Enzyme Assembly inside Nanotube Forest Films for Self-Powered Biodevices

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Controlling the electrical contact of redox enzymes with electrodes is a critical issue for enzymatic biodevices such as biofuel cells and biosensors. The mutual positioning between enzyme molecules, mediator molecules (not always necessary), and electrode surface determines the efficiency, reproducibility, and stability of the bioelectrocatalysis systems. We present herein an enzyme/mediator/electrode ordered ensemble that shows both "high turnover rate" and "large catalytic current". In order to satisfy both of th ese requirements, the larger amount of enzymes than monolayer should be immobilized with keeping effective contact with electrodes. We realize such ideal condition by taking advantage of a film of well-aligned carbon nanotube forest (CNTF) [1] consisting of single-walled CNTs arrayed wi th a pitch of 16 nm.

We have previously reported the incorporation of fructose dehydrogenase (FDH) and Laccase (LA C) as the anodic and cathodic electrode catalysts, respectively [2]. By connecting the FDH-CNTF anode and the LAC-CNTF cathode showed the world highest power density of 1.8 mW cm^{-2} (at 0.45 V) in stirred 200 mM fructose, 84% of which could be maintained after continuous operation for 24 h.

In this work, the molecularly ordered composites of polyvinylimidazole-[Os(bipyridine)$_2$Cl] (PVI-[Os(bpy)$_2$Cl]) and glucose oxidase (GOD) are assembled inside a film of the CNTF. The structure of the prepared GOD/PVI-[Os(bpy)$_2$Cl]/CNT composite film is entirely uniform and stable; more than 90% bioelectrocatalytic activity could be maintained even after storage for 6 days [3]. Owing to the ideal positional relationship achieved between enzyme, mediator and electrode, th e prepared film shows a high bioelectrocatalytic activity for glucose oxidation (ca. 15 mA cm^{-2} at 25 °C) with an extremely high electron turnover rate (ca. 650 s^{-1}) comparable to the value for the GOD solutions, indicating almost every enzyme molecules entrapped within the ensemble (ca. 3 × 10^{12} enzymes in a 1× 1 mm^2 film) can work to the full. The free-standing, flexible composite film can be used by winding on a needle device, for example, a self-powered sugar monitor, that changes the blinking interval of an LED [4] upon simply being inserted into a grape.

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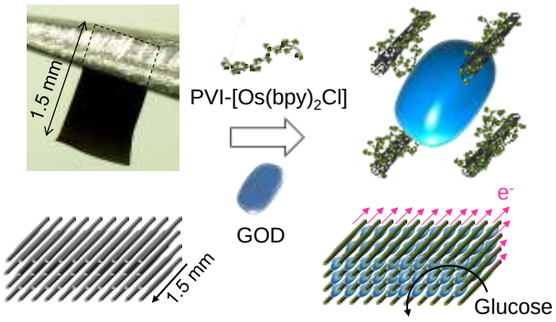

Figure 1. Schematic illustration of the stepwise process for constructing bioelectrocatalytic composite inside a CNTF film.

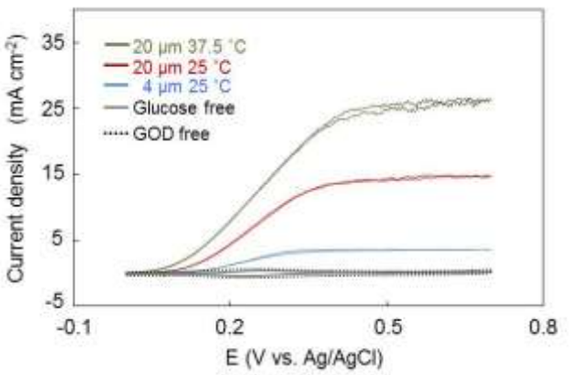

Figure 2. Cyclic voltammograms of GOD/PVI-Os/CNTF ensemble films at 10 mV s^{-1} in stirred air-saturated 25°C (or 37.5°C) PBS containing 200 mM D-glucose. The thickness of CNTF films were 4 μm or 20 μm.

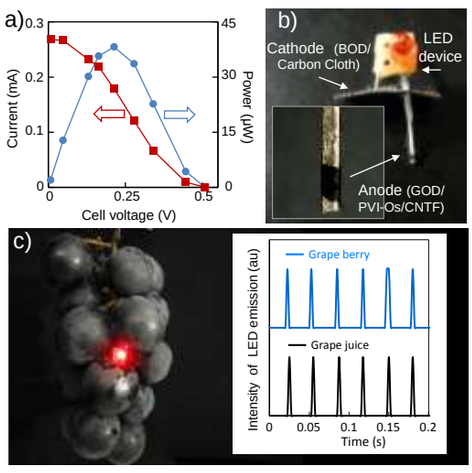

Figure 3. (a) Performance of a biofuel cell composed of an anode of GOD/PVI-[Os(bby)$_2$Cl]/CNTF film (20μm thickness) and a cathode of BOD-modified carbon cloth (1cm × 1cm) in 200 mM glucose PBS solution. (b) Photograph of the LED-based self-powered sugar indicator, at the tip of which the GOD/PVI-[Os(bby)$_2$Cl]/CNTF film was wound. (c) The device assembly was inserted in a grape and the LED blinking was measured (inset). The time course of LED emission, taken using an extracted juice, is also shown.