Application of Nano-modified Electrode in Glucose Biofuel Cell

Cao Meng, Zhou Yao*, Yan Qing
Danlian University, Danlian, 116622, China

*Corresponding author e-mail: 348237548@qq.com

Abstract. With the continuous consumption of energy and the worsening of the environment, new energy devices, such as glucose fuel cell, have also developed rapidly. The latest development of nanomaterials has also brought new opportunities for the field of biological fuel cell. This paper mainly introduces the latest research achievements of nano-modified electrode in the glucose fuel cell in recent years.

1. Introduction
Glucose is a very rich resources in nature. It is cheap, non-toxic, ready to use and environmentally friendly. In addition, the oxidation reaction of glucose can generate a lot of energy. And because glucose is a common energy currency in the organism, the biological fuel cell based on glucose is a potential source of biomimetic implants. It is well worth looking forward to develop an effective bioelectrocatalytic system for glucose oxidation and oxygen reduction. The glucose biological fuel cell consists of two half-reaction reactions shown as follows:

Equation 1 (anode): $\text{C}_6\text{H}_12\text{O}_6 + 24\text{OH}^- \rightarrow 6\text{CO}_2 + 18\text{H}_2\text{O} + 24\text{e}^-$
Equation 2 (cathode): $6\text{O}_2 + 12\text{H}_2\text{O} + 24\text{e}^- \rightarrow 24\text{OH}^-$
Total reaction: $\text{C}_6\text{H}_12\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$

The main research direction of glucose biological fuel cell is the design of the catalyst needed for the oxidation of glucose in the anode. In this paper, the application of nano-modified electrode in glucose biofuel battery at home and abroad in recent years is summarized.

2. Enzyme Biological Fuel Cell (EBFC)
In recent years, The glucose enzyme biological fuel cell (EBFC) have attracted worldwide attention, it due to it can directly convert glucose into electric energy and use it as an implantable power supply because it can directly use enzymes in biological fluids to catalyze the oxidation of glucose.

In the construction of EBFC, the immobilization of most of oxidoreductase on bare electrode is difficult because of the instability of biological substrate when interacting with the electrode surface. In order to achieve better bioelectrocatalysis effect, the hydrophobicity and stability should be considered when immobilizing the enzyme on the electrode. Various methods have been reported on how to enhance the electrochemical contact between enzymes and electrodes, such as the use of electron transfer mediator and the entrapment of enzymes in conductive polymers. Recently, the rapid development of nanomaterials has provided strong support for the solution of problems. The large surface area and high conductivity of nanomaterials are beneficial to the immobilization of the enzyme
on the surface of the electrode and the transfer of electrons. In addition, nanomaterials can provide a favourable microenvironment, which is beneficial to the retention of enzyme bioactivity.

Carbon nanotubes (CNT) are widely applied in nanomaterials because of their large specific surface area and high conductivity. In addition, a number of studies have shown that nitrogen doped carbon can effectively enhance the stability of materials. On the other hand, the graphite nitride carbon nanomaterials (g-C₃N₄ NSs) have become a promising material because of their high nitrogen content, low cost and controllable structure. In that case, Gai has prepared a porous and high-nitrogen-containing ternary complex of CNTs/g-C₃N₄ NSs. It is a kind of carbon nanotube, g-C₃N₄ NSs and gold nanoparticles (Au NPs) formed by the superposition and electrostatic interaction of the pi-pi and it were synthesized and used as electrode materials to modify EBFCs (Fig.1). In the preparation process, CNT and g-C₃N₄ NSs were first assembled by ultrasonic treatment to get CNTs/g-C₃N₄ NSs complex. Then, the Au NPs functionalized by carboxyl group was modified to CNTs/g-C₃N₄ NSs by electrostatic force, and CNTs/g-C₃N₄ NSs/Au NSs/Au was obtained. It is worth noting that the amino in the enzyme structure condensate with the carboxyl group on the surface of Au NPs, thereby realizing the binding of the enzyme to the ternary complex.

The authors first examined the electrochemical impedance spectroscopy (ESI) of the CNTs/g-C₃N₄ NSs/Au NPs modified electrode. The results showed that this ternary complex exhibited excellent electron conductivity. Next, the cyclic voltammogram (CV) of the enzyme electrode proved that the ternary complex can effectively enhance the bioelectrocatalytic activity of the enzyme, that is, the oxidation of glucose on the anode is more likely to occur. The control experiments showed that the introduction of g-C₃N₄ NSs into CNTs/Au NPs showed better catalytic activity. The authors further optimized the mass percentage of g-C₃N₄ NSs in the ternary complex. The results show that the effect is best when the mass percentage of g-C₃N₄ NSs is 50wt. %. This is due to a large amount of electron-rich pyridine nitrogen and quaternary nitrogen in CNTs/g-C₃N₄ NSs can provide sufficient free electrons to enhance the electron transfer efficiency, thereby facilitating the electro catalytic reaction of the enzyme. An excess of g-C₃N₄ NSs reduces the conductivity of the complex and blocks the porous structure and ultimately affects the electron transfer. To profit from the porous structure of the ternary complex and its high nitrogen content, the authors designed a membrane-free, medium-free glucose/O₂ EBFC based on an enzyme-modified ternary composite electrode. The cell was tested to have open circuit voltages and maximum power densities of 0.55 ± 0.03 V and 249 ± 4.2 μW cm⁻², respectively, in 0.1 M PBS solution containing 5 mM glucose.

