



Short communication

Binder/surfactant-free biocathode with bilirubin oxidase for gas-diffusion-type system

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ABSTRACT

Direct electron transfer (DET)-type bioelectrocatalysis of dioxygen (O_2) reduction is an essential process for constructing a biocathode for use in an enzymatic biofuel cell. In this study, a gas-diffusion-type electrode without any binders or surfactants, which are both known to interfere with DET-type bioelectrocatalysis, was constructed. Bilirubin oxidase (BOD), a promising catalyst for DET-type O_2 reduction, and water-dispersed multiwalled carbon nanotubes compatible with BOD were used. The electrode displayed high kinetic performance in the DET reaction and large steady-state current density under quiescent conditions. In addition, the electrode provided a platform that was eight times more suitable for BOD than a traditional electrode.

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1. Introduction

Enzymatic biofuel cell is an energy conversion system in which enzymes oxidize a substrate or reduce dioxygen (O_2) at the bioanode or biocathode, respectively [1–3]. Owing to the properties of enzymes, the device can operate under very mild and safe conditions such as neutral pH, room temperature, and atmospheric pressure [1–3]. Furthermore, biofuel cells can be used in micropower devices to extract energy from biological sources and are expected to find applications in implantable biomedical power devices [4–7]. Multicopper oxidases (MCOs) catalyze four-electron reduction of O_2 into H_2O and are utilized as biocatalysts [8,9]. In addition, several MCOs are classified as direct electron transfer (DET)-type enzymes that can shuttle electrons to or from an electrode without any redox mediators [9–12]. Therefore, DET-type enzymatic biofuel cells are suitable for realizing efficient and compact energy conversion systems [13,14].

The low solubility and low diffusion coefficient of O_2 cause limitations in the catalytic current and result in a decrease in power in O_2 reduction with MCOs in solution. A gas-diffusion-type electrode, which can supply a gaseous substrate from the gas phase, has been utilized to solve this problem [15–22]. A simple numerical simulation has predicted that the limiting catalytic current continues to increase with the thickness of the gas-diffusion-type electrode up to millimeter thickness [22]. Accordingly, it is invaluable for the achievement of efficient

DET-type bioelectrocatalysis with MCOs in the limited layer of the gas-diffusion-type electrode.

Hydrophobized carbon materials such as Ketjen black (KB), carbon black with Teflon[®], and carbon nanotubes (CNTs) [23] are often utilized for constructing gas-diffusion-type electrodes [15–22]. Teflon[®] is frequently used as a binder between carbon particles and as a hydrophobic material; however, Teflon[®] is known to act as an insulator. Therefore, enzymes adsorbed onto the Teflon[®] cannot directly communicate with the electrode. On the other hand, most CNT suspensions contain surfactants for dispersion. Surfactants are considered to strongly adsorb onto the CNT surface and interfere with the DET reaction between an enzyme and the electrode [24,25]. To enhance the performance and efficiency of DET- and gas-diffusion-type electrodes, it is necessary to avoid using these additives.

Among MCOs, bilirubin oxidase (BOD) is a promising enzyme for DET-type bioelectrocatalysis [26] because it has a high bioelectrocatalytic activity in DET-type O_2 reduction. The type I Cu site acts as the electron accepting site, and its formal potential of BOD is relatively close to that of the H_2O/O_2 redox pair [26]. Because the rate constant of the DET reaction decreases exponentially with the tunneling distance between the electrode and the active site of an enzyme [27], a suitable orientation of the adsorbed enzyme is essential for fast electron transfer [28,29]. Focusing on the type I Cu active site of BOD to communicate with an electrode, several approaches have been reported to realize efficient DET-type bioelectrocatalysis with BOD [21,25,30–35]. Premodification of the electrode with negatively charged chemical compounds has been reported as an effective method. This includes covalent modification by diazonium

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Table 1
Characteristics of BOD-adsorbed electrodes^a.

BOD-adsorbed electrodes	Amount of MWCNT/mg	$-j$ (at 0 V, 60 s)/mA cm ⁻²	Relative electroactive surface area (A) ^b	Efficiency ($-j/A$)
CNT1	1.4×10^{-3}	0.0007	0.03	0.023
CNT2	0.14	7 ± 1	0.12 ± 0.02	58 ± 13
CNT3	0.28	10 ± 0.9	0.25 ± 0.02	40 ± 5
CNT4	0.56	12 ± 2	0.42 ± 0.01	28 ± 5
CNT5	1.26	13.3 ± 0.5	1	13.3 ± 0.5
KB/PTFE	N/A	11.4 ± 0.6	1.5 ± 0.1	7.6 ± 0.6

^a The errors were evaluated by Student's *t*-distribution at 90%-confidence level.

^b The relative electroactive surface areas were evaluated from the amplitude of non-faradic charging current on CVs under Ar-saturated conditions.

coupling [30] or by oxidation of amines [31], physical adsorption of bilirubin [21,32,33] or other aromatic compounds [34], and the utilization of functionalized CNT such as pyrene-functionalized CNTs [35] or water-soluble CNTs of length 1–4 μm [25].

In this study, we aimed to construct a gas-diffusion-type electrode that meets the aforementioned requirements. Binder/surfactant-free CNTs, which are highly compatible with BOD [25], were deposited on a water-proof carbon cloth (WPCC) base to construct a gas-diffusion-type biocathode with BOD. We characterized the biocathodes via microscopic and bioelectrochemical analysis.

