Catal Lett (2012) 142:469–479
DOI 10.1007/s10562-012-0783-7

Direct Biomass Fuel Cell (BMFC) with Anode/Catalyst Comprising a Nanocomposite of a Mesoporous n-Semiconductor Film and a Metal Thin Layer: A New Concept of Catalyst Design

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Received: 24 November 2011 / Accepted: 12 February 2012 / Published online: 6 March 2012
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Abstract We designed an efficient direct biomass fuel cell (BMFC) anode and prepared a nanocomposite [base electrode/mesoporous n-semiconductor (SC) thin film/metal thin layer]. A Pt thin layer was photodeposited onto a mesoporous 20-μm thick TiO_2 thin film having a roughness factor of 2000, which was coated on an F-doped tin oxide/glass base electrode (FTO). This anode/catalyst nanocomposite was efficient at decomposing aqueous solutions of glucose and other biomass-related compounds in combination with an O_2-reducing cathode the other side of which was exposed to ambient air. The nanocomposite exhibited sharp optimum conditions at the atomic ratio of Pt/Ti = 0.33 in the BMFC, generating high electrical power of 2 mW cm^{-2} without any light irradiation or bias potential when using a 1 M glucose aqueous solution. This output power is 20 times as large as that generated by a mesoporous TiO_2 film anode under UV-light (18 mW cm^{-2}) irradiation. At this ratio, the coated Pt specifically exhibited metallic luster, and its average Pt thickness on the mesoporous TiO_2 nanostructure was calculated to be 0.40 nm. The high BMFC activity was interpreted by the simultaneous Schottky-junction/Ohmic contact nature of the nanocomposite. Other biomass compounds such as sucrose, ethanol and polysaccharides were also effective as direct fuels for the BMFC. Immediately after soaking this composite anode without a cathode in a glucose aqueous solution, continuous evolution of H_2 bubbles was observed from the anode surface. The electrical power generation and H_2 production are easily changed by connecting and disconnecting a cathode, respectively. Based on a simple design and calculation, the present system with glucose fuel has the potential to construct a module stack of 2 kW m^{-3}. Simultaneous material/energy circulation by using the BMFC with biomass and its waste fuel is proposed for application in future social systems.

Keywords Biomass fuel cell · Glucose · Mesoporous semiconductor · Titanium dioxide · Platinum thin layer

1 Introduction

Our current rate of consumption of fossil fuels is unsustainable and according to the first law of thermodynamics (energy can be transformed, i.e. changed from one form to another, but cannot be created or destroyed), human society on Earth faces tremendous challenges in meeting its energy requirements. Moreover, according to the 2nd law of thermodynamics, entropy (a parameter representing the degree of disorder) always increases in the course of spontaneous chemical processes in a closed system, and our social systems will disintegrate someday in the future due to increased entropy. These two thermodynamic laws do not allow the present state of society to continue eternally due to the limited energy resources as well as to the increasing entropy of the Earth as a closed system. Nevertheless, organisms have continued to live on the Earth for 3.5 billion years supported by solar irradiation either directly or indirectly through photosynthesis, as the Earth is not a closed system but open to solar irradiation.

Photosynthesis is a photochemical process producing $C_6H_{12}O_6$ structure compounds such as glucose, sucrose, polysaccharides, and cellulose from carbon dioxide and water.

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$$CO_2 + 2H_2O + 8\,\text{visible-light photons} \rightarrow 1/6(C_6H_{12}O_6) + O_2 + H_2O \quad (1)$$

$\Delta G^\circ = 480$ kJ $(CO_2\ \text{mol})^{-1}$, $\Delta H^\circ = -467$ kJ $(CO_2\ \text{mol})^{-1}$, $\Delta S^\circ = -43.6$ J K^{-1} $(CO_2\ \text{mol})^{-1}$.

As a result of this photosynthesis, positive free energy and negative entropy (=negentropy) are produced. The free energy produced is utilized as an energy resource by living things, and the negentropy compensates for the entropy increase caused by their metabolic processes. It is now urgent to develop a sustainable energy resource system based on solar irradiation instead of consuming the fossil fuels built up over hundreds millions of years. An artificial photosynthetic system producing chemical energy such as hydrogen from solar irradiation and water is a candidate, but it would take a long time to develop such a system and make major changes to our energy system infrastructure for practical use. On the other hand, utilization of biomass itself produced by solar irradiation is a promising candidate for practical use in the near future. The oxidative decomposition of biomass and its related compounds, which corresponds to the reverse reaction of Eq. 1, is a down-hill process that can in principle take place without providing any energy such as photons if a proper active catalyst is developed.

The details are described in Sect. 4. A tremendous amount of biomass waste (about 130 EJ year^{-1} world^{-1} where E is 10^{18}) is present in society as a serious environmental pollutant, yet it has the potential to meet nearly 1/3 of our primary energy demand (480 EJ year^{-1} w^{-1}). It is extremely important to decompose and clean this biowaste pollutant in order to protect our environment against pollution, during which a large amount of free energy is liberated corresponding to the backward reaction of Eq. 1. Thus, simultaneous environmental cleaning and sustainable energy resource creation are possible if technology is developed that produces energy by decomposing biomass materials. Such a system resembles the activities of living things on Earth.

Biomass energy conversion systems are already applied to use ethanol produced from corn and sugar cane, etc. as fuel for automobiles. Problems of biofuel are its cost, the energy needed to produce a pure fuel compound from biomass, as well as acquirable net energy from the fuels based on lifecycle assessment (LCA) about energy. This LCA should include also necessary energy to recycle all the industrial facilities and instruments to produce the fuels. For this reason, it is desirable to develop a direct biomass fuel cell (BMFC) that decomposes biomass or even biomass waste to generate electrical power.

Glucose and other compounds with the repeating unit ($C_6H_{12}O_6$) are the most basic biomass compounds (see Eq. 1). One glucose fuel cell has been investigated by using a Pt-Ru catalyst supported on carbon [1]. However, in this glucose fuel cell only $2e^-$ glucose oxidation was reported among the total $24e^-$ decomposition of glucose to CO_2 producing mainly gluconic acid due to the limited oxidation ability of the catalyst; the situation is the same for an enzymatic biofuel cell. In addition to this, microbial fuel cells (MFCs) have also been investigated, but the drawback of MFCs is the low power density, e.g., 4.6 μW cm^{-2} [2]. These direct biomass FCs are in many cases fuel-specific, and, moreover, only selective and partial decomposition of fuel has been possible.

