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Research Article

Research on Flexible Thin-Disk Glucose Biofuel Cells Based on Single-Walled Carbon Nanotube Electrodes

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Glucose biofuel cell (GBFC) is a power supply device which has attracted considerable attention because of its green environmental protection and high economic benefits. Fuels like glucose and oxygen are ubiquitous in physiological fluids, allowing the direct harvest of energy from human bodies. Compared with conventional batteries such as Li-Po, GBFC is a more promising alternative to power medical devices without the need to be replaced or refueled. However, the energy conversion efficiency of the existing GBFCs still needs to be further improved for practical applications. In this paper, the performance of the GBFC was studied based on single-walled carbon nanotubes (SWCNTs), which have relatively high conductivity and large specific surface area that could improve the activity of enzymes immobilized on the electrode surface and thus realize the direct electron transfer (DET). After optimization of the catalysts' amount, the GBFC based on SWCNTs performed well with two Pt layers sprayed on one side of the proton exchange membrane (PEM) and 1.5 mL glucose oxidase (GOx) dropped on the other side, which attained the highest open-circuit potential (OCP) of 0.4 V. After being encapsulated with a flexible porous enclosure made by polydimethylsiloxane (PDMS), the biological compatibility of the completed GBFC has been successfully improved, which provides great potential for powering wearable or implantable devices.

1. Introduction

Biofuel cell (BFC) is a power supply device that can convert the chemical energy of the biological organic matter directly into electric energy by using enzymes as the catalyst [1–4]. The development of glucose biofuel cells (GBFCs) is driven by the ever-increasing need of wearable or implantable medical devices, such as micropumps, cardiac pacemakers, or artificial organs, to generate an electrical power output inside human bodies [5]. Indeed, conventional batteries such as Li-Po [6] have been used in heart pacemakers but not for more flexible applications, which are mainly due to their less environment friendly, the need of surgical replacement and incompatibility [7]. Instead, GBFCs have attracted considerable attention because of their wide range of raw materials, green environmental protection, good biological compatibility, and high economic benefits [8, 9]. Fuels such as glucose and oxygen are ubiquitous in the extracellular body fluids at constant levels and biocatalysts such as enzymes are greener alternative to traditional organic synthesis under mild reaction conditions [10]. The reaction products of GBFCs only contain gluconolactone, H^+, and water, all of which are nontoxic and green [11, 12]. Accordingly, GBFCs seem to be a more promising alternative to power medical devices, without the need to be replaced or refueled.

Nevertheless, GBFCs suffer from severe limitations. One of the major challenges is that their energy conversion efficiency still needs to be further improved. In fact, a GBFC is composed of two bioelectrodes modified with cathodic and anodic enzymes, respectively, to complete the concomitant oxidation and reduction processes [13]. The redox active site

