Conductive multilayered polyelectrolyte films improved performance in microbial fuel cells (MFCs)

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HIGHLIGHTS
- GE and PAH multilayered films were used to modify the anode in MFCs.
- The modification method was based on layer-by-layer (LBL) self-assembly technique.
- The modified anodes could produce a higher level of electricity output.
- The ITO/(PAH/GE)2 anode electrode could output stable and the highest energy.

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ABSTRACT
Microbial fuel cells (MFCs) are bioelectronics devices that can directly convert the chemical energy from organic matter to electricity by the catalytic activity of living microorganisms. The performance of the MFCs could be influenced by many factors, such as anode materials and surface structure. Based on our previous work, in this paper, graphene (GE) nanosheets and poly(allylamine hydrochloride) (PAH) multilayered films were used to modify the anode in MFCs via layer-by-layer (LBL) self-assembly technique. Compared with the bare anode method, the multilayered films could improve the conductive ability between the bacteria and the anode so that produce a higher level of electricity output. The electrochemical performances of anodes modified with different (PAH/GE)n in the MFC were investigated. The results demonstrated that the ITO/(PAH/GE)2 anode produced a much higher and more stable current level. The electrode modified with the (PAH/GE)6 is promising for the development of MFCs in the future.

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1. Introduction

There are many factors that influence the performance of the MFC, including electrode materials, microbial source, electrolyte compositions, and reactor configurations [1–3]. MFC anodes need certain properties such as (i) good biocompatibility to support microbial growth, (ii) high electrical conductivity and (iii) electrochemically inert [4] to be suitable as a bio-anode. But bad adhesion of microorganisms and poor electron transfer capability limit the application of the conventional anode material. In order to achieve that, many materials and methods have been used in MFC electrode modification [5,6]. Anode modification with nano-materials is one of the best ways to improve these properties. After modification, the specific surface area, surface biocompatibility, conductivity and electrochemical activity of the anode are improved obviously, thus the power output of the MFC is increased [7]. Sun et al. [8] also advocated that the fabrication materials of electrode played a profound role in influencing power generation by determining the actual accessible area for bacteria to anchor and affecting the interfacial electron transfer resistance. Hence, modifying the anode surface with an appropriate material that can facilitate electron transfer is essential. Nano-structured materials, which have unique
electrical and structural properties, e.g. carbon nano-tubes and carbon nanoparticles were found to be efficient modifiers for such function [9]. Traditionally, CNT is considered to be the perfect electrode modifier as anodes in MFCs due to their chemical stability and good biocompatibility [10–13]. Recently, emerging graphene materials were gradually applied to modify the electrode because of its excellent physical and chemical characteristics. Compared with the CNT, graphene has better electrical properties and higher surface area, which is more suitable to modify MFC anode than CNT.

However, graphene without any treatment is hydrophobic and not conductive to microbial load on its surface. To improve their biocompatibility and dispersion properties, it is necessary to treat graphene with mixed acids [14–16]. By pre-treatment, various different oxygen functional groups have been grafted onto the surface of the graphene.

Nowadays, there is a growing concern on the polymer electrolyte, which is used as a key component in the development of the performance of MFC [17], Park et al. [18] found that the polymer electrolyte could not only lower the internal resistance, but also increase the surface area in MFC. Khan [19] assessed ionically cross-linked polyelectrolyte complex membranes of cationic chitosan/anionic poly(acrylic acid) on fuel cells and found the membranes exhibited high ion exchange capacity, high proton conductivity, low methanol permeability, and adequate thermal and mechanical stability. In our previous work [20], chitosan were used to modify the anode, and the modified anode within the polymer matrix could produce a higher quantity of electricity output. In addition, the high ionic conductivity of PAH was applied in this work to modify the anode.

The LBL self-assembly technique is a versatile approach to fabricate nanostructure thin films and is typically accomplished by alternating the adsorption of mutually interacting polymers on surfaces, it was first introduced in the early 1990s by Decher, Moehwald and Lsv [21–24]. This method is based on non-covalent intermolecular interactions among charged or hydrocarbon-modified moieties. The LBL technique has been used as a new approach to produce multilayered thin films for such uses as fuel cells and sensors. Recently, Sun et al. used multiwall carbon nanotube (MWNT) and poly(ethyleneimine) (PEI) multilayered films to modify a carbon paper electrode based on LBL self-assembly technique, they found that the MFCs with the modified anode could produce a 20% enhancement power density comparing with the bare TP anode [8]. LBL film may improve biocompatibility and may be advantageous in the fabrication of the biofilm between the bacteria and the electrode, which could be used to magnify the current output in the MFC system.