In order to create an efficient anode catalyst for a direct biomass fuel cell, we designed and developed a new catalysis concept. We found that a mesoporous n-semiconductor (SC) forms simultaneously a Schottky junction and an Ohmic contact with a redox electrolyte aqueous solution [3]. The Schottky junction makes the conduction band bend near the SC surface forming a depletion layer (=space charge layer) where the majority of carriers, electrons for n-SC, are depleted, and the Ohmic contact enables a conventional redox response on the SC surface, as mentioned later in Sect. 3.1 and shown in Fig. 5. In addition, if a sufficient number of electrons are injected from the biomass (electron donor) present in the contacted water phase into the conduction band of a mesoporous n-SC, the injected electrons work as charge carriers making the SC highly conductive like graphite even if the SC itself is nearly insulating [4].

Based on our previous report, we designed an efficient fuel cell (FC) anode/catalyst nanocomposite comprising a mesoporous n-semiconductor and a metal thin layer. This nanocomposite catalyst is capable of efficiently decomposing biomass and its related compounds as described in Sect. 3.1. This article reports the preliminary results, and proposes a possible sustainable energy resource system based on biomass and its waste, which has the potential to meet a large part of the energy demands of society.

2 Experimental

2.1 Materials

To prepare a nanoporous TiO_2 film, Ti-nanoxide (T/SP) paste (average particle size 13 nm, anatase ~90% and rutile ~10%) was purchased from Solaronics Co., Ltd. F-doped SnO_2 conductive glass (FTO, surface resistance 10 Ω/sq cm) was purchased from AGC Fabritec Co., Ltd. All other chemicals were of commercially available purest grade, and used as received.

2.2 Preparation of Electrodes

Commercially available Ti-nanoxide (T/SP) paste was used for mesoporous TiO_2 thin film preparation. The paste was coated on a fluorine-doped SnO_2 coated glass (FTO, 2 cm × 1 cm size) by a squeeze coating method with a coated area of 1 cm × 1 cm. For this process, adhesive tape (thickness 140 μm) was used as a spacer to adjust the TiO_2 film thickness usually to 20 μm obtained after calcination. The TiO_2 paste layer on FTO was dried at room temperature, and then calcined at 450 °C for 30 min, giving a mesoporous TiO_2 thin film of 20-μm thick having a roughness factor of ca.2000. This roughness factor was estimated from the monomolecularly adsorbed amount of bis(bipyridyl)-Ru dye. The effective surface area of 10-μm mesoporous TiO_2 film was 1,000 cm^2 in comparison to the apparent surface area of the TiO_2 (1 cm^2), which equates to a 2,000 roughness factor for a 20-μm film. This measured roughness factor is reasonable when considering a standard roughness factor of around 1,000 for a 10-μm mesoporous TiO_2 thin film [5]. The mesoporous TiO_2 thin film itself is nearly the same as the material utilized in a dye-sensitized solar cell [6], and is used as an electron acceptor from I_3^-/I^- redox electrolytes dissolved in a liquid organic medium. This mesoporous TiO_2 thin film has a nanocrystalline structure with Ti^{4+} [5]. In order to prepare a nanocomposite of a mesoporous TiO_2 thin film and a Pt metal layer, Pt metal was photochemically deposited from an aqueous $K_2{}^+[Pt(IV)Cl_6]^{2-}$ solution in the presence of a methanol electron donor onto a mesoporous TiO_2 thin film (thickness 20 μm) at the atomic ratio of $Pt/Ti = 0\text{–}0.50$ under UV-light irradiation in ambient air. To control the ratio, a certain amount of $K_2{}^+[Pt(IV)Cl_6]^{2-}$ was dissolved in 5 mL water containing 3 vol% methanol, and reductive photodeposition of Pt onto a mesoporous TiO_2/FTO was conducted completely using 500 mW cm^{-2} white light from a 500 W xenon lamp. More than 99% Pt was photodeposited onto the TiO_2 as concluded from the disappearance of the absorption maximum at 261 nm of the remaining Pt salt in the solution. The deposited Pt amount was confirmed also by weight after drying the formed TiO_2/Pt nanocomposite on FTO at 50 °C. For instance, at the peak ratio of $Pt/Ti = 0.33$, 26.8 μmol Ti was contained in a 20-μm TiO_2 film, so that $Pt = 26.8\ \mu mol \times 0.33 = 8.84\ \mu mol = 1.72$ mg. We obtained this theoretical weight increase for the TiO_2 film after photodeposition. The accuracy in the weight measurement is ±2%. Electrochemical deposition of Pt from the same Pt complex aqueous solution did not give good results, with much Pt having been deposited as a suspension in the solution phase in this case.

In order to bring another side of the Pt-mesh cathode into contact with air, a membrane electrode assembly (MEA) (1 cm × 1 cm) purchased from FC Development Co., Ltd., Japan, was used. This MEA is composed of three layers, i.e., [carbon paper/Pt-carbon catalyst-dispersed Nafion 117 (cation exchange sulfonated perfluoroalkyl polymer) membrane/Pt-carbon catalyst-dispersed carbon paper], for which the first layer is in contact with the electrolytes liquid, and the last layer is exposed to ambient air (see also Fig. 1). The Pt-mesh is used for both electric communication with the anode via the outer circuit and stabilization of the MEA membrane; this Pt-mesh can be substituted with Ti- or SUS (stainless steel)-mesh in future.

2.3 Cell and Measurements

A cell (1 cm × 1 cm × 3 cm) was designed and fabricated by poly(methyl methacrylate) plastic plates as shown in Fig. 1. The cell chamber contains water with solubilized or suspended glucose or other related compounds used as fuel, and the side of the O_2-reducing cathode (MEA) faces ambient air.

In an aqueous solution of 1 M ($M = mol\ L^{-1}$) glucose containing also 1 M NaOH (pH 14) and 0.1 M Na_2SO_4 electrolytes, an anode/catalyst nanocomposite comprising [FTO base anode electrode/mesoporous TiO_2 thin film/Pt thin layer] at various Pt/Ti atomic ratios and the MEA O_2-reducing cathode mentioned in the last section were soaked as shown in Fig. 1. One side of the cathode is in contact with the liquid phase and the other side is in contact with the ambient air phase. Cyclic voltammograms were measured against Ag–AgCl reference electrode under ambient air, and current density (*J*)–potential (*V*) characteristics (*J*–*V* curve) were measured without a reference electrode by a potential scanning method. When the anodic and the cathodic scans exhibit hysteresis in the *J*–*V* curve, average values for the forward and the backward scans were adopted to obtain *J*–*V* parameters. All the measurements were conducted at 25 °C.