Figure 1. Schematic illustration of assembly of the ternary hybrid and fabrication of the membrane-less and mediator-less glucose/O₂ EBFC.
3. glucose-powered non-enzymatic biofuel cell

EBFC, which uses glucose as its energy source, relies on a specific enzyme, that is, the oxidation of glucose oxidase at the anode. At the same time, other enzymes are required on the cathode to catalyze the reduction of O₂, such as lactase or bilirubin oxidase (BOD). However, the high specificity of enzymes, to a large extent, restricts the effective utilization of other types of biofuels, such as other sugars, in biomass and biological fluids. On the other hand, the inability of binding between the enzyme and the electrode will affect the performance of the fuel cell, it is often necessary to introduce a redox mediator into the EBFC. More importantly, unstable enzymes and redox mediators can greatly affect the stability of EBFC, thus limiting the practical application of EBFC. Non-enzymatic fuel cells have rekindled interest and have been further developed due to their excellent long-term stability and high power density.

Guo and others have resigned a PtBi binary modified nanoporous gold (NPG-PtBi) electro catalyst for anodes in glucose fuel cells. NPG-PtBi is prepared by sequential electroless plating and electrochemical plating on a NPG by sequentially coating a Pt layer with Bi particles. The authors constructed a simple glucose fuel cell with NPG-PtBi as anode and commercial Pt/C as cathode. Under the condition of an anode noble metal loading of only 0.45 mg cm⁻² (Au 0.3 mg and Pt 0.15 mg), the open circuit voltage reached 0.9 V, The maximum power density of 8 mW cm⁻². In addition, the authors compared the performance of fuel cells using NPG-PtBi with the same Pt loading and commercial electro catalyst JM-Pt/C (60%) as the anode. The maximum weight power density of NPG-PtBi is 18 mW mg⁻¹, about 4.5 times higher than commercial Pt/C.

Zhao and others have used a three-dimensional Nan composite electrode for implantable glucose biofuel cells, and the designed cell showed good performance. The power density in the physiological environment was 2.3 mW cm⁻² and the open circuit voltage was 0.70V. In addition, the fuel cell solution showed good stability. The whole fabrication process of three-dimensional Nan composites is electrochemical deposition of three-dimensional flower-like platinum (Pt) Nan clusters onto multi-walled carbon nanotubes (MWCNTs) by electrodeposition. The size of nuclei can be adjusted by adjusting the potential range as well as the distance between the clusters. Electrochemical studies showed that the novel three-dimensional Pt clusters prepared had significantly higher electro catalytic activity and better stability to glucose oxidation reaction and oxygen reduction reaction than Pt nanoparticles dispersed alone.

In the use of precious metal catalysts, especially Pt for the design of biofuel batteries, catalyst poisoning is an important aspect to be solved urgently. In order to avoid this problem, Zhao et al further deposited 3D PtNi/MWCNTs catalyst on multi-walled carbon nanotubes (MWCNTs) by depositing three-dimensional flower-like platinum (Pt). Polarization curves, cell performance and stability tests showed that the 3D PtNi/MWCNTs catalyst has higher performance and stability for implantable GBFC than the 3DPt/MWCNTs and the uniformly dispersed PtNi/MWCNTs, and the Pt/When the atomic ratio of Ni was 3/7, the constructed biofuel cell exhibited the highest power density and open circuit potential in the physiological environment of 3.12 ± 0.04 mW cm⁻² and 0.786 ± 0.005 V, respectively (FIG. 2 shows the cell Schematic diagram of the role of principle). This new approach has made this 3D PtNi/MWCNTs a promising next generation fuel cell catalyst candidate for operation under mild conditions.
Xu and others have utilized a nano porous gold (NPG) structure as an effective electro catalyst for glucose oxidation to construct a biofuel cell. The surface cleansing NPG structure was first reduced by H\textsubscript{2}AuCl\textsubscript{4} by sodium citrate (Na\textsubscript{3}Cit) in an ice-water bath and then by kinetic-controlled self-assembly. The preparation method breaks through the traditional trisodium citrate thermal reduction chloroauric acid method and can be realized without heating the reaction. It is worth noting that under the same conditions, the surface-cleaved NPG structure produces a highly enhanced catalytic activity in glucose electro oxidation with a current density of about 9 A cm\textsuperscript{-2} mg\textsuperscript{-1}. The remarkable electro catalytic activity of NPG can be attributed to the large electrochemically active surface area, the clean surface and the highly active sites of the porous structure. The use of surface-cleaned NPG for glucose biofuel cells has seen significant improvements in performance, indicating that NPG has great potential for use in biofuel cells.