In this research, graphene nanosheets and poly(allylamine hydrochloride) (PAH) were modified on the anode in MFCs based on LBL self-assembly technique in order to study anode modification on the performance of MFCs.

2. Experimental

2.1. Chemicals and materials

The ITO was purchased from KangDaKe Photoelectric Technology Co. Ltd. The Shewanella loihica PV-4 was purchased from the American Type Culture Collection (ATCC). The PAH and Graphene were purchased from Aldrich Company. The sodium bicarbonate (NaHCO3) obtained from Tianjin OumChemical Development Center, calcium chloride (CaCl2) obtained from Shanghai MeiXing Chemical Industry Co. Ltd., ammonium chloride (NH4Cl) obtained from Shanghai Chemical Reagent Co, Ltd., magnesium chloride hexahydrate (MgCl2·6H2O) and sodium chloride (NaCl) obtained from Shantou LongXi Chemical Industry Co. Ltd., sodium lactate (CH3C6H5O7Na) obtained from Bio Basic Inc.

2.2. The ITO modified with the layer-by-layer (LBL) self-assembly technique

First, the charged ITO glass was treated. The ITO was immersed in 3.95% potassium hydroxide (KOH) in Acetic acid (CH3COOH) solution and treated 5 min with ultrasound. Then, the ITO electrode was treated with ethyl alcohol and ultrapure water for 5 min. The ITO was negatively charged after the treatments. Second, in order to make graphene convenient for self-assembly in the following step, graphene was acidified to obtain oxygen-containing functional groups. Graphene was sonicated in concentrated nitric acid and sulfuric acid (v/v, 1:3) mixed solution for 24 h, the large particles of graphene were removed with filter paper.

The ITO/(GE/PAH)n (n = 0, 2, 4, 6) were prepared as follows. 1 mg/mL Graphene and PAH solution were prepared, respectively. First, the ITO conductive glass was immersed in PAH solution for 15 min, the positively charged PAH will be adsorbed on the negatively charged ITO glass and the glass surface will be positively charged (it is marked as ITO/PAH). Then, the excess PAH was removed with water. Second, the ITO/PAH was immersed in GE solution for 15 min and the negatively charged GE will be adsorbed on the ITO/PAH. Then the ITO/PAH/GE was soaked in ultrapure water for 5 min to remove the excess GE. Third, the above steps will be repeated expected times, the electrode ITO/(PAH/GE)n (n = 0, 2, 4, 6) will be obtained.

2.3. Cell cultivation

The S. loihica PV-4 were first cultivated in 10 ml Difco marine broth 2216 for 24 h at 37 °C. Then, the bacterial solution was centrifuged at 10,000 rpm for 10 min and dissolved in 10 ml cultivation solution. The cultivation solution consisted of 2.5 g NaHCO3, 0.06 g CaCl2, 1 g NH4Cl, 0.2 MgCl2·6H2O, 10 g NaCl, and 1.7 ml CH3COONa per liter for 48 h at 37 °C. The optical density value (OD value) was measured; an Eppendorf AG 22331 spectrophotometer (Eppendorf, Hamburg, Germany) was used to measure the OD value of the liquid culture medium. The wave-length for measuring S. loihica PV-4 is 600 nm. The OD value was 0.8, and the solution containing the bacteria was injected into the reactor.

2.4. Measurements of scanning electronic microscopy (SEM)

Surface morphology images of the electrode surfaces were taken with a Zeiss Ultra Plus field emission SEM operating at 0.8 kV (Zeiss, Oberkochen, Germany).

2.5. MFCs reactor construction

The experimental device was a single-compartment MFC (Fig. 1). The bare ITO (denoted as the ITO anode) and LBL assembled ITO/(PAH/GE)n (n = 0, 2, 4, 6) were used as working anodes. Each anode surface with certain electro active species was about 0.8 cm². A Pt electrode and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The chamber was cubic, with an internal volume of 13 ml, and filled with 4 ml cultivation solution. The cultivation solution was used for bacterial growth and also served as the working solution for the electrochemical test. The CH3COONa was the electron donor.

2.6. Electrochemical measurement

All the current–time curves and cyclic voltammetry were measured by the electrochemical workstation (CHI 660d CHI instruments Inc., Shanghai, PR China). The applied potential of ITO for current measurements was 0.2 V. The scan rate of the CV
measurements was 0.1 V/s. All of the mentioned measurements were performed for the anode system.