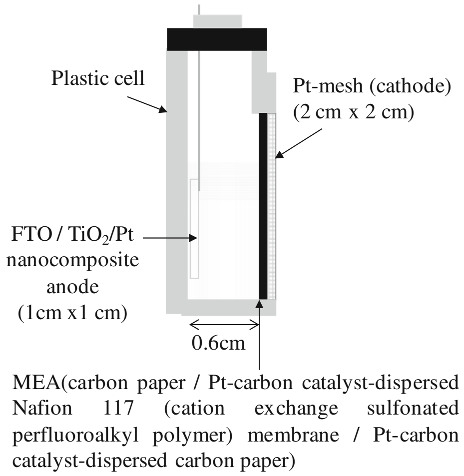

Fig. 1 Side view of a direct biomass fuel cell (BMFC) (inside 2.5 cm × 2.5 cm × 0.6 cm = 3.75 cm^3) used for CV (with Ag–AgCl reference electrode), and *J*–*V* measurements with membrane electrode assembly (MEA)/Pt-mesh cathode without reference electrode. One side of the cathode is in the aqueous solution and the other side faces ambient air via the Pt-mesh

3 Results and Discussion

3.1 Design of an Anode/Catalyst Nanocomposite [FTO Anode/n-Semiconductor (SC)/Metal Thin Layer Catalyst] for BMFC by Utilizing Simultaneous Schottky Junction/Ohmic Contact Behavior Between Mesoporous n-SC and Metal Thin Layer

Our present strategy is to utilize a possible simultaneous Schottky-junction/Ohmic contact of a mesoporous n-SC thin film coated with a metal thin layer, as inferred from our previous report on a mesoporous TiO_2 thin film in contact with an aqueous electrolyte solution [3]. Such nanocomposite is expected to work as an anode/catalyst for a BMFC without inputting any external energy such as light or bias potential. The design focused on the following points (see also Fig. 5 shown later):

(1) A large effective surface area of a mesoporous n-SC thin film (e.g., 2,000 times the effective surface area as much as the apparent one for a TiO_2 thin film with 20 μm thickness calcined from average 13 nm size TiO_2 particles): this mesoporous n-SC film was expected to form a nanocomposite with a metal catalyst (Cat) layer such as Pt for biomass decomposition.

(2) Ability to form a Schottky junction/Ohmic contact between a mesoporous n-SC and a metal catalyst (Cat) layer.

(3) Intermediate complex formation or interaction of biomass present in the contacted aqueous phase with the metal Cat layer followed by electron transfer from the biomass into the Cat layer.

(4) Active transport of the injected electrons from the coordinated or interacted biomass through the Cat into the n-SC bulk conduction band (CB) by utilizing the Ohmic contact and the bended band of the Schottky junction in the depletion layer (regarding the Schottky junction, see also Fig. 5), which could shift the equilibrium of the intermediate complex of $[\text{Cat/biomass}]_{\text{complex}}$ towards products;

$$\text{Cat} + \text{biomass} \rightleftarrows [\text{Cat-biomass}]_{\text{complex}} \rightarrow \text{Cat}^- + \text{product}^+ \quad (2)$$

$$\text{Cat}^- \rightarrow \text{Cat} + \text{efficient}\,e^-\,\text{transport through the Ohmic contact and Schottky junction from the n-SC interface into the SC bulk,} \quad (3)$$

(5) Transport of the injected electrons from the SC bulk conduction band through the base electrode (=FTO) and the outer circuit towards the O_2-reducing cathode.

Even if a SC is nearly insulating like TiO_2 (original conductivity less than 10^{-10} S cm^{-1}), the injected electrons from biomass make the SC highly conductive. For instance, we showed that a mesoporous TiO_2 thin film exhibits a high conductivity of 2.3×10^4 S cm^{-1} (the same or even higher than graphite) due to the injected electrons from a contacted glycine aqueous solution under UV-light irradiation. This conductivity was calculated from the resistance of 0.43 Ω at a 10-μm thick TiO_2 thin film as investigated by alternating current impedance spectroscopy [4]. We also showed that the carrier (e^-) density in a mesoporous TiO_2 thin film in contact with a methanol aqueous solution is 6.96×10^{19} cm^{-3} under UV-light irradiation [3], which is a larger order of magnitude than graphite ($\sim 10^{18}$ cm^{-3}). These facts imply that, when a sufficient amount of electrons is injected from a contacted liquid phase into the mesoporous TiO_2 thin film, the TiO_2 works as an even better electric conductor than graphite. These results also demonstrate that the resistance between SC particles is negligible.

Based on this concept, we designed a new nanocomposite anode, and prepared it from a mesoporous n-SC thin film and metal catalyst thin layer as follows.

3.2 Preparation of an Anode/Catalyst nanocomposite ([FTO/Mesoporous TiO_2 Film/Pt Thin Layer) for BMFC and its Characteristics with Glucose Fuel

TiO_2 is often loaded with Pt metal to enhance its photocatalytic activity. In this case the loading ratio is limited to ca. 2 wt%, which corresponds to an atomic ratio of ca. Pt/Ti = 0.01, because the deposited Pt-black has a strong filter effect to hinder UV light irradiation on the TiO_2. We aimed not to enhance its photocatalytic activity, but to fabricate a new composite catalyst working without irradiation by making a nanocomposite between a mesoporous TiO_2 film and a Pt metal layer, so we started at a higher ratio from Pt/Ti = 0.01.

In an aqueous $K_2{}^+[Pt(IV)Cl_6]^{2-}$ solution containing methanol as a reductant, Pt metal was photochemically deposited onto a mesoporous TiO_2 thin film (20 μm thickness, coated on an FTO) by changing the atomic ratio of Pt/Ti, under UV-light irradiation in ambient air. The Pt/Ti ratio was calculated as follows. The Ti-nanoxide (T/SP) paste contains TiO_2 fine powder with an average diameter of 13 nm composed of 90% anatase (density = 3.90 g cm^{-3}) and 10% rutile (density = 4.23) giving an average density of 3.93. By measuring the average weight of coated TiO_2 films (e.g., 10 cm^2 with 17 μm thickness, 16 cm^2 with 13 μm thickness, etc.), the TiO_2 weight was determined as 107 μg $μm^{-1}$ cm^{-2}, which results in TiO_2 = 2.14 mg (=26.8 μmol TiO_2 repeating unit) for a

Table 1 The effect of atomic ratio Pt/Ti on output electrical power using 1 M glucose aqueous solution at pH 14 (+0.1 M Na_2SO_4)

