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A highly flexible self-powered biosensor for glucose detection by epitaxial deposition of gold nanoparticles on conductive bacterial cellulose

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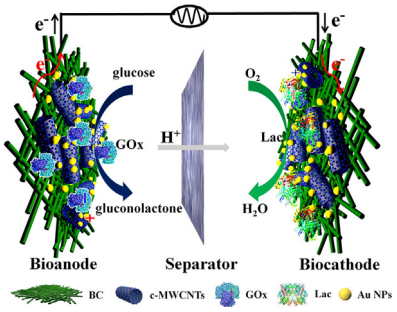
HIGHLIGHTS

- This self-powered biosensor is herein reported for the first time.
- The device shows acceptable range and ultralow detection limit.
- This work expands application scopes of both BC and sensors.

GRAPHICAL ABSTRACT



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ABSTRACT

An Enzyme (glucose/O_2) BioFuel Cell (EBFC) was developed using glucose oxidase (GOx)-based bioanode and a laccase (Lac)-based biocathode with carboxylic multi-walled carbon nanotubes (c-MWCNTs) and gold nanoparticles (AuNPs)-modified bacterial cellulose (BC) electrode as the substrate. The open circuit potential (OCP) of the EBFC was inhibited and later activated by the self-powered electrochemical device. The device not only provided high power density (345.14 μW cm^{-3}), but also exhibited an unprecedented broad linear dynamic range from 0 to 50 mM with a lower detection limit of 2.874 μM for glucose concentrations in biological media. This result was attributed to a synergistic mechanism between the enzymes, c-MWCNTs, and AuNPs in which direct electron transfer (DET) was facilitated from the catalytic centers of enzymes to the electrode surface. The BC-based nanocomposites may have great promise as flexible electrodes in the field of self-powered biosensors.

1. Introduction

Sensors are widely used in society to gather information and provide continuous feedback loops. By integrating thousands or more into a network with information processing modules, definitive conclusions can be made from the high amount of information obtained and simultaneously analyzed. Sensors have paved the way for the *internet of things* and similar sensing networks [1]. However, the challenge that

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remains is determining how to power them within variegated environments. Typically, they receive their power via DC batteries. Yet, not only is lifetime of the sensor network limited, but sensors of different types consume energy at different rates, which require additional efforts to match batteries and sensors for energy saving; not to mention that replacing all the batteries for the numerous sensors involves requires additional expenditures of time and resources. An additional drawback is found with biosensors implanted in vivo because most batteries contain toxic ions like Pb^{2+}, Hg^{+}, etc.

To address the latter two drawbacks, enzymatic biofuel cells (EBFCs) have attracted interest for their ability to harvest electricity from renewable biofuels. EBFCs are more complex than traditional fuel cells, because typically open circuit potentials are significantly lower than theoretical due to mediator redox potentials, enzyme redox potentials and cofactor redox potentials [2]. Recently, EBFCs based self-powered sensors have attracted considerable attention because they operate without external power sources and are well-suited for device miniaturization. The sensing mechanism is based on parameters of EBFCs, such as: the power density and open circuit potential (OCP) are dependent on target concentration. Meanwhile, compared with traditional electrochemical sensors, construction of the sensing platform is challenging. To date, many kinds of self-powered platforms have been constructed for chemical and biological sensing, including for detection of Hg^{2+}, cyanide, glucose, etc. Katz et al. first explored BFC-based self-power glucose sensors by optimizing glucose concentration and power output [3]. Gu et al. reported an EFC-based self-powered homogeneous immunosensing platform via strategy-induced glucose release [4]. Gai and coauthors reported one-compartment EBFCs-based self-powered aptasensing platform for antibiotic residue detection [5]. Yan and coauthors reported a photocathode-based photocatalytic fuel cell (PFC) as a self-powered sensor to detect p-nitrophenol (p-NP) with a wide concentration range from 0.05 μM to 20 μM [6]. Recently, Xu and coauthors reported a self-powered electronic-skin (e-skin) for detecting glucose level in body fluid [7]. Zhang and coauthors developed a self-powered implantable skin-like glucometer for real-time detection of blood glucose level in vivo [8].

