic tube having many pinholes was inserted into the cell to introduce air into the sample solution during the photochemical reaction. It should be added here that the Cell 2 was efficient in photodecomposing samples due to its large photoanode area for irradiation, but it was not suited for analyzing product gas due to its open-air structure.

2.4. Irradiation and measurements

The TiO_2 film was irradiated at $100\,mW\,cm^{-2}$ light intensity with a 500 W xenon lamp through an IR-cutoff filter (HA-50), which contained UV-A (290–390 nm) region light with the intensity of $8.6\,mW\,cm^{-2}$. This UV intensity was close to that from a solar simulator (PEC-L10 from Peccell Technologies, Inc.) at the irradiance of AM 1.5 G and $100\,mW\,cm^{-2}$ (UV-A was about $7\,mW\,cm^{-2}$). The UV-A region light intensity was measured by a UV-light meter (model UV-340, CUSTOM Co. Ltd.). The gases (CO_2 and N_2) formed were analyzed by a gas chromatograph (Shimadzu, GC-8A) with a 5A molecular sieve column at $30\,°C$ using argon carrier gas, and CO_2 was analyzed with a silica gel column. For obtaining the total amount of the formed CO_2, the gas volume in the gas phase was corrected by its solubility in water. All the photoelectrochemical reactions were performed at $25\,°C$. NH_4^+ was analyzed by an ion chromatograph (Dionex Dx-AQ) by using a cation exchange column (Ion Pac CS12A) with an eluate CH_3SO_3H and an electric conductance detector.

The I–V characteristics of a biophotochemical cell (BPCC) were measured by a two-electrode system, i.e., with a nanoporous TiO_2 photoanode and a Pt black-coated Pt plate cathode either in a cylindrical cell (Cell1) or in a thin layer cell (Cell 2) at $25\,°C$.
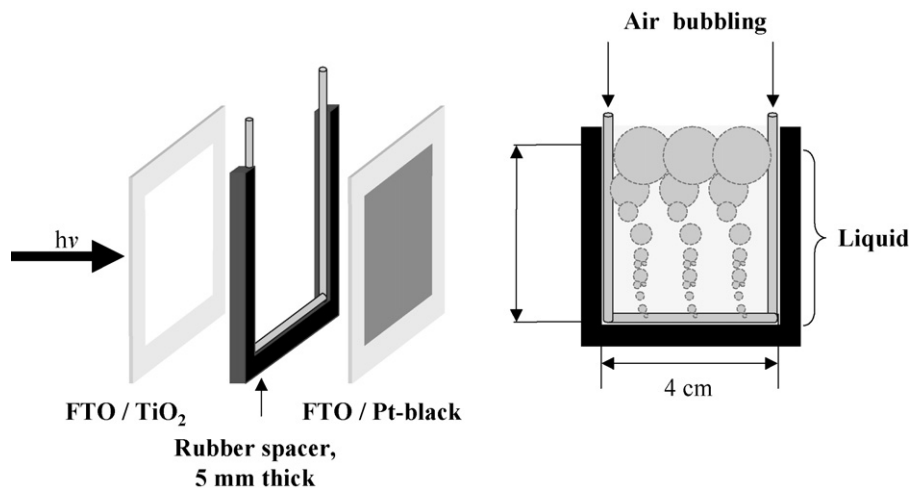

Fig. 1. Thin layer cell (Type 2); size $5\,cm \times 5\,cm$ (effective electrode area = $4\,cm \times 4\,cm$).
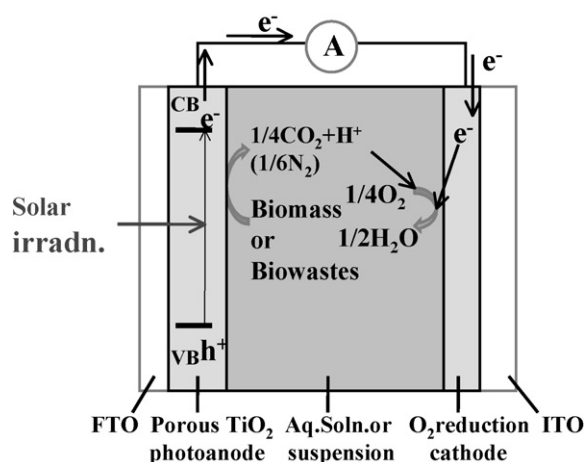
Fig. 2. Principle of biophotochemical cell (BPCC) for solar decomposition of biomass and its wastes with simultaneous electrical power generation.