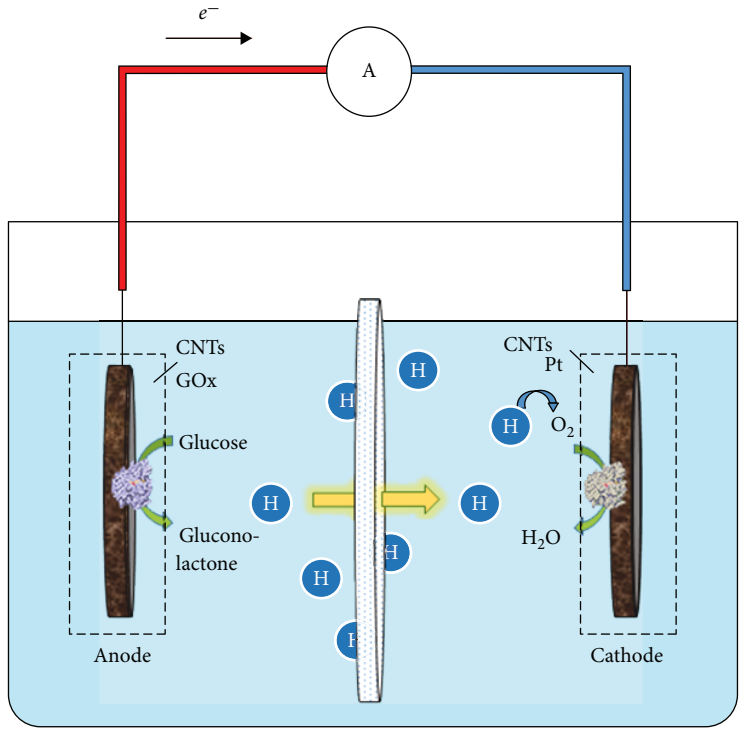

Figure 1: Schematic of a GBFC equipped with two bioelectrodes based on SWCNTs (not to scale).

of enzymes usually hides in a thick coat of protein, thus hindering the direct electron transfer (DET) between the electrodes and the enzymes [14]. To date, the open-circuit voltage (OCV) and power density acquired currently are far below the levels required to supply implantable biomedical and health care applications [13]. Initially, redox mediators such as osmium complexes, 2, 2′-azino-bis (3-ethylbenzthiazoline)-6-sulfonic acid, and ferrocyanide were employed as electron acceptors between the enzyme and the electrode surface to increase the power density [15]. However, the application of electron transfer mediators also often brings a decrease to the theoretical open-circuit potential (OCP) and causes toxicity to implantable devices [14, 16–19]. For these reasons, new research aspect transfers to the realization of efficient DET with the employ of novel carbon nanomaterials [20–23]. Another main challenge of GBFCs exists in the enclosure of the electrodes. To date, most GBFCs were designed with nonflexible encapsulating materials such as silicon or hard polymer, which do not fit human bodies. The complex preparation process and high cost of GBFCs also hinder their development to a large extent.

Single-walled carbon nanotubes (SWCNTs) have a wide range of applications in electrochemical sensors, biosensing, and electrode fabrication because of their many unique properties, such as very large specific surface area and excellent conductivity [24, 25]. These advanced properties also greatly contribute to remedy the gap between the electrode and the active site of enzymes, thus accomplishing DET without involving the harmful electron mediators and finally enhancing the OCV as well as the power density [26, 27]. With these improvements, GBFCs are expected to be an alternative power supply for low-power-consuming portable devices, such as medical sensors [28]. Cosnier et al. reported the first implantable GBFC employing CNTs as the electrodes. They implanted the GBFC into the retroperitoneal space of a rat and finally delivered a power output of 38.7 μW [27]. However, the performance of GBFCs still needs to be further improved, which also includes cost saving and the biological compatibility.

We herein demonstrate a flexible thin-disk GBFC equipped with one side containing Pt particles and another side containing glucose oxidase (GOx). As shown in Figure 1, a piece of proton exchange membrane (PEM) was used to separate the anodic and cathodic compartments. In addition, we used SWCNTs as the electrode to realize DET between the electrode surface and the active site of enzymes. After being catalyzed by enzymes, the anodic reactants released hydrogen ions, which transferred to the cathode through the PEM. The process is illustrated in the following reactions:

$$\begin{aligned} \text{Anode} &: 2\text{Glucose} \rightarrow 2\text{Gluconolactone} + 4\text{H}^+ + 4\text{e}^- \\ \text{Cathode} &: \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \\ \text{Overall} &: 2\text{Glucose} + \text{O}_2 \rightarrow 2\text{Gluconolactone} + 2\text{H}_2\text{O} \end{aligned} \quad (1)$$

Finally, the GBFC exhibited an OCP of 0.4 V. After the optimization of catalyst amount, the completed thin-disk electrodes of the GBFC were fixed on a flexible enclosure composed of polydimethylsiloxane (PDMS) to increase the