3. Results and discussion

Graphene, however, just like other carbon materials, is unfavorable for bacteria adhesion as its highly hydrophobic. Thus we decorated the surface of graphene with hydrophilic conducting polymer PAH through in situ polymerization in order to promote bacteria adhesion and form the biofilm. The surface structure of the ITO/(PAH/GE)$_2$ and ITO/(PAH/GE)$_4$ electrodes at different magnifications are shown in Fig. 2. There were many irregular shape PAH/GE nanosheets attached firmly on the surface of the anodes which indicated the PAH/GE was self-assembly on electrode successfully. What’s more, the surface area of the electrode was enhanced. Theoretically this kind of surface structure could be rather beneficial to MFC system, because it could maximize the available surface area for bacteria to immobilize. What’s more, the graphene may also help to facilitate efficient electron transfer between the endogenous mediators and electrode by means of the extraordinary electrical conductivity of graphene. But there were differences between the two modification electrode, the image of the ITO/(PAH/GE)$_2$ clearly displayed an amorphous, networked rod nanostructure without any aggregation (Fig. 2A), its corresponding

![Fig. 1. Schematic diagram of MFC (A); photograph of MFC (B).](image)

![Fig. 2. SEM images of the ITO/(PAH/GE)$_2$ at low magnification (A), at high magnification (B). The ITO/(PAH/GE)$_4$ at low magnification (C), at high magnification (D).](image)
higher magnification image (Fig. 2B), appeared rougher, which benefited sufficient bacterial hold on it. There were many pore structures emerged in the electrode surface of ITO/(PAH/GE)$_4$ (Fig. 2C and D), which was not conducive to the growth of bacteria. Regardless of the electron transfer mechanism between the bacteria and electrons, the anode surface structure and its ability to interact with the bacteria seem to be of critical importance [8, 25–27], that may be the reason why the ITO/(PAH/GE)$_2$ had the best electrochemistry properties.

Fig. 3 shows the current–time curves of the MFCs with different layers of (PAH/GE)$_n$. Compared with the blank ITO anode system, anode system modified with (PAH/GE)$_n$ could output larger and more stable current. It is because the graphene has stable electrochemical properties, larger specific surface area, good conductivity and high carrier mobility rate so that provide sufficient sufficiency for bacteria to adhesion and facilitate efficient electron transfer between the endogenous mediators and electrode. What’s more, PAH is positively charged in neutral solutions, it can electrostatically interact with the negatively charged bacteria membrane. That could improve the bio-compatibility and be advantage to fabricate the bio-film between the bacteria and the electrode, which could be used magnify the electricity generation in the MFC system.

Further observation graph could find that, as the number of modified layers increased, the electricity generation firstly became bigger, and the ITO/(PAH/GE)$_2$ could output the largest energy. It because the (PAH/GE)$_2$ has the specific surface structure, which could provide a better environment conducive to bacterial growth. When the layers continued to increase, the electricity generation became lower. It may because that thicker film on electrode tends to pile up together and the surface structure changed to not conducive to microbial adsorption [28], which result that the electricity generation in MFC become lower.

Cyclic voltammetry was used to evaluate the electrochemical activity of the anodes after current–time test. Fig. 4 shows the results of the CVs, There was a pair of well-defined redox waves on every electrode. The potential separation ($\Delta E_p$) between the anodic and cathodic peaks ($E_{pa} - E_{pc}$) was 290 mV, and such a large peak-to-peak separation may be caused by the rough and uneven macroscopic structure of the ITO electrode surface. As the number of the PAH/GE multilayered films increased, the anodic and cathodic redox peak potentials shifted slightly to more negative in negative pole and more positive in positive pole, respectively, which could be a result of increasing microscopic roughness of the electrode surface [8]. Both the anodic and cathodic peak currents on modified electrode were enhanced remarkably compared with the bare anode, that may because (i) the presence of the PAH/GE could absorb more bacteria thus produce more electric energy and (ii) the graphene could promote a higher electric conductivity between the bacteria and the electrode so that reduce the power loss in transmission. In addition, the anode with the ITO/(PAH/GE)$_2$ had the highest redox peak potential. This finding is in agreement with the result of the current–time curves.

4. Conclusions

Utilizing the layer-by-layer (LbL) self-assembly technique, graphene and PAH multilayered film were successfully modified on the ITO conductive glass. The microstructure and electrochemical performances of the ITO/(PAH/GE)$_n$ films were studied in this work. SEM test showed that ITO/(PAH/GE)$_2$ electrode surface displayed an amorphous, networked rod nanostructure. As the number of modified layers increased, there were many pore and aggregation structures emerged in the electrode surface, which was not conducive to the growth of bacterial. The current–time curves and Cyclic voltammetry proved that graphene and PAH multilayered film modified on the electrode surface could significantly improve the electricity generation performance of MFC, and the ITO/(PAH/GE)$_2$ anode electrode could output more stable and the high energy.

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