3. Results and discussion

3.1. Photochemical decomposition by BPCC and its application to biomass wastes

The photochemical decomposition mechanism of biomass in a biophotochemical cell (BPCC) composed of a highly porous TiO_2 film photoanode and an O_2-reducing cathode is schematically depicted in Fig. 2. It has been reported by our group [7–9] that aqueous solutions and suspensions of organic compounds including biomass and biowastes (human urine, waste paper slurry in water, etc.) can be photodecomposed by UV-light with simultaneous generation of electrical power. The reasons for the high activity of the BPCC capable of photodecomposing high concentration solutions or suspensions up to 0.1–1 M could be explained as follows:

(1) A highly porous semiconductor was used as a photoanode film that has a roughness factor of about 1000 when the thickness is about 10 μm.
(2) At the cathode O_2 works as electron acceptor forming either H_2O or H_2O_2, for which the redox pontentials are 1.23 V (vs. SHE at pH 0) or 0.68 V, respectively. When considering also over potential of around 0.3 V for these redox couples, natural high bias potential from 0.9 to 0.4 V (vs. SHE at pH 0) would be applied to the semiconductor photoanode, which could cause its high reactivity even without any artificial applied potential.

In the following investigations many models of biomass and biowastes such as vegetable juice, yogurt, tomatoes, orange, weeds, dead leaves, orange rind, banana rind, and pig urine, either in an aqueous solution, suspension or slurry in water, have been decomposed by solar simulator irradiation under AM 1.5 G and 100 mW cm^{-2} conditions generating simultaneously electrical power. Important procedures and methods needed for practical use of the BPCC were investigated and improved a great deal in the present paper.

Photodecomposition of human urine and other natural substances by a BPCC was reported in our previous communication [9]. As a model solution for urine, a 0.4 M urea aqueous solution (5 mL) was photodecomposed by a BPCC using a cylindrical cell (Cell 1) under 1 atm O_2 atmosphere with 100 mW cm^{-2} white light irradiated conditions. It should be noted here that the Cell 1 is not suited for efficient photodecomposition, but was used to analyze produced gases because this cell can be airtight. The amounts of CO_2 and N_2 formed by the decomposition of urea after 12 h were 12.9

Table 1
Photodecomposition of 0.17 M ammonia aqueous solution by a thin layer cell (5 cm × 5 cm; effective area = 4 cm × 4 cm) under 500 W Xenon lamp with IR cutoff filter (HA-50) at 100 mW cm^{-2} during air bubbling: I–V characteristics.

Time	Jsc/mA cm^{-2}	Voc/V	FF	Output power/mW cm^{-2}
At start	0.28	0.78	0.33	0.07
After 9 h 92% reaction	0.21	0.61	0.30	0.04

and 13.9 μmol, respectively, indicating nearly quantitative CO_2/N_2 molar ratio of 1/1 at the decomposition yield of 0.67%. During this 12 h's photodecomposition 7.8 C were passed at the outer circuit showing high charge injection yield of 97% from urea to the outer circuit when calculated based on the formed N_2 (corresponding to decomposition charges of 8.05 C) since a urea molecule is decomposed to CO_2 and N_2 by a 6e$^-$-oxidation process. This is a good result exhibiting that urea can generate nearly quantitative photocurrents by photodecomposition in the BPCC.