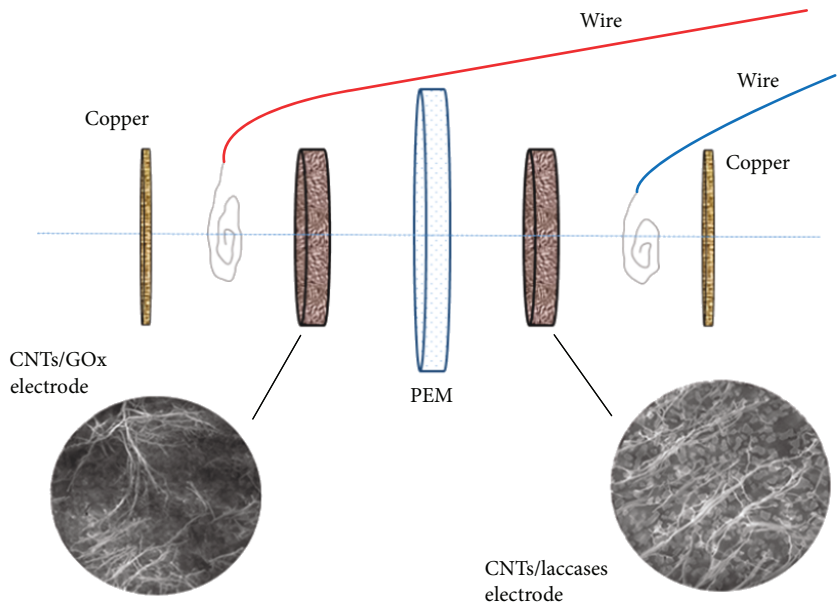

Figure 2: Exploded view of the internal structure of the bioelectrodes (bioanode with CNTs/GOx and biocathode with CNTs/laccase).

flexibility and compatibility. The final results showed that the GBFC is promising to be used for wearable or implantable devices.

2. Materials and Methods

2.1. Chemicals and Reagents. GOx from Aspergillus niger (200 U mg^{-1}solid) and laccase from Trametes versicolor (0.5 U mg^{-1}solid) were purchased from Sigma-Aldrich and used as received without further purification. α-D-Glucose was prepared in phosphate buffer 0.1 M (pH 7.0) at least 24 h before its use. Nafion 212 membranes (DuPont) were pretreated at 80°C with 5 wt% H_2O_2 and 5 wt% H_2SO_4 solutions for 2 h, rinsed, and then stored in D.I. water. SWCNT solution purchased from NanoIntegris Technologies was used after an ultrasonic dispersion. Unless otherwise noted, all chemicals and reagents in this study were of analytic grade.

2.2. Characterization of SWCNTs Used as Electrode Materials. The tested GBFC was composed of two electrodes that were synthesized by, respectively, mixing GOx (1 mg, dissolved in 0.5 mL of phosphate buffer) and laccase (1 mg, dissolved in 0.5 mL of phosphate buffer) with SWCNT solution (1 mL). No redox mediator was added in this work. Nafion 212 membrane played a fixed role in the middle of the electrodes while avoiding short circuit of the battery. To immobilize the mixed electrode on the PEM, it was added into a dropper, followed by depositing the electrode solution to both sides of the PEM. Then, the PEM with two electrodes was dried in air under room temperature. A drop of Nafion solution was finally added to both sides of the PEM to improve contact among the surfaces of PEM, enzymes, and SWCNTs.

Figure 2 shows the internal structure of the completed bioelectrodes. Two pieces of round copper were stuck to the PEM, which contributed to the implementation of electrical signal transmission. The surface of the GBFC was planar and smooth, with the thickness as thin as about 1 mm.

Figure 3 shows the morphology of the bioelectrodes observed by scanning electron microscopy (SEM). Enzyme agglomerates were widely distributed among the SWCNTs, suggesting the possible realization of direct electron transfer (DET).

To compare the performance with and without SWCNTs, we designed two experiments including the tests of SWCNT-based biofuel cell and carbon nanomaterial-free biofuel cell. The preparation methods of two different electrodes were the same, and the same amounts of enzymes and SWCNTs were used. Although no carbon nanomaterial was added to the control experiment, 1 mL dispersion (without any carbon nanomaterial) was dropped on the PEM and dried in air to exclude the interference of the dispersion of SWCNTs. After the bioelectrode fabrication, two pieces of round copper foil (red copper, 200 meshes, 3 cm in diameter) were stuck to the PEM with conductive silver adhesives.