Atomic ratio/Pt/Ti	J_{sc}/mA cm^{-2}	V_{oc}/V	*FF*	Output power/mW cm^{-2}	Note
0	0	0	0	0	
0.008	0.20	0.88	0.25	0.04	
0.083	2.0	1.04	0.38	0.78	
0.17	2.4	0.62	0.32	0.47	
0.25	1.0	0.42	0.12	0.05	
0.29	1.9	0.45	0.25	0.21	
0.30	1.8	0.42	0.25	0.19	
0.31	5.6	0.82	0.25	1.15	Metallic luster surface
0.32	2.3	1.02	0.55	1.29	Metallic luster surface
0.33	5.1	1.29	0.30	1.97	Metallic luster surface
0.34	5.0	0.79	0.25	0.99	Metallic luster surface
0.42	0.82	0.53	0.25	0.11	
0.50	2.7	0.54	0.18	0.26	
(Pt foil only)	0.08	0.70	0.01	0.04	TiO_2 film partially destroyed

1 cm^2 and 20-µm thick film. In a photoreductive deposition of Pt from its complex (see Experimental Sect. 2.2), it was confirmed that almost all the Pt was deposited onto the mesoporous TiO_2 film. The Pt/Ti atomic ratio of 0.33 gave the best results as shown later in Fig. 4. Since the effective surface area of the 1 cm^2 TiO_2 with 20 µm thickness is 2,000 cm^2 (roughness factor = 2000), the average coated thickness of the Pt atom on TiO_2 is calculated to be 0.40 nm by using the Pt metal density of 21.5 g cm^{-3} (see also Sect. 2.2). Such calculation was also conducted based on the total number of the average TiO_2 particles in a 1 cm^2 and 20-µm thick film. In this case, when assuming that 20% of the total particle surface is occupied by connection with neighboring particles, the thickness coated on the mesoporous thin film is calculated to be the same as that calculated above (0.40 nm thick). It was further calculated based on the Pt metal density that the 0.40 nm thick Pt layer is composed on average of only one layer of Pt atoms.

The formed TiO_2/Pt nanocomposite film was opaque and homogeneously black-colored with metallic luster at a ratio of Pt/Ti = 0.33, in contrast to the initial colorless and transparent TiO_2 thin film. When the surface exhibited a metallic luster, the catalytic activity was specifically high as shown in Fig. 4 and Table 1. In the initial stage of the Pt photodeposition, dull Pt-black (powders) was deposited, but afterwards near the ratio of Pt/Ti = 0.31, the TiO_2 surface started to become metallic luster while keeping the black-color of the TiO_2/Pt film. Then, the metallic luster became clearer like a Pt metal surface at Pt/Ti = 0.33 while still keeping the black color behind.

The metallic luster indicates the existence of free electrons in the Pt layer, strongly suggesting that a Pt thin layer lattice structure grew until metallic free electrons appeared. From the ratios above Pt/Ti = 0.34, Pt-black particles started to deposit on the TiO_2 surface, making the surface dull again and then the BMFC activity decreased dramatically at Pt/Ti = 0.42. Only the photodeposition of Pt induced such metallic luster appearance and good BMFC results. Electrochemical Pt deposition did not produce an efficient anode, since much Pt was deposited as Pt-black powder suspension in the aqueous phase.

As for fuel, glucose was mainly used in the present study since it is the most fundamental compound among the photosynthetic products as shown in Eq. 1; polysaccharides such as cellulose are composed of glucose units. In order to investigate cyclic voltammogram, the nanocomposite anode of (FTO/mesoporous TiO_2 film/Pt layer) and a Ag–AgCl reference electrode were soaked in an aqueous solution of 1 M glucose also containing 1 M NaOH (pH 14) and 0.1 M Na_2SO_4 electrolytes in the cell

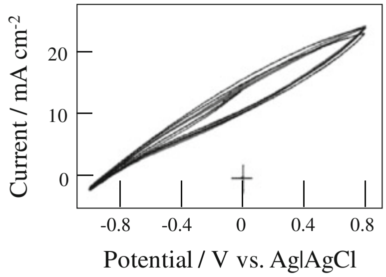

Fig. 2 Cyclic voltammogram of 1.0 M glucose aqueous solution (pH 14, +0.1 M Na_2SO_4) at the mesoporous TiO_2/Pt (Pt/Ti = 0.34) (1 cm × 1 cm) nanocomposite thin film anode under ambient air with MEA/Pt-mesh as a cathode and Ag|AgCl as a reference electrode. Scan rate, 50 mV s^{-1}

(Fig. 1) for which one side of the O_2-reducing cathode faces an ambient air phase.

The cyclic voltammogram (CV) of 1 M glucose aqueous solution (pH 14) at the Pt/Ti atomic ratio of 0.34 is shown in Fig. 2. The CV exhibits an unusual nearly straight line with a slope and a slight hysteresis without any current peak demonstrating the Ohmic nature of the current. This implies also that a diffusion-limited process, which is usual in conventional CVs, is not involved in the present CV. This CV feature is entirely different from the known CVs of glucose fuel cells at Pt–Ru catalyst dispersed in a carbon paper/Nafion/graphite anode. In such conventional cases using a Pt–Ru anode catalyst, CV typically exhibits three distinct anodic peaks at −0.79, −0.36 and 0.054 V and cathodic ones at −0.32 and −0.8 V vs. Ag–AgCl due to oxidation and reduction of glucose [1]. In this reported glucose fuel cell only a small part of the glucose energy (2 e^- among the total 24 e^-) was converted to electricity. However, as shown in Fig. 2, the Ohmic nature of the straight line shows most probably that successive electron injection from glucose into the Pt takes place at the anode.

Without a reference electrode, the current density (*J*) vs. potential (*V*) characteristics was measured under potential scan conditions (50 mV s^{-1}), and the *J*–*V* curve is shown in Fig. 3.

UV light irradiation did not affect the CV and *J*–*V* characteristics in Figs. 2 and 3, respectively. Only when the *J*–*V* characteristics did not indicate a good output when the Pt/Ti is below 0.1, UV-light irradiation increased the current to some extent (details omitted). Figure 3 also shows a straight line with only a slight hysteresis, implying also the Ohmic nature of the overall electron transport involving e^- injection from glucose into the Pt catalyst layer. This result supports successive injection of the e^- from glucose to Pt and then from the Pt layer into the TiO_2 layer, and further e^- transport via FTO and the outer circuit to the cathode reducing O_2 to H_2O there. We previously reported [7] that, when glucose was activated by holes formed under irradiation of a mesoporous TiO_2 thin film photoanode, both CV and *J*–*V* curves showed straight lines, which is the same finding as the present data in Figs. 2 and 3. In that article we showed that once glucose was activated by the photochemically formed holes by a mesoporous TiO_2 thin film, the activated glucose undergoes successive $24e^-$ oxidation forming CO_2 [7]. Although the present anode system operated without irradiation is different from such photoactivated glucose decomposition, a similar mechanism should act on the Pt surface as revealed by the same CV and *J*–*V* straight lines with Ohmic nature.