Among the livestock wastes, urine from pigs is a serious pollutant. One pig excretes around 3 L urine containing around 0.4 M urea as a main component averagely per day. After washing the pig urine with four times as much water as the urine, it becomes around 15 L urine/water mixture containing 0.08 M urea. Since urease is present everywhere in nature, the urea in urine is rapidly decomposed into ammonia producing 0.16 M ammonia after complete conversion of 0.08 M urea by urease, so that decomposition of ammonia is also an important subject to photodecompose and clean urine. A 0.17 M NH_3 aqueous solution (4 mL) (NH_3 = 680 μmol) was photodecomposed in a thin layer cell (Cell 2, effective TiO_2 and Pt coated area = 4 cm × 4 cm) of 5 cm × 5 cm outer size, a pretype cell for a submodule, under 100 mW cm^{-2} irradiated conditions while bubbling air. It was confirmed that the N_2 formed photochemically in the BPCC corresponded quantitatively to the decrease of NH_4^+ ion determined by an ion chromatography. The decrease of NH_4^+ in the aqueous solution after 9 h was 624 μmol indicating therefore that the photodecomposition yield of ammonia was (624/680=) 92% in 9 h. The I–V characteristics of the ammonia BPCC at the photoreaction start and after 92% decomposition are shown in Table 1. It should be noted that even after 92% decomposition, the characteristics as a photochemical cell did not change much in comparison to the large decrease of the ammonia concentration from 0.17 to 0.014 M. From these results we can estimate that solar decomposition of 0.17 M NH_3/15 L urine/water mixture for one pig/day is possible in a 92% yield by using 3 m^2 irradiation area in 9 h. This is an encouraging result at the present first stage of the trial application showing that the solar decomposition of urine from livestock wastes is a possible and realistic target for the BPCC.

Commercially available conventional photocatalyst powders can treat usually concentrations of pollutants only up to 100 ppm both in gas and liquid phases, but the present BPCC can treat pollutants up to 10^4 ppm with much less TiO_2 (more than two orders less than a powder system) coated as a thin film on an electrode. Therefore in a rough estimation, the present BPCC activity is more than four orders of magnitude as high as that of conventional TiO_2 powder photocatalysts.

3.2. The effect of air bubbling

In order to investigate the effect of air bubbling in a thin layer type cell (Cell 2; effective electrode area = 4 cm × 4 cm), an aqueous solution of 0.5 M glycine (+0.1 M Na_2SO_4 electrolytes) was used, and the results are shown as I–V characteristics in Fig. 3 without and with air bubbling. Quantitative formation of CO_2 and N_2 was already reported by us before [8]. Without air bubbling the I–V curves degraded quickly with time probably due to the rapid O_2 consumption at the O_2-reducing cathode. It is clear that air bub-
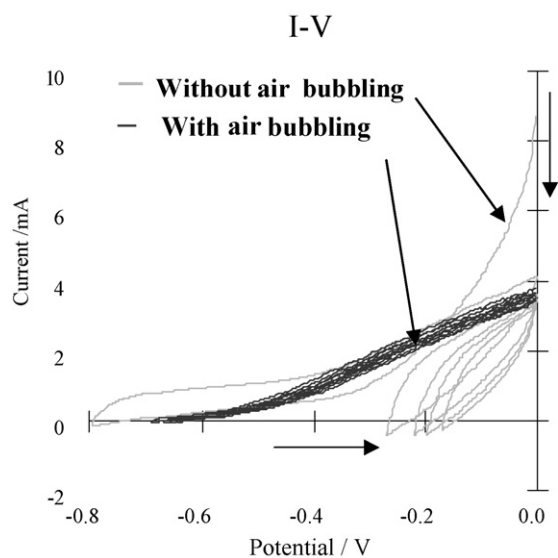
Fig. 3. Effect of air bubbling for a 0.5 M glycine aqueous solution (+0.1 M Na_2SO_4 electrolytes) in a thin layer type cell (5 cm × 5 cm) under 100 mW cm^{-2} irradiation. The I–V curves without air bubbling (grey lines) decayed quickly, while the I–V curves with air bubbling (black lines) showed much better and stable behavior.

bling improved remarkably the I–V characteristics exhibiting much more stable behavior and higher fill factors under air bubbling than those without air bubbling. The slight and gradual degradation of the I–V curves with time under air bubbling is ascribable to the water evaporation due to the bubbling as observed by the decrease of the solution in the cell.