Saturated glucose buffer (pH 7) was prepared over 24 h before the experiments. The bioelectrodes remained attached while being immersed in the buffer, which can be attributed to the immobilization of the copper. The maximum OCV produced by the SWCNT-based biofuel cell was 0.4 V, confirming the realization of DET. The control experiment was performed on a carbon nanomaterial-free biofuel cell and almost no current existence was observed, proving that the SWCNTs do play a role in the current generation.

2.3. Bioelectrode Fabrication. The final bioelectrodes of the GBFC were fabricated by, respectively, loading GOx and Pt particles with SWCNT dispersion, followed by a sonication bath.

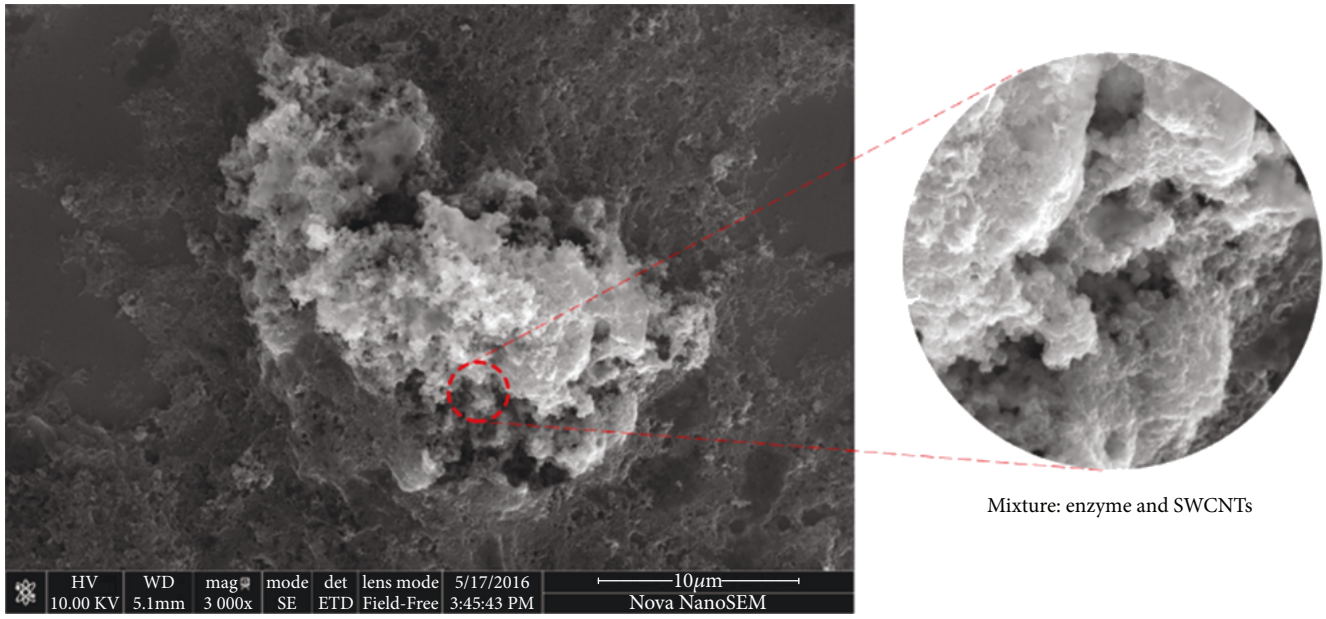

Figure 3: SEM micrograph of the bioelectrode (with enzymes and single-walled carbon nanotubes).

Biocathode Fabrication. In this experiment, the biocathode was fabricated layer by layer with SWCNTs and Pt particles loaded by turns. The PEM was coated at room temperature by a spray gun (3 mm caliber) filled with SWCNT alcoholic solution, which brings a better dispersion and makes it easier to be dried with a heater. An ion sputtering apparatus (Gaten, America) was used to sputter the Pt particles to the PEM, with the deposition speed of 0.1 nm/s.