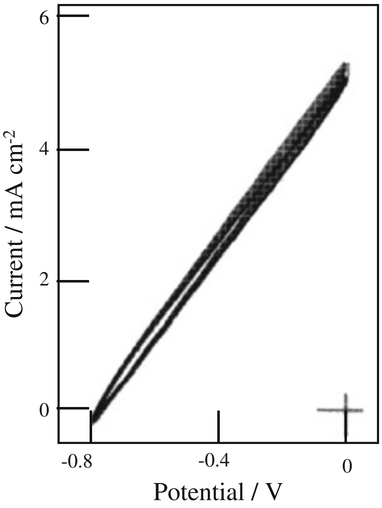

Fig. 3 *J*–*V* characteristic of 1.0 M glucose aqueous solution (pH 14, +0.1 M Na_2SO_4) at the mesoporous TiO_2/Pt (Pt/Ti = 0.34) nanocomposite thin film anode under ambient air with an MEA cathode. Scan rate, 50 mV s^{-1}

Figure 3 gives a short circuit current density (J_{sc}) of 5.0 mA cm^{-2}, open circuit potential (V_{oc}) of 0.79 V, and fill factor (*ff*) of 0.25, where *ff* is the ratio of the maximum real output wattage (*W*) on the *J*–*V* curve versus ideal maximum output (= $J_{sc} \times V_{oc}$). Depending on the anode nanocomposite composition and/or reaction conditions, CV and *J*–*V* characteristics sometimes showed hysteresis, in which case we took the average *J*–*V* values of the forward and the backward scans of the curve to obtain the *ff* value. The maximum power output can be calculated to be $W = J_{sc} \times V_{oc} \times FF = 5.0$ mA $cm^{-2} \times 0.79$ V $\times 0.25 = 0.99$ mW cm^{-2} at Pt/Ti = 0.34. The effect of the Pt/Ti atomic ratio from 0 to 0.50 on the output parameters is shown in Table 1. Without Pt, the mesoporous TiO_2 thin film itself did not work at all as an FC anode as shown in the first line data of Table 1.

By a slight change of the Pt/Ti ratio from 0.34 to 0.33, the *J*–*V* curve gave a J_{sc} of 5.1 mA cm^{-2}, V_{oc} of 1.29 V, and *ff* of 0.30 generating 1.97 mW cm^{-2}. This output wattage is almost 20 times as large as that (0.10 mW cm^{-2}) generated at a mesoporous TiO_2 thin film photoanode in a Photo Fuel Cell (PFC) under about 18 mW cm^{-2} UV region-light irradiation [8]. The present output is 1.4 times as much as the reported value of 1.38 mW cm^{-2} at 0.2 M glucose concentration with Pt–Ru/C catalyst for which, however, only $2e^-$ decomposition of glucose to gluconic acid has been reported [1] based on cyclic voltammograms exhibiting three typical anodic peaks as mentioned above. Our output data are greatly superior to the reported values, and the anode/catalyst nanocomposite is applicable also to other biomass compounds as shown later in Sect. 3.3.

The Pt/Ti ratio-dependent tendencies of the FC parameters (J_{sc}, V_{oc}, *FF*) are not simple to interpret due to the delicate mechanistic processes as mentioned later, but Table 1 exhibits a clear tendency of the output power dependence on the Pt/Ti ratio. Since the dependence is remarkable, the output power is plotted against the Pt/Ti

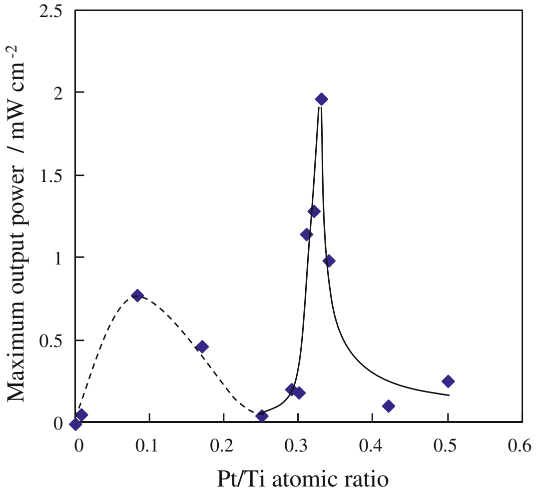

Fig. 4 Pt/Ti atomic ratio dependent maximum output power obtained by *J–V* characteristics of the glucose fuel cell with TiO_2/Pt (Pt/Ti = 0–0.5) nanocomposite thin film anode

atomic ratio in Fig. 4 in order to demonstrate it more clearly.

An atomic Pt/Ti ratio around 0.33 gave a very sharp optimum point for the output power, indicating that delicate conditions exist as to the high activity of the TiO_2/Pt composite film as an efficient BMFC anode/catalyst. When the Pt/TiO_2 nanocomposite surface exhibited metallic luster, the activity was high, but when the ratio exceeded 0.34, excess Pt-black was deposited on the lustrous Pt/TiO_2 composite film making the metallic luster dull, and at the same time the activity decreased dramatically. When the ratio was 0.50, the TiO_2 film was partially destroyed probably due to excessively deposited Pt.

It is inferred that the lustrous Pt structure appearing clearly at the Ti/Pt ratio of 0.33 is important for the FC anode/catalyst activity. The metallic luster implies the existence of free electrons in a crystalline Pt structure, showing therefore most probably conversion of the Pt layer to crystalline Pt at this ratio. Such crystalline Pt structure, the conductivity of which should be high (10^5 S cm^{-1} order), must be favorable to transport electrons injected from the substrate (glucose) through the Pt layer into the TiO_2 mesoporous layer mainly via Ohmic channels (see Fig. 5).

Figure 4 shows a broad activity peak at the Pt/Ti ratio of around 0.1 for which the average Pt layer thickness is calculated to be 0.11 nm. The output parameters were not reproduced well at this region of Pt/Ti = 0–0.2, and the CVs exhibited generally redox peaks of glucose demonstrating only partial decomposition. Moreover, UV-light irradiation enhances J_{sc} to some extent different from those at a higher Pt/Ti ratio for which no irradiation effect was observed at all. It is inferred that the nanocomposite structure around the region of Pt/Ti <0.25 must be different from that over Pt/Ti ~0.25, so we do not discuss this broad peak around 0.1 in the present preliminary stage.