The BPCC is regarded as a kind of fuel cell for which theoretical energy conversion efficiency from the fuel energy to electrical power can be represented by $\eta = (\Delta G^\circ / \Delta H^\circ) \times 100\%$. Its conversion efficiency (η) is usually very high in comparison to conventional electrical power plants that simply combust fuels and utilize the produced heat to rotate dynamo generating electrical power whose conversion efficiency is usually only 40% in a maximum case. However, for fuel cells, theoretical η is 83% for hydrogen fuel cell, 89% for ammonia, 97% for methanol, and 100% for graphite. Another type cell was used which is composed of FTO/TiO_2/3 mm thick spacer/MEA cathode (containing Pt-carbon catalyst, see Section 2)/stainless steel mesh/air phase, in order to use air phase O_2 for reduction at the cathode. This type cell with a 0.5 M glycine (+0.1 M Na_2SO_4 electrolytes) aqueous solution under 100 mW cm^{-2} irradiation gave the performance, Jsc = 0.47 mA cm^{-2}, Voc = 1.08 V, and FF = 0.57. As mentioned before, the BPCC can in principle produce charges at the outer circuit nearly quantitatively from the organic compounds. When assuming a charge injection efficiency from glycine into the outer circuit to be 97% mentioned before for a urea case, the above result demonstrates that the energy conversion efficiency from glycine to electrical power can be 50% (=0.97 × (1.08 V/1.2 V) × 0.57(=FF) × 100, where 1.2 V is the theoretical photovoltage generated by glycine) in the present non-optimized preliminary case, which is already higher than a conventional electrical power plant.

3.3. Fabrication of larger size cells

For a practical use of the biophotochemical cell, it is of importance to enlarge the cell size to fabricate a module (a basic device for practical use) without decreasing the cell performance. In a usual solar cell such as a dye-sensitized solar cell (DSSC), enlargement of a cell size decreases the cell performance if the cell size is enlarged, mainly due to the enhanced charge

Table 2
Effect of electrode area in the performance of BPCC for a 0.5 M glycine aqueous solution (+0.1 M Na_2SO_4) on the I–V characteristics.

Effective electrode area/cm × cm (cm^2)	Isc/mA	Jsc/mA cm^{-2}	Voc/V	FF
1 × 1 (1)	0.31	0.31	0.82	0.21
2 × 2 (4)	0.93	0.23	0.70	0.25
4 × 4 (16)	3.75	0.23	0.68	0.22
5 × 5 (25)	6.97	0.28	0.73	0.25
9 × 7 (63)	18.7	0.30	0.67	0.28
19 × 16 (304)	39.7	0.13	0.68	0.25

UV-light intensity, 8.3 mW cm^{-2} for 1, 4, 16, 25, and 63 cm^2 cells, and 3 mW cm^{-2} for the 304 cm^2 cell.

recombination. In the present BPPC it was tried by using a 0.5 M glycine (+0.1 M Na_2SO_4 electrolytes) aqueous solution to simply enlarge the size of the thin layer type cell (Cell 2 with using Ti-nanoxide paste to prepare a TiO_2 film) from the cell size of 2 cm × 2 cm (effective electrode area of 1 cm × 1 cm), to 3 cm × 3 cm (2 cm × 2 cm), 5 cm × 5 cm (4 cm × 4 cm), 6 cm × 6 cm (5 cm × 5 cm), 10 cm × 10 cm (9 cm × 7 cm), and finally to 20 cm × 20 cm (19 cm × 16 cm), and the results are shown in Table 2. Note that the irradiation conditions for the cells from 2 cm × 2 cm to 10 cm × 10 cm were 8.3 mW cm^{-2} UV region light irradiated either with a xenon or Xe–Hg lamp, but that the cell (20 cm × 20 cm) was irradiated by different UV intensity of 3 mW cm^{-2} with a high pressure Hg lamp due to a technological problem of obtaining a large irradiated area to cover the whole large cell. Table 1 exhibits clearly that enlargement of the cell size does not change much the cell performance except the 19 cm × 16 cm (effective area) size cell that adopted weaker light intensity. For the BPCC this result is promising for future since this device might need to circulate biomass solution or suspension in water, which would not be easy if small size cells have to be combined for fabricating a module. We could now conclude that the 10 cm × 10 cm or the 20 cm × 20 cm cell can be a submodule, so that based on this submodule a module can be fabricated easily, simply by connecting more than two submodules in an electrically series or parallel way, e.g., combination of four pieces of 20 cm × 20 cm submodules makes a 40 cm × 40 cm module, and nine submodules can make a 60 cm × 60 cm module.

