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On/off states of a microbial fuel cell controlled by an optical switching system†

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An optical signal was successfully employed to reversibly switch the on/off states of a microbial fuel cell via an optical switching system consisted with a functionalized electrode and a photoacid. Using this switching system as the controlling component can achieve an effective, fast and reliable control of a MFC.

Microbial fuel cells (MFCs) are gaining great interest from researchers in different areas, due to the potential applications in wastewater treatment, bioelectrochemical synthesis and biosensor areas.[1-4] Achieving an effective and reliable control of a MFC is an important issue for its applications.[5, 6] The most suitable parameter for controlling a MFC is the electric current. But there is still little work reported about how to control the current production of a MFC. In recent years, enzymatic fuel cells based on stimuli-responsive electrodes have been developed and proposed for applications in signal processing, biofuel cells power switching and information storage and transduction.[7-11] However, the core parts of these enzymatic fuel cells were electrochemically active enzymes. Compared to enzymatic fuel cells, MFCs are more difficult to be controlled by external signals. It is because the electrochemically active bacteria, the core parts of MFCs, are more robust than enzymes. Thereby, external signals are more difficult to affect bacterial activities and eventually control the MFC. Also, the complexity of bacterial genetic regulation system and the metabolism processes would make the response sluggish.[12] Therefore, to our knowledge, the best way to control a MFC is controlling the electrodes rather than the bacteria. Stimuli-responsive functionalized interfaces provide us the possibility.[13-16]

Typical stimuli-responsive functionalized interfaces are fabricated by grafting stimuli-responsive chemical matrix on conductive electrode material. For example, pH sensitive interfaces are the most mature stimuli-responsive interfaces, which are usually made by modifying the bare electrode with a pH sensitive polymer layer and the electrode conductivity can be controlled by the degree of the polymer layer swelling or shrinking. Swelling or shrinking of the polymer layer was depending on the environmental pH condition. Thereby, to control the electric current production of a MFC equipped with a pH-sensitive interface modified electrode, the pH of the medium should be artificially tuned to a certain level.[17] In most cases, the pH sensitive interface is controlled by dosing acids/alkalis or other chemicals can be transformed to acids or alkalis by specific reactions, *e.g.*, glucose oxidation and urea degradation.[18, 19] Afterwards, to reset the MFC, pH should be tuned back to the initial level.[20] Thus, other chemicals are needed to be dosing into the system, which would result in chemicals and by-products accumulation and decreasing the system stability and reproducibility. Instead of these invasive signals, using non-contact signals, *e.g.*, light, temperature and magnetic field, to trigger the pH shift and then controlling the current production would be more ideal, due to the following advantages: 1) has less side effects; 2) easier to control; 3) more compatible with different types of control units. Most environmental factors, *e.g.*, light and temperature, are non-contact signals. Thus, developing a MFC controlled by non-contact signals provides the possibility of building “smart” MFCs that can be self-regulated according to environmental variations.

In our work, we demonstrated an optical switching system for controlling a MFC. To bridge the optical signal and the electric current production of a MFC, the optical switching system involves two components: photoacid and an ITO electrode with poly (4-vinyl pyridine) (P4VP) modified interface. The photoacid can reversibly undergo photo-isomerization upon light illumination, which releases protons and therefore decreases the solution pH.[21] When the light illumination is removed, the photoacid reunites with protons, which increases the pH to the initial level. Through the photo-isomerization processes of the photoacid, the photoacid can transduce an optical signal to a pH shift; the conductivity of the ITO electrode with poly (4-vinyl pyridine) (P4VP) modified interface is sensitive to pH value. Thereby, combining these two components into a cathode chamber of a MFC can switch the current production of the MFC by an optical signal.

To investigate the performance of the synthesized photoacid and the fabricated electrode, the properties of the photoacid and the polymer modified electrode were firstly tested separately. The photoacid, a merocyanine with propyl sulfonate group on the nitrogen of the indoline moiety, could reversibly change the solution pH by optical signals based on photo-isomerization reactions (Fig.1a): in the case of no illumination, the photoacid (MEH) solution is predominant in the form of protonated merocyanine (ME), which is a weak acid. In the case of being under illumination (λ_{max}=419), ME isomerizes rapidly undergo a 6π-electrocyclic ring closing reaction and then causes proton complete dissociation.[22] This process transforms the MEH from ME state to SP^+ state, which is a strong acid and thus decreases the solution pH. These transformations caused by the optical signal were reversible.

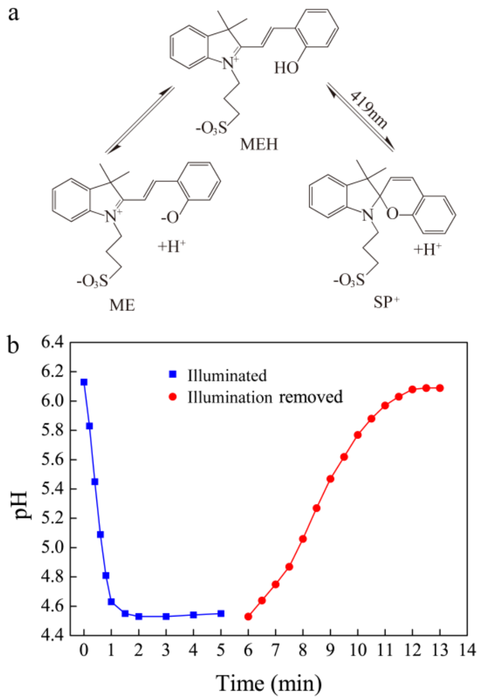

Fig.1 (a) The transformation of the photoacid among MEH, ME and SP^+ states; (b) The pH variation of the photoacid solution (600 μM) with/without the illumination (λ=405 nm).

In our illumination test, the initial photoacid solution pH was adjusted to 6.1 to obtain the largest ON/OFF current ratio. When the photoacid solution (600 μM) was under illumination (a laser transmitter, λ=405 nm, 100mW), the pH dramatically dropped from 6.1 to 4.5 and then the pH was stable at 4.5. When the illumination was removed, the pH value was recovered to the initial level (pH=6.1) (Fig.1b). Besides the eligible pH variation range for controlling the pH sensitive interface, our photoacid has another two merits: 1) Fast photo-isomerization. 600 μM photoacid can release enough protons to decrease the solution pH from 6.1 to 4.5 in 2 minutes and 6 minutes for the pH recovery, which allows to conduct a quick switch of the pH sensitive interface; 2) The long-lived photo-isomerized state of the photoacid (at least 5 minutes) leaves enough time to activate the pH sensitive interface. Even after the pH variation experiments were repeated 15 times, the pH variation was still stable (data not shown). Based on the obtained results, the photoacid was qualified to trigger the activation of the pH sensitive interface.