Bioanode Fabrication. In this experiment, the bioanode was fabricated by mixing GOx and SWCNTs together in the alcoholic dispersion, followed by a sonication bath for 30 min. The well-mixed solution was poured into the 5 mm caliber spray gun and loaded onto the PEM, followed by drying in the heater.

2.4. GBFC Encapsulation with Polydimethylsiloxane. The work presented a flexible porous enclosure on the GBFC based on polydimethylsiloxane, designed as three centimeters in diameter (Figure 4). Both sides of electrodes should be in full contact with the respective reactant. Thus, thin-disk biofuel cells were designed to have one side with a sealed cavity and another side with a porous lid. The headspace of the cavity could be used to store biofuels for reaction at the anode while the bottom of it was designed to have a circular inlet which conveniently allowed the supplement of glucose solution. The holes on the surface of the lid guaranteed an adequate supply of oxygen, which made sure the catalytic reaction at the cathode could be proceeded exactly.

The porous structure of the lid was fabricated by pouring the PDMS (10 g mixed with curing agent) onto a printed circuit board with multi-micropillars, followed by heating in a constant temperature oven, while the sealed cavity was made by a columned mold. These two parts of the enclosure could be bonded with epoxy glue in the presence of a piece of thin-disk electrode on the middle floor. Figure 5 shows the integral flexible enclosure of the GBFC, which makes it beneficial for the application on wearable or implantable devices.

3. Results and Discussion

Researchers worldwide have exerted considerable efforts to realize DET by taking advantage of carbon nanomaterials, and further investigation has turned to the selection of electrode materials. In this study, we measured the OCP among two GBFCs which were fabricated with and without SWCNTs. The blank control group exhibited almost no voltage in the initial measurement, whereas the SWCNT-based biofuel cell generated a voltage growth prominently, which proved that the SWCNTs played an important role on the DET, without the need for an electron transfer mediator. In addition, the GBFC with SWCNTs displayed a good OCP value, which peaked at over 0.4 V.

The method employed above to immobilize the electrode mixture was moving it into a spray gun followed by sputtering it onto the PEM. In fact, the operation in solution facilitated the mixture of the SWCNTs and enzymes thoroughly by magnetic stirring and sputtering with a small-caliber spray gun then can accelerate the evaporation of alcohol. Meanwhile, the amounts of SWCNTs and enzymes immobilized on each electrode had less mass than 2 mg, which could significantly reduce the cost spent on the electrode preparation. Although the performance of the GBFC described above was still not optimal, the simple operation and low cost made it a great prospect to promote its practical application.

3.1. Biocathode Measurement. Biocathodes with different amounts of loaded Pt layers were compared and analyzed by the cyclic voltammetry (Figure 5). The sample loaded with Pt showed greater current density compared with the normal