3.4. MnO_2 for O_2-reducing catalyst in place of precious Pt

It is important to use a low cost catalyst for O_2 reduction at the cathode in place of precious Pt catalyst. It was found that MnO_2 can work as an O_2-reducing catalyst almost the same as Pt. The characteristics of a thin layer type biophotochemical cell (BPCC with closed conditions under O_2 or Ar) with either Pt or MnO_2 cathode catalyst in combination with a nanoporous TiO_2 photoanode were investigated in an aqueous solution of 0.1 M glycine (+0.1 M Na_2SO_4 electrolyte), and the results are shown in Fig. 4. For this study MnO_2-carbon composite material was used as the catalyst (see Section 2). Although Voc was lower for the MnO_2 catalyst, Jsc was higher for MnO_2 than the Pt case. Both the catalysts therefore exhibit similar conversion efficiency. It should be noted here that both Voc and Jsc tended to decrease with time during repeated I–V scanning, which can be interpreted by rapid O_2 consumption in the photoelectrochemical reaction because the present cells were operated in O_2 or Ar atmosphere under closed conditions. The hysteresis of both the I–V characteristics is ascribed to a slow charge transfer process of the 9e$^-$-electron decomposition of glycine, which was often observed in the BPCC reported earlier by us [7–9]. Under Ar atmosphere for the MnO_2 catalyst the I–V characteristics were only low, but they produced some electrical power, which could be caused by a small amount of air leaked in the cell due to the difficult sealing of the thin layer type cell.
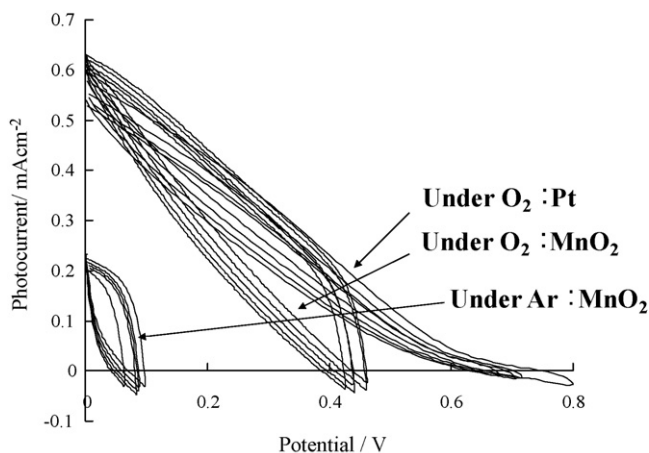
Fig. 4. Characteristics of a thin layer type biophotochemical cell (BPCC, with closed conditions under O_2 or Ar) with Pt or MnO_2 cathode catalyst in combination with a nanoporous TiO_2 photoanode; both the electrodes were in contact with an aqueous solution of 0.1 M glycine (+0.1 M Na_2SO_4 electrolyte). Light source: Xe lamp with an IR cutoff filter HA-50 at the white light intensity of 100 mW cm^{-2}. Sweep direction, $0 \rightarrow 0.8 \rightarrow 0$ V.

In another experiment the irradiation (at 100 mW cm^{-2}) of a 1 cm^2 TiO_2 anode and a C/MnO_2 cathode thin layer BPCC containing 0.5 M ammonia under air gave the I–V characteristic parameters; Jsc 0.31 mA cm^{-2}, Voc 0.88 V, and FF 0.37, which was also comparable to those with a Pt-coated cathode. The turnover number of the MnO_2 catalyst used in a 0.1 M glycine aqueous solution in a cylindrical cell under O_2 atmosphere (Cell 1) was 3.0 in 6.5 h as estimated from the used MnO_2 and formed CO_2 indicating that the MnO_2 can work as a catalyst for O_2 reduction.

3.5. Towards utilizing solar visible light in future

Up to present only a nonsensitized TiO_2 porous film has been used for this BPCC, so that the energy conversion efficiency based on the total incident solar energy is only low since the energy fraction of the UV-light utilizable by the TiO_2 is limited (only 4–5% UV-light in the total solar irradiation on the earth). It is desirable to use visible light to enhance photodecomposition and electrical power generation. Although it is not the aim of the present paper to use visible light for the BPCC, the first trial was conducted to prove that sensitized BPCC is in principle possible. It has been well known in the Graetzel's cell [6] that sensitization of a porous TiO_2 film is effective if I$^-$ is used as a donor for the oxidized Ru complex sensitizer formed after injecting an electron from the photoexcited sensitizer to the porous TiO_2. It is important in the BPCC if an oxidized form of a sensitizer can oxidatively decompose organic compounds or biomass to CO_2. It is known that Ru(bpy)$_3$$^{2+}$ complex, a famous sensitizer theoretically capable of photodecomposing water by visible light, has a high oxidation ability in its oxidation state of Ru^{3+} (1.27 V vs. SHE at pH 7) [10]. The question now is if its 3+ complex can decompose organic compounds to CO_2. In order to prove this, an aqueous phase photochemical reaction of glycine was conducted by using Ru(bpy)$_3$$^{2+}$ and an acceptor, $K_2S_2O_8$, by using visible light. We have already reported by observing an *in situ* visible absorption spectral change under visible light irradiation that the Ru(bpy)$_3$$^{2+}$ complex is photochemically oxidized to 3+ complex very rapidly in the presence of $K_2S_2O_8$ under irradiation since the $K_2S_2O_8$ can