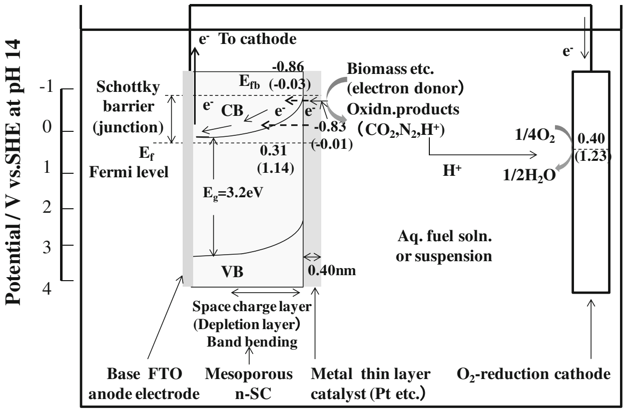

Fig. 5 Catalysis mechanism and estimated energy diagram of the nanocomposite (Base FTO electrode/mesoporous TiO_2 film/metal thin layer catalyst) forming a Schottky barrier (junction) at the interface between TiO_2 and metal as an efficient anode/catalyst for direct biomass fuel cell. The anode nanocomposite symbolizes only a surface part of one particle composing a mesoporous TiO_2 film. The numbers are reduction potential (V vs. SHE) at pH 14 and pH 0 (in the parentheses): E_g = Bandgap, VB (valence band) and CB (conduction band) bend at the interface. The *broken line arrows* indicate Ohmic e$^-$ injection. The Pt layer thickness (0.40 nm) was calculated under the Pt/Ti = 0.33 conditions for the 20-µm thick TiO_2 film

Before proposing a possible mechanistic scheme for the present device, it should first be mentioned that the present TiO_2 film is an n-type semiconductor as proved in the Refs. [3, 4, 6–10]. It has been established [11] that, when an n-SC contacts metal or an aqueous electrolyte solution the Fermi-level (E_f) of which is located between the conduction band (CB) edge and the valence band (VB) edge of the n-SC, the n-SC forms a depletion layer where majority carriers (electrons for n-SC) are depleted (also called a space charge layer). In this case both the CB and VB bend towards positive potential when going from the SC/metal interface into the SC bulk as shown in Fig. 5. Such a barrier formed at the interface between SC and metal (or aqueous electrolyte solution) is called a Schottky-junction (or liquid-junction). We have already reported Schottky barrier formation between a mesoporous TiO_2 thin film and an aqueous electrolyte solution by investigating Mott–Schottky plots, and found that when using a nanostructured mesoporous TiO_2 thin film as a n-SC, the contact exhibits both the Schottky junction/Ohmic contact nature [3]. This implies that there should be Ohmic electron injection channels from the aqueous phase via the Pt layer into the n-SC in the present nanocomposite. Moreover, enhanced electron transport channels should also exist from the SC/Pt interface towards the FTO base electrode in the space charge layer formed in the n-SC due to band bending.

These two kinds of electron transport channel (Ohmic contact and bended bands) would interconnect with each other making the present nanocomposite device (TiO_2 thin film/Pt thin layer) efficient as a BMFC anode.

For the present TiO_2/Pt contact we investigated Mott-Schottky plots proving Schottky-junction formation as well as simultaneous Ohmic contact behavior, obtaining the depletion layer thickness of 0.29 nm at 0 V vs. Ag–AgCl. This depletion layer is unusually thin due to the nanostructured TiO_2 film in comparison to conventional depletion layer thickness. However, these Mott–Schottky plots showed the complicated behavior of the present device, discussion of which is beyond the scope of the present Letter, so this will be reported elsewhere.

The flat band potential (E_{fb}) is determined by the surface energy state of the SC; it usually does not change if the surface state is not changed. The E_{fb} of a conventional TiO_2 electrode is −0.03 V vs. SHE at pH 0 (−0.86 V at pH 14) when soaked in an aqueous electrolyte solution. If adopting this E_{fb} value now, the E_{fb} is slightly more negative than the H^+/H_2 reduction potential (=0 V vs. SHE at pH 0) as shown in Fig. 5. The work function of Pt metal is 5.64 eV, and the electrochemical H^+/H_2 reduction potential is around −4.50 V vs. vacuum level at pH 0, which correlates the electrochemical potential and work function. Therefore, the Fermi level of Pt metal is 1.14 V vs. SHE at pH 0, which should be the same as the E_f of the TiO_2 film after forming contact with the Pt metal layer. The O_2 reduction potential for the O_2/H_2O at the cathode is 1.23 V vs. SHE at pH 0 (0.40 V vs. SHE at pH 14). The redox potential of glucose was calculated from the thermodynamic data for the reaction, glucose/CO_2 ($\Delta G = -394$ kJ CO_2 mol^{-1}), to be −0.013 V vs. SHE at pH 0 (−0.83 V vs. SHE at pH 14). In Fig. 5, these estimated potential values (vs. SHE at pH 14) are shown together with those at pH 0 (in the parentheses). According to Fig. 5, the theoretical V_{oc} should be 0.40–(−0.86) = 1.26 V, which is nearly the same as the V_{oc} value of 1.29 V at Pt/Ti = 0.33 shown in Table 1 supporting the finding that the E_{fb} value would be reasonable even though these V_{oc} values are not strictly the same.

The detailed mechanism of the glucose decomposition was not determined in the present preliminary study, but it is inferred as follows. First, glucose would form a kind of complex with the catalyst Pt, and then electron(s) would be injected from the glucose into the Pt in an intermediate complex state. After such e^- injection, since E_{fb} is nearly the same or even more negative than the glucose reduction potential, the Schottky barrier would hinder transport of the injected electron(s) into the TiO_2 layer in the conventional case. However, since the present n-SC/Pt contact would also have the same Ohmic nature as that (mesoporous TiO_2 thin film in contact with electrolytes aqueous solution) reported in our previous paper [3], the injected electron(s) in the Pt layer would further be injected into the n-SC layer through Ohmic channels. The very thin depletion layer (e.g., 0.29 nm at 0 V vs. Ag–AgCl for Pt/Ti = 0.33 as mentioned above) would also facilitate such electron transport from Pt to n-SC. Thus, the bended band structure that must be interconnected with Ohmic channels should facilitate injected electron transport to the FTO conducting layer, and finally via the outer circuit to the cathode reducing O_2 to H_2O there. The decomposition intermediates of glucose should have various potential values depending on the structure, but such Ohmic channels distributing widely within the whole range from E_{fb} to E_f would make electron injection from various potential conditions of glucose intermediates to TiO_2 possible. The unusual Ohmic linear CV and J–V characteristics shown in Figs. 2 and 3 support such multi-electron catalysis processes via Ohmic channels.