Bacterial cellulose (BC), synthesized by *Komeigatabacter xylinus (K. xylinus)*, possesses a 3D interconnected porous structure composed of nanofibrous networks characterized as a layer-by-layer arrangement. BC has attracted significant attention for its excellent biocompatibility, high permeability, mechanical strength, and flexibility [9]. To date, it has been widely used in biomedical areas such as artificial skin [10], artificial blood vessels [11], bio-scaffolding [12], and wound dressings [13] because of its flexibility, high biocompatibility, excellent stability, and mechanical properties that allow it to maintain its structure during tissue cultivation. In combination with conductive materials (such as carbon nanotubes (CNTs), graphene, conductive metal and polymer), it can display multifunctional conductivity, making it ideal for flexible electrodes in lithium ion batteries, supercapacitors, and sensors [14–18]. To date, some researchers believed that CNTs have therefore been utilized as the conducting nanowires to facilitate direct electron transfer (DET) from the catalytic centers of enzymes to electrode taking advantages of their chemical inertness, electro-chemical stability, excellent conductivity, and molecular dimensions that enables intimate interaction with the enzymes [19–21]. Many kinds of CNTs-based platforms have been constructed for electrochemical biosensor. Kenath et al. reported a novel EBFC equipped with enzyme-functionalized 3D graphene-single walled carbon nanotubes (SWCNTs) hybrid electrodes using the naturally abundant glucose as the fuel and oxygen as the oxidizer [22]. However, Bartlett et al.'s work implied that the surface redox peaks usually attributed to DET to GOx actually arise from flavin, and possibly catalase, impurities present in the as supplied commercial enzyme that are adsorbed at the electrode surface [23].

Importantly, noble metal nanoparticles such as gold nanoparticles (AuNPs) display rich electronic and optical properties in addition to their pronounced biocompatibility and chemical inertness, which there can be widely applied in food safety inspection [24], catalysis [25], bioanalytical chemistry [26], cell imaging [27] and photothermal therapy [28]. It is noted that, because of their low toxicity, high chemical stability and high surface area, AuNPs have been used to ligate biomolecules such as enzymes to the surface of electrode for biosensing predicated on direct electron transfer (DET) between the electroactive center of enzyme and electrode [29]. Xiao et al. reported that AuNPs acts as an electron relay or "electrical nanoplug" for the alignment of the enzyme (GOx) on the conductive support and for the electrical wiring of its redox-active center, which has been published in "Science" [30]. Zhang et al. constructed a novel H_2O_2 biosensor using the obtained Au-BC nanocomposites as excellent support for horseradish peroxidase (HRP) immobilization, which allows the detection of H_2O_2 with a detection limit low than 1 μM [31]. However, due to its large specific surface area, direct introduction of AuNPs tends to lead to aggregation. Meanwhile, separation and recovery of AuNPs from the reaction solution media are difficult. Therefore, to address aggregation, AuNPs are loaded not only into porous inorganic materials, but polymer substrates, a very attractive means for controlling AuNPs growth and structural stability.

Renewable polymers are attractive AuNP supports because of biodegradability and biocompatibility as evidenced by Chen et al. who first reported bacterial cellulose-based AuNP membranes functionalized by amidoxime [32]. Zhang et al. prepared AuNPs utilizing the porous structure of cellulose that were able to absorb $AuCl_4^-$ ions which were reduced by an appropriate reducing agent [33]. However, those approaches were inconvenient and suffered from a lack of control. Therefore, to enhance the interaction between AuNPs and cellulose, work in modified cellulose by introduction of poly(diallydimethylammonium) (PDDA), poly(ethylenimine) (PEI) and other functional groups ($-NH_3$, $-COOH$) has emerged. Herein, inspired by the revious literatures, efforts have been made to achieve synergistic integration of CNTs and AuNPs in which DET was facilitated from the catalytic centers of enzymes to the electrode surface for EBFC application. An ideal self-powered biosensor by using glucose oxidase (GOx)-based bioanode and laccase (Lac)-based biocathode decorated with c-MWCNTs and AuNPs-modified BC electrode is reported. Experimental results showed that BC with an ultrafine nanofiber, three dimensional (3D) network structure and high stability would be a very promising support for self-powered biosensors.

2. Experimental

2.1. Reagents and materials

Lac (activity ≥10 U/mg) and GOx (having an activity ≥800 U/mg) were purchased from Sigma-Aldrich (USA). PEI (poly(ethyleneimine), M_w = 25,000) was obtained from Aldrich (USA). The c-MWCNTs (Purity, > 95%) was purchased from Nanjing XFNANO Materials Tech Co., Ltd. (Nanjing, China). *Komeigatabacter xylinum* (ATCC 10245) was obtained from the American Type Culture Collection. Yeast extract, bacto-peptone and ABTS (2,2′- azino-bis-(3-ethylbenzthaiazoline-6-sulfonic acid)) were purchased from Sigma-Aldrich (USA). D-mannitol sodium, hydrochloroauric acid trihydrate ($HAuCl_4{\cdot}3H_2O$, 99.9%), and sodium chloride (NaCl, 99.5%), were supplied by the Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). Nafion (5 wt%) was purchased from DuPont Company (USA). 0.1 M acetate buffer solution at various pH values were of analytical grade and used as received. Fluorescein isothiocyanate (FITC) was purchased from Aldrich (USA). All of the chemicals were of analytical grade and solutions were prepared using deionized water (DIW).

2.2. Synthesis of BC [34]

BC was produced by *Komeigatabacter xylinus* (K. xylinus) (ATCC 10245), which was inoculated into 10 mL of a Hestrin and Schramm