2. Experimental

2.1. Materials

Water-dispersed multiwalled CNTs (MWCNTs; outer diameter: 10–15 nm, length: 1–4 μm without surfactant) were kindly donated by Nitta Corp. (Japan). WPCC (EC-CC1-060T) was purchased from Toyo Corp., (Japan), and carbon paper (CP, TGP-H-120) was purchased from Toray Industries, Inc., (Japan). KB EC300J was kindly donated by Lion Corp., (Japan). Poly(1,1,2,2-tetrafluoroethylene) (PTFE, 6-J) fine powder was purchased from Du Pont-Mitsui Fluorochemicals Co., Ltd., (Japan). PTFE sheets (EN0701405) were obtained from Nippon Donaldson, Ltd. (Japan). BOD (EC 1.3.3.5) from *Myrothecium verrucaria* was donated by Amano Enzyme Inc. (Japan) and used without further purification. All other chemicals used in this study were of analytical grade unless otherwise specified and all solutions were prepared with distilled water.

2.2. Electrode preparation

The MWCNT suspension was applied to one-side of WPCC sheets and dried at 55 °C to prepare MWCNT-modified WPCC electrodes (labeled CNT1–CNT5 depending on the amount of MWCNTs on the WPCC electrode, as characterized in Table 1). The KB-modified CP electrode (KB/PTFE) was prepared at KB:PTFE = 6:4 (w/w) according to the literature [21]. The PTFE sheet was attached to the opposite side (without MWCNT) of the WPCC electrodes by pressure bonding to completely hold electrolysis solutions. Subsequently, 300 μL (1 L = 1 dm³) BOD solution (20 mg mL⁻¹) dissolved in 10 mM (1 M = 1 mol dm⁻³) phosphate buffer (pH 7) was applied to the MWCNT-mounted electrode surfaces (CNT1–CNT5 and KB/PTFE), which were dried for 2 h under reduced pressure at room temperature.

2.3. Microscopic and electrochemical measurements

Scanning electron microscopy (SEM) was performed on a Hitachi S-4300. Cyclic voltammetry and chronoamperometry were carried out on an electrochemical analyzer BAS CV 50W and ALS 714C. A handmade gas-diffusion-type electrolysis cell identical to that reported in a previous paper [21] was used for the measurements. The projected surface area of the working electrode was set to 1.0 cm². The electrode was set as the PTFE sheet-attached side facing to gas phase. A Ti mesh served as a current collector, and was attached to the MWCNT-mounted and BOD-adsorbed side of the working electrode. A Pt mesh and an Ag|AgCl|sat. KCl electrode were used as counter and reference electrodes, respectively. All potentials in this study are in reference to the reference electrode. The measurements were performed in 1.5 M citrate buffer (pH 5) at 40 °C under quiescent and O₂ atmospheric conditions.

3. Results and discussion

3.1. Characterization of the MWCNT-based gas-diffusion-type electrodes

Fig. 1A shows photographs of the BOD solution on the WPCC and CNT1–CNT5. Since the surface of WPCC is very hydrophobic, the BOD solution on the WPCC and CNT1 was strongly repelled. The electrode surface became more hydrophilic with an increasing amount of MWCNTs on the WPCC (CNT1–CNT5), at which point the BOD solution soaked more easily on the inside of the electrodes.

SEM was conducted to BOD-adsorbed CNT5 from the top and vertical views (Fig. 1B and C, respectively). Fig. 1B shows that the WPCC

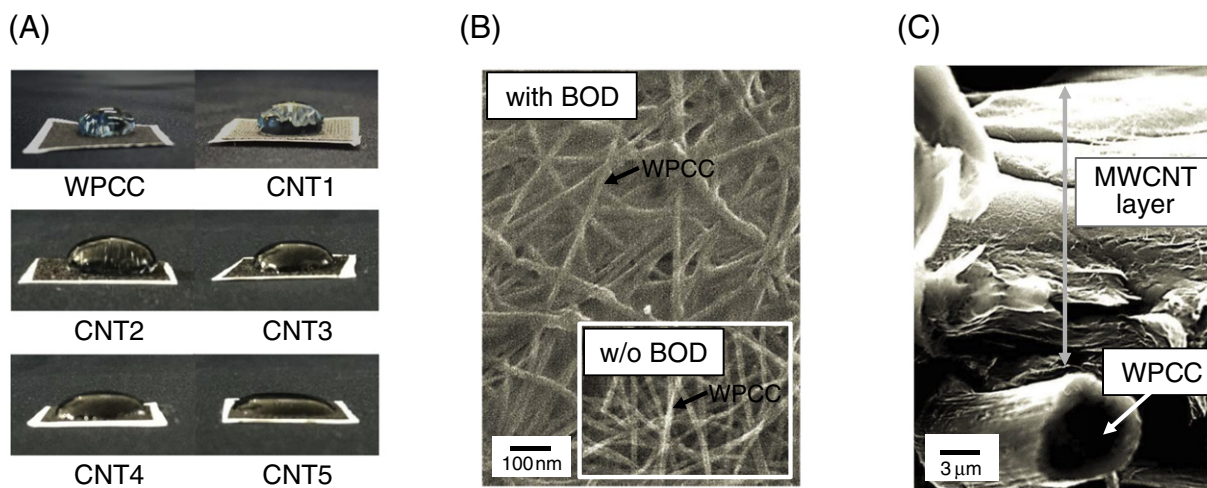


Fig. 1. (A) Photographs of BOD solution deposited on the WPCC and MWCNT-based WPCC electrodes (CNT1–CNT5). Before BOD deposition, the PTFE sheet is attached to the opposite side of each electrode. (B) SEM of BOD-adsorbed CNT5 from the top view. The inset shows the SEM of CNT5 without BOD. The black arrows indicate the MWCNT. (C) SEM of BOD-adsorbed CNT5 from the vertical view. The white arrow indicates a fiber of the WPCC. The accumulated MWCNT layer is indicated by the bidirectional arrow.

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