The effects of the mesoporous TiO_2 film thickness, pH, and glucose concentration are shown in Table 2.

Table 2 Effect of TiO_2 film thickness, pH, and glucose concentration on the output power

TiO_2 film thickness/μm	Pt/Ti atomic ratio	pH	Glucose conc./M	J_{sc}/mA cm^{-2}	V_{oc}/V	FF	Output power/ mW cm^{-2}	Result
5	0.31	14.0	1.0	0.44	0.50	0.23	0.051	Effect of TiO_2 film thickness is large
10				2.4	0.62	0.24	0.51	
20				5.3	0.77	0.27	1.08	
30		TiO_2 film unstable						
20	0.33	2.1	1.0	0.2	0.04	0.25	0.002	Effect of pH is large
		8.4		0.6	0.05	0.25	0.008	
		11.8		2.2	0.67	0.25	0.37	
		14.0		5.1	1.29	0.30	1.97	
	0.31	14.0	0.01	2.5	0.70	0.25	0.44	Effect of glucose conc. is not very large
			0.1	2.6	0.74	0.25	0.48	
			1.0	5.3	0.77	0.27	1.10	

The output power was higher when the film was thicker up to 20 μm, which could be interpreted simply by the higher effective surface area of the device (2,000 cm^2 for a 20-μm TiO_2 film), but when it is 30 μm, the film was unstable and easily detached from the FTO. The effect of the glucose solution pH was large, giving a much higher output power at a higher pH. Glucose is much more unstable under alkaline conditions than acidic conditions, undergoing various changes such as the formation of carboxylic acid and cleavage of C–C bonds, which would be a reason for the higher efficiency at higher pH. The effect of glucose concentration is not large, e.g., two orders of magnitude lower glucose concentration (0.01 M) generated as much as 40% electrical power as that by 1.0 M concentration glucose, suggesting a catalysis-limited process rather than a substrate diffusion-limited process in the present FC.

3.3 BMFC Characteristics of Other Biomass-Related Compounds

Electrical power generation by other biomass-related compounds such as sucrose, ethanol, ammonia, and polysaccharides (soluble starch, carrageenan, and soluble carboxymethyl cellulose) were investigated, and the results are shown in Table 3. A 10 wt% ethanol aqueous solution gave 0.48 mW cm^{-2} at pH 14, which is 24% of the output power by glucose, as shown in Table 1, but 7.5 times larger than that (0.064 mW cm^{-2}) by a photoirradiated mesoporous TiO_2 film alone under 18 mW cm^{-2} UV region-light irradiation [8]. Ammonia was not suited to the present mesoporous TiO_2/Pt metal composite film. Soluble starch, carrageenan and carboxyl methyl cellulose generated small electrical power, but even polymeric compounds can be decomposed and used to generate electrical power. Since other metals could be used to fabricate efficient anode/catalyst composites, investigation of other metal layers instead of the precious Pt is underway.

The nanocomposite of the mesoporous TiO_2 thin film with a Pt thin layer was stable in repeated use for more than 1 month without change.

3.4 Evolution of Continuous H_2 Bubbles Simply by Soaking only the TiO_2/Pt Nanocomposite Anode in a Biomass Aqueous Solution

Continuous evolution of H_2 bubbles was observed from the anode surface simply by soaking an FTO/TiO_2/Pt nanocomposite anode without a cathode in a biomass compound aqueous solution under anaerobic conditions. Immediately after soaking a 1 cm^2 FTO/mesoporous TiO_2/Pt nanocomposite anode (Pt/Ti = 0.34) in a 1 M glucose solution (5 mL, pH 14) in a closed 12 mL cylindrical cell under an argon atmosphere, bubbles were evolved continuously from the anode surface, and the generated gas was analyzed to be H_2 by gas chromatography. Since this composite anode would show both a Schottky junction and Ohmic contact behavior as shown in Fig. 5, when the cathode is not connected, the electrons injected from biomass via Pt into the mesoporous TiO_2 must be transported back to the Pt layer due to the partial Ohmic contact nature, and therefore protons are reduced to H_2 on the Pt surface. The evolved H_2 gas was 13.0 μmol cm^{-2} after 1 h. By simply connecting and disconnecting with a cathode, electrical power and H_2 generation were easily switched, respectively, which on the other hand supports the working principle of the present device shown in Fig. 5. When using a Pt foil coated with Pt-black, H_2 bubbles were not observed, and the H_2 evolved was about 1/10 of that by the mesoporous TiO_2/Pt nanocomposite.

Even under aerobic conditions H_2 was obtained, but in this case O_2 reduction to H_2O took place competitively. Other biomass compounds were investigated in the same manner as glucose and the findings also confirmed the H_2 evolution.

Table 3 BMFC characteristics of other biomass-related compounds in an aqueous solution at pH 14 (+0.1 M Na_2SO_4) with atomic ratio of Pt/Ti = 0.33 and TiO_2 film thickness of 20 μm

Compound (conc./M)	J_{sc}/mA. cm^{-2}	V_{oc}/V	*FF*	Output power/mW cm^{-2}	Note
Sucrose (1 M)	1.3	0.65	0.21	0.21	Decreased with time
Ethanol (10 wt%)	0.67	0.49	0.24	0.079	pH ~8
	3.2	0.63	0.24	0.48	pH 14
Ammonia (1 M)	0.21	0.09	0.25	0.005	
Soluble starch (10 mM repeating unit)	0.45	0.14	0.25	0.016	
Carrageenan (0.1 mM repeating unit)	0.50	1.2	0.24	0.14	Decreased with time
Carboxymethyl cellulose (0.1 mM repeating unit)	~0.2	~0	0.25	~0	
Glucose (1 M)	5.1	1.29	0.30	1.97	From Table 1

4 Proposal of Sustainable Energy Resource Creation Using Biomass and its Waste Directly as a Fuel as a Materials/Energy Circulation System for Future Society

The present article reports the preliminary results of creating a direct biomass fuel cell (BMFC) anode/catalyst nanocomposite comprising a mesoporous n-SC thin film and Pt metal thin layer, using biomass and biomass-related compounds as a fuel. Although only the first and the preliminary stage of the device achievements are reported, the present BMFC with a nanocomposite structure would have the potential to remove the need for energy derived from atomic power plants and reduce the consumption of fossil fuels if concentrated research and development were conducted in this direction. Even at the present stage, the following estimation is possible.