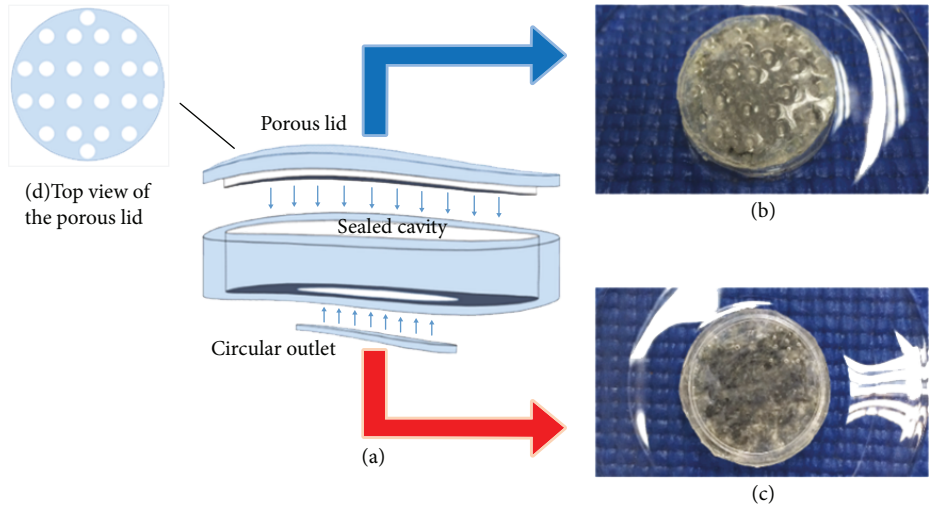

Figure 4: (a) Whole structure of the flexible porous enclosure fabricated by PDMS. (b) Photo of the entire GBFC encapsulated by PDMS: porous side. (c) Photo of the entire GBFC encapsulated by PDMS: glucose side. (d) Sketch of the porous lid.

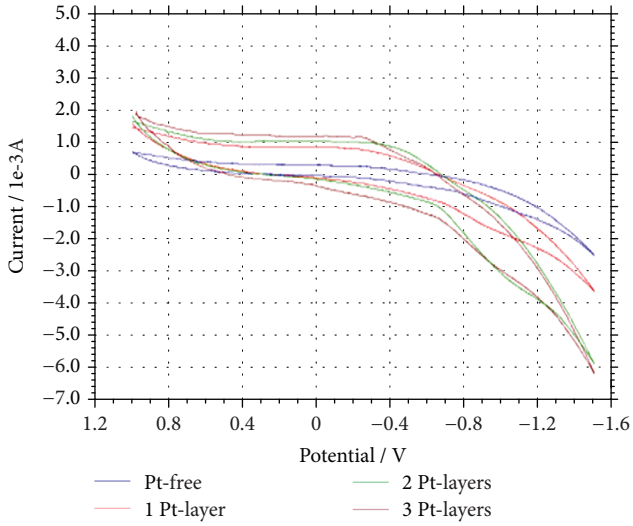

Figure 5: Cyclic voltammograms in 0.5 M glucose PBS with various Pt layers.

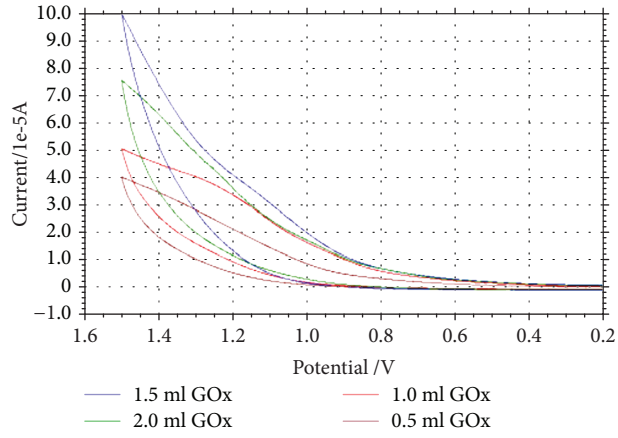

Figure 6: Cyclic voltammograms in 0.5 M glucose PBS with different amount of enzymes (GOx).

group. The increase in current density between the electrode with two Pt layers and that with three was not significant. Under comprehensive consideration, the electrode with two Pt layers was chosen as a part of the final GBFC.

3.2. Bioanode Measurement. Bioanodes with different amounts of loading enzymes were compared and analyzed by the cyclic voltammetry (Figure 6). Results indicated that the current density boosted with the addition of enzyme but decreased when its amount increased to 2 mL. Finally, the anode with 1.5 mL GOx was chosen.

3.3. PDMS Encapsulation. For practical applications on wearable and implantable devices, the enclosure of the GBFC was designed to be thin and flexible with a circular shape. At the anode, the GBFC was powered by the decomposition of glucose, which exists widely in human bodies, food, and nature and thus could be easily replenished. At the cathode, one side of the electrode could be thoroughly exposed to the air environment with the porous structure. Indeed, the decrease in quantity of electrode materials led to the volume reduction of the whole battery, thus diminishing the thickness of the GBFC to a level that fits better to human bodies. In addition, the flexible PDMS enclosure outside the flexible membrane electrodes also opened new possibilities for being attached onto the skin surface, without affecting the normal movement of human, or being implanted inside bodies to power implantable medical devices using the glucose in human blood as fuel.