work as a strong acceptor for the photoexcited Ru(bpy)$_3$$^{2+}$ forming its 3+ complex [11]. It was confirmed that photochemical decomposition of 0.1 M glycine aqueous solution (5 mL) in the presence of 0.1 mM Ru(bpy)$_3$$^{2+}$ and 10 mM $K_2S_2O_8$ takes place rapidly under Ar with visible light irradiation (intensity 100 mW cm^{-2}) forming 835 µL CO_2 in 1 h (=34.1 µmol CO_2, formation of $2CO_2$ from glycine is a 6e$^-$ process, so that it corresponds to 102 µmol e$^-$ process) that corresponds nearly quantitatively to the 50 µmol $K_2S_2O_8$ (2e$^-$ oxidant, so that it is totally 100 µmol e$^-$ oxidant) used in the reaction mixture. Moreover, it has already been established in our previous paper that NH$_3$ is decomposed by Ru(bpy)$_3$$^{3+}$ to N$_2$ under alkaline conditions over pH 9.24 (refer pK_a of NH$_4$$^+$ = 9.24) [10]. It has therefore been proved that the complex can work as a good sensitizer for the BPCC for visible light decomposition of organic compounds to CO_2 and N$_2$ if it can stably be attached to a TiO_2 porous structure while the TiO_2 works as an acceptor for the photoexcited Ru complex. Since stable attachment of the complex onto a nanoporous TiO_2 film was not easy and needs still research time, it should be the subject for near future investigation.

4. Conclusion

In the present paper it was demonstrated by developing more efficient methods and cells as well as high cost-performance MnO_2 O_2-reducing catalyst that BPCC can be practically used to photodecompose and clean biomass wastes under solar irradiation (at present UV region light) with simultaneous generation of electrical power. It was estimated that the present BPCC system is much more active than conventional powder photocatalyst systems by more than four orders of magnitude if based on the amount of the TiO_2 used. Moreover, it was elucidated that module production involves in principle no problem by enlarging the thin layer cell. It has also been shown that utilization of solar visible light would in principle be possible for generating a larger scale electrical power from biomass wastes in the near future.

References

[1] C.J. Stevens, N.B. Dise, J.O. Mountford, D.J. Gowing, Science 303 (2004) 1876.
[2] Biomass Handbook, Society of Energy, Japan ed., 2005.
[3] H. Gerischer, Z. Phys. Chem. 26 (1960) 325.
[4] K. Honda, A. Fujishima, Nature 238 (1972) 37.
[5] A. Fujishima, K. Hashimoto, T. Watanabe, TiO$_2$ Photocatalysis—Fundamental and Applications, BKC Inc., Tokyo, 1999.
[6] B. O'Regan, M. Graetzel, Nature 353 (1991) 737.
[7] M. Kaneko, J. Nemoto, H. Ueno, N. Gokan, K. Ohnuki, M. Horikawa, R. Saito, T. Shibata, Electrochem. Commun. 8 (2006) 336.
[8] J. Nemoto, M. Horikawa, K. Ohnuki, T. Shibata, H. Ueno, M. Hoshino, M. Kaneko, J. Appl. Electrochem. 37 (2007) 1039.
[9] M. Kaneko, H. Ueno, K. Ohnuki, M. Horikawa, R. Saito, J. Nemoto, Biosens. Bioelectron. 23 (2007) 140.
[10] M. Kaneko, I. Okura (Eds.), Photocatalysis—Science and Technology, Kodansha/Springer, 2002.
[11] M. Kaneko, N. Katakura, C. Harada, Y. Takei, M. Hoshino, Chem. Commun. 2005 (2005) 3436.