The present preliminary glucose fuel cell produced electrical power of about 2 mW cm^{-2} as shown in Table 1. If based on a simple and preliminary calculation, a larger scale module could be prepared as follows. For example, after a simple calculation, a 20 cm × 20 cm (=400 cm^2) anode thin film would produce 0.8 W/400 cm^2 electrical power. By installing 20 pieces of this 400 cm^2 nanocomposite anode in an 8-L glucose aqueous solution (20 cm × 20 cm × 20 cm = 8,000 cm^3), each anode being separated by 1 cm, the 8-L module unit produces 0.8 W × 20 = 16 W/8 L electrical power. By accumulating 125 pieces of this 8-L module to an about 1 m^3 size module stack, 2.0 kW m^{-3} electrical power is produced, which suffices for 2 persons' average electrical power demand at home in Japan. The present device is able to operate for 24 h per day (=average 2.0 kW m^{-3} day^{-1}) even based on the present preliminary stage. This is different from solar cells with a capacity of 0.1 kW m^{-2}, which generate electrical power on average 2–3 h per day at most (=average 0.01 kW m^{-2} day^{-1}) when considering night and cloudy/rainy days in a year. For an average Japanese house, 3 kW is the standard electrical power demand, which is produced by a 1.5 m^3 stack of modules (=about 1.2 m × 1.2 m × 1.2 m) by the present BMFC.

In addition, in accumulation of energy by a form of H_2 fuel, roughly 300 L H_2/h would be generated by a 1 m^3 stack of modules (=7.2 m^3 H_2/m^3 module stack, day) based on a simple calculation.

These calculations are just based on the first and the preliminary stage of BMFC conversion efficiency.

In nature, organisms acquire energy by ingesting, digesting, and burning (=oxidative decomposition with O_2) foods that are photosynthetic products either directly or indirectly, the processes of which correspond to the reverse reaction of the photosynthetic reaction of Eq. 1. This means that creation and recycling of energy and materials are coupled with each other in nature. It is important to learn from nature in order to design future social systems for acquiring/recycling of energy/materials that are compatible with nature. Biomass waste remains a serious environmental pollutant all over the world, which is still not easy to clean up and treat. The total energy of such biomass waste is huge, around 130 EJ $year^{-1}$ w^{-1} [12], among which livestock, agricultural and forestry waste each account for 1/3, amounting to nearly 27% of world primary energy demand of ca. 480 EJ $year^{-1}$ w^{-1} in 2010. If such biomass waste were dry, we could recover energy simply by combustion, but energy recovery by combustion is possible only when the water content is less than 85% due to the water vaporization latent heat. Since much of the biomass waste is wet with a water content of more than 85%, it cannot be used for energy recovery merely by combustion. The current energy problems are estimated roughly below.

At present, fossil fuels (oil, gas and coal) and wood comprise more than 90% of world primary energy use. The average energy conversion efficiency of using these fossil fuels/woods is not easy to estimate, but it could be about 25%; such energy conversion from fuels is comprised of electrical power plants (average maybe roughly 35% conversion efficiency based on 40% by oil/gas, 30% by coal and 25% by wood), automobiles (maybe average less than 15%), refining industries for producing metals from metal ores (maybe ca. 30%) and much smaller conversion efficiencies just for burning to obtain heat. On the other hand, the theoretical biomass conversion efficiency to electrical power by a fuel cell (=$\Delta G°/\Delta H°$) is large, nearly 100% due to its highly positive entropy term (e.g., 97% for ethanol and $\sim$100% for glucose). We have for example obtained a 50% energy conversion efficiency of glycine to electrical power in a preliminary experiment by using a Photo Fuel Cell (PFC) comprising a mesoporous TiO_2 thin film photoanode and a Pt black-based O_2-reducing cathode [9]. In addition to the present biomass waste, many industries have started to produce fuels and other materials from biomass, which is increasing the amount of biomass waste tremendously. This suggests the possibility of meeting more than 50% of world energy demand from biomass waste if it could be converted directly to electrical power by devising an efficient BMFC operating without inputting external energy.

In addition to biomass waste, conventional biomass materials, even their suspensions (green algae was photodecomposed in a PFC [10]), could also be used as fuel if efficient BMFCs were realized. Moreover, the BMFC could be coupled with a PFC by which stable biomass including cellulose and lignin [8], even solid suspensions, is at first photodecomposed by solar UV region light to smaller compounds, and the decomposed smaller molecular weight products could be accumulated and thereafter converted to electrical power by a BMFC without inputting any external energy. That is, an efficient BMFC with the help of a PFC could provide the potential to meet a large portion of world energy demand by only biomass and its waste while cleaning/cycling them to mineralization. This application has the potential to remove the need for energy derived from atomic power plants and reduce the consumption of fossil fuels, which is considered to be the primary reason for the serious global climate change.

5 Conclusion

We designed and prepared an efficient direct biomass fuel cell (BMFC) anode comprised of a [base electrode (FTO)/ mesoporous n-semiconductor (SC) thin film/metal thin layer] nanocomposite. A Pt thin layer was photodeposited onto a mesoporous 20-μm thick TiO_2 thin film having a roughness factor of 2,000 coated on an F-doped tin oxide/ glass base electrode (FTO). This anode/catalyst nanocomposite was used to decompose aqueous solutions of glucose and other biomass-related compounds in combination with an O_2-reducing cathode, the other side of which was exposed to ambient air. The nanocomposite exhibited sharp optimum conditions at the atomic ratio of $Pt/Ti = 0.33$ as an anode/catalyst for a BMFC generating high electrical power from a 1 M glucose aqueous solution giving 2 mW cm^{-2} output without any light irradiation or bias potential. This output is 20 times as large as that generated by a simple mesoporous TiO_2 film anode under UV-light irradiation. At this $Pt/Ti = 0.33$ ratio the coated Pt specifically exhibited metallic luster, and its average Pt thickness on the mesoporous TiO_2 nanostructure was calculated to be 0.40 nm. The high BMFC activity was interpreted by both the Schottky-junction/Ohmic contact nature of the nanocomposite comprised of a mesoporous TiO_2 thin film and a Pt thin layer. Other biomass compounds such as ethanol and polysaccharides were also effective as direct fuels for the BMFC. Finally, we proposed a simultaneous material/energy circulation for application in future social systems based on development of the present BMFC and by using biomass and its waste fuel, which would have the potential to remove the need for energy derived from atomic power plants and reduce the consumption of fossil fuels.

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