4. Conclusions

A novel flexible thin-disk GBFC based on a SWCNT-GOx bioanode and a SWCNT-Pt biocathode was researched. It attained the highest OCP of 0.4 V, as a result of the relatively large surface area of SWCNTs for more enzymes to load on and then to catalyze the chemical reactions with the existence of glucose/O_2. The electrode solution with an optimized

amount of catalysts was sputtered on the PEM and dried in air in order to make a thin-disk cell, which simplified the process and reduced the consumption of costly electrode materials at the same time. Besides, the use of a PDMS porous enclosure on the membrane-type electrodes successfully improved the flexibility and the biological compatibility of the cell. Therefore, the developed GBFC provides great potential for powering wearable or implantable medical devices.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no conflict of interest.

Authors' Contributions

X. Y., Y. L., and W. X. conceived and designed the experiments; Y. L. and C. Z. performed the experiments and analyzed the data; X. Y. and W. X. guided the experiments and contributed reagents/materials/analysis tools; Y. L. wrote the paper; X. Y. modified the manuscript of the paper.

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References

[1] I. Willner and E. Katz, "Integration of layered redox proteins and conductive supports for bio-electronic applications," *Angewandte Chemie, International Edition*, vol. 39, no. 7, pp. 1180–1218, 2000.

[2] M. T. Meredith and S. D. Minteer, "Biofuel cells: enhanced enzymatic bioelectrocatalysis," *Annual Review of Analytical Chemistry*, vol. 5, no. 1, pp. 157–179, 2012.

[3] L. Halamkova, J. Halamek, V. Bocharova, A. Szczupak, L. Alfonta, and E. Katz, "Implanted biofuel cell operating in a living snail," *Journal of the American Chemical Society*, vol. 134, no. 11, pp. 5040–5043, 2012.

[4] F. Davis and S. P. J. Higson, "Biofuel cells: recent advances and applications," *Biosensors & Bioelectronics*, vol. 22, no. 7, pp. 1224–1235, 2007.

[5] A. Zebda, C. Gondran, A. le Goff, M. Holzinger, P. Cinquin, and S. Cosnier, "Mediatorless high-power glucose biofuel cells based on compressed carbon nanotube-enzyme electrodes," *Nature Communications*, vol. 2, no. 1, article 370, 2011.

[6] G. Zhou, F. Li, and H. M. Cheng, "Progress in flexible lithium batteries and future prospects," *Energy & Environmental Science*, vol. 7, no. 4, pp. 1307–1338, 2014.

[7] W. Jia, X. Wang, S. Imani et al., "Wearable textile biofuel cells for powering electronics," *Journal of Materials Chemistry A*, vol. 2, no. 43, pp. 18184–18189, 2014.

[8] C. H. Kuo, W. H. Huang, C. K. Lee et al., "Biofuel cells composed by using glucose oxidase on chitosan coated carbon fiber cloth," *International Journal of Electrochemical Science*, vol. 8, pp. 9242–9255, 2013.

[9] B. L. Horecker, "Pathways of carbohydrate metabolism and their physiological significance," *Journal of Chemical Education*, vol. 42, no. 5, p. 244, 1965.

[10] M. Alcalde, M. Ferrer, F. J. Plou, and A. Ballesteros, "Environmental biocatalysis: from remediation with enzymes to novel green processes," *Trends in Biotechnology*, vol. 24, no. 6, pp. 281–287, 2006.

[11] A. Heller, "Miniature biofuel cells," *Physical Chemistry Chemical Physics*, vol. 6, no. 2, pp. 209–216, 2004.

[12] J. Ryu, H. S. Kim, H. T. Hahn, and D. Lashmore, "Carbon nanotubes with platinum nano-islands as glucose biofuel cell electrodes," *Biosensors and Bioelectronics*, vol. 25, no. 7, pp. 1603–1608, 2010.