Navaee has prepared a highly efficient catalyst for glucose oxidation, FePt nanoparticles, by introducing transition metal iron. The authors studied the effect of Fe ratio and particle size on the electro catalytic activity. The results showed that the small size Fe\textsubscript{15}Pt\textsubscript{85} had the highest glucose oxidation activity. The Pt biodegradable nitrogen-doped grapheme was used as a cathode and the Fe\textsubscript{15}Pt\textsubscript{85} was used as an anode, glucose biofuel cell with an open-circuit voltage of 0.64V, and the maximum power density is 95 mW cm\textsuperscript{-2} when the battery voltage is 0.44 V.

It has been shown that the Co\textsubscript{3}O\textsubscript{4} nanostructures also have excellent catalytic ability for glucose oxidation. Therefore, Co\textsubscript{3}O\textsubscript{4} nanostructures can be used as a stable alternative to glucose oxidase. With precious metal nanomaterials, Co\textsubscript{3}O\textsubscript{4} has the advantage of being inexpensive, which makes Co\textsubscript{3}O\textsubscript{4} more widely available. However, Co\textsubscript{3}O\textsubscript{4} is different from other metal oxides, its conductivity is poor, and conductive nano-materials and Co\textsubscript{3}O\textsubscript{4} complex will be able to effectively solve this problem. So chen has designed a unique fuel cell by combining the new conducting nanomaterials grapheme and Co\textsubscript{3}O\textsubscript{4}. The cell was able to efficiently collect electricity from various sweet biofuels (glucose, sucrose, or lactose) with two non-enzymatic electrodes coated with three-dimensional graphene composite based on Co\textsubscript{3}O\textsubscript{4} as the anode and the cathode, respectively, as shown in FIG. Utilizing the double catalytic ability of Co\textsubscript{3}O\textsubscript{4} nanostructures for glucose oxidation and oxygen reduction and the unique structural characteristics of 3D graphene, the open circuit voltage can reach 1.1 V at a glucose concentration of 200 mM, close to the theoretical limit of 1.2 V, and the output power density reached 2.38 ± 0.17 mW cm\textsuperscript{-2}. In addition, since the glucose fuel cell does not contain enzymes and redox mediators, it shows good stability. After 30 days, the open circuit voltage dropped only 27%.

**Figure 2.** The GBFCs equipped with 3D PtNi/MWCNTs catalysts.
Zhang has also reported the use of Co$_3$O$_4$ as an electro catalyst for the oxidation of glucose to be used in biofuel batteries. Unlike Chen and other research, Co$_3$O$_4$ is a cobalt oxide hollow nan dodecahedron (Co$_3$O$_4$-HND) obtained by simple thermal conversion of a Co-based metal-organic framework (Co-MOF, ZIF-67) template. Co$_3$O$_4$-HND showed high catalytic activity when tested as an electro catalyst for glucose oxidation reactions. Based on the non-enzymatic oxidation of glucose, Co$_3$O$_4$-HND can be used as a non-enzymatic and non-noble metal electro catalyst in glucose biofuel cell due to its excellent electrochemical performance, low cost and simple preparation. Table 1 summarizes the non-enzymatic biofuel cell performance of the above five nano-modified electrodes.

| Literature | Anode Catalyst | Open Circuit Voltage | Output Power Density |
|------------|----------------|----------------------|---------------------|
| [1]        | NPG-PtBi       | 0.9 V                | 8 mW cm$^{-2}$      |
| [2]        | 3D Pt/MWCNTs   | 0.70V                | 2.3 mW cm$^{-2}$    |
| [3]        | 3D PtNi/ MWCNTs| 0.786±0.005V         | 3.12±0.04 mW cm$^{-2}$ |
| [4]        | Fe$_{13}$Pt$_{85}$ | 0.64V             | 95 mW cm$^{-2}$     |
| [5]        | 3D graphene-Co$_3$O$_4$ | 1.1V              | 2.38 ± 0.17 mW cm$^{-2}$ |

**4. Summary**

In this paper, the latest research results of the nano-modified electrode in the glucose biofuel battery are summarized. From the current development perspective, nanomaterials can serve as electrode substrates in enzyme biofuel cells to promote electron transfer between the enzyme and the electrode. More importantly, various types of nanomaterials, such as noble metal nanomaterials, metal oxide nanomaterials and carbon nanomaterials, have also been proved to be good alternatives to enzyme catalysts to improve the performance of BFC, especially stability. The role of nanomaterials in glucose fuel cells is as follows: a). Nanomaterials provide larger specific surface areas, thereby providing more redox sites; b). Nanomaterials have high electrical conductivity that promotes Electron transfer and electrode surface catalytic process; c). Nanomaterials showed higher stability conducive to the maintenance of fuel cell performance. However, in the design of non-enzymatic biofuel cells, more research is still on precious metal-based catalysts such as gold and platinum. In summary, the introduction of new nanomaterials, especially non-noble metal nanomaterials, will be even more important in the design of glucose biofuel cells.
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