[13] A. Zebda, S. Cosnier, J. P. Alcaraz et al., "Single glucose biofuel cells implanted in rats power electronic devices," *Scientific Reports*, vol. 3, no. 1, 2013.

[14] M. Holzinger, A. le Goff, and S. Cosnier, "Carbon nanotube/enzyme biofuel cells," *Electrochimica Acta*, vol. 82, pp. 179–190, 2012.

[15] S. Cosnier, A. le Goff, and M. Holzinger, "Towards glucose biofuel cells implanted in human body for powering artificial organs: review," *Electrochemistry Communications*, vol. 38, pp. 19–23, 2014.

[16] P. Cinquin, C. Gondran, F. Giroud et al., "A glucose BioFuel cell implanted in rats," *PLoS One*, vol. 5, no. 5, article e10476, 2010.

[17] S. Kerzenmacher, J. Ducrée, R. Zengerle, and F. von Stetten, "Energy harvesting by implantable abiotically catalyzed glucose fuel cells," *Journal of Power Sources*, vol. 182, no. 1, pp. 1–17, 2008.

[18] S. Holmberg, A. Perebikovsky, L. Kulinsky, and M. Madou, "3-D micro and nano technologies for improvements in electrochemical power devices," *Micromachines*, vol. 5, no. 2, pp. 171–203, 2014.

[19] G. Güven, P. Lozano-Sanchez, and A. Güven, "Power generation from human leukocytes/lymphocytes in mammalian biofuel cell," *International Journal of Electrochemistry*, vol. 2013, Article ID 706792, 11 pages, 2013.

[20] Z. Liu, X. Lin, J. Y. Lee, W. Zhang, M. Han, and L. M. Gan, "Preparation and characterization of platinum-based electrocatalysts on multiwalled carbon nanotubes for proton exchange membrane fuel cells," *Langmuir*, vol. 18, no. 10, pp. 4054–4060, 2002.

[21] X. Sun, R. Li, D. Villers, J. P. Dodelet, and S. Desilets, "Composite electrodes made of Pt nanoparticles deposited on carbon nanotubes grown on fuel cell backings," *Chemical Physics Letters*, vol. 379, no. 1-2, pp. 99–104, 2003.

[22] C. Wang, M. Waje, X. Wang, J. M. Tang, R. C. Haddon, and Yan, "Proton exchange membrane fuel cells with carbon nanotube based electrodes," *Nano Letters*, vol. 4, no. 2, pp. 345–348, 2004.

[23] Y. Yao, Y. Ding, L. S. Ye, and X. H. Xia, "Two-step pyrolysis process to synthesize highly dispersed Pt-Ru/carbon nanotube catalysts for methanol electrooxidation," *Carbon*, vol. 44, no. 1, pp. 61–66, 2006.

[24] H. Kataura, Y. Kumazawa, Y. Maniwa et al., "Optical properties of single-wall carbon nanotubes," *Synthetic Metals*, vol. 103, no. 1-3, pp. 2555–2558, 1999.

[25] S. Cheraghi, M. A. Taher, H. Karimi-Maleh, and E. Faghih-Mirzaei, "A nano-structure label-free DNA biosensor for ciprofloxacin analysis as a chemotherapeutic agent: an experimental and theoretical investigation," *New Journal of Chemistry*, vol. 41, no. 12, pp. 4985–4989, 2017.

[26] C. Liu, S. Alwarappan, Z. Chen, X. Kong, and C. Z. Li, "Membraneless enzymatic biofuel cells based on graphene nanosheets," *Biosensors and Bioelectronics*, vol. 25, no. 7, pp. 1829–1833, 2010.

[27] C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam, and A. Govindaraj, "Graphene: the new two-dimensional nanomaterial," *Angewandte Chemie, International Edition*, vol. 48, no. 42, pp. 7752–7777, 2009.

[28] M. Holzinger, Y. Nishina, A. Le Goff, M. Tominaga, S. Cosnier, and S. Tsujimura, "Molecular design of glucose biofuel cell electrodes," *Molecular Technology: Energy Innovation*, vol. 3, pp. 288-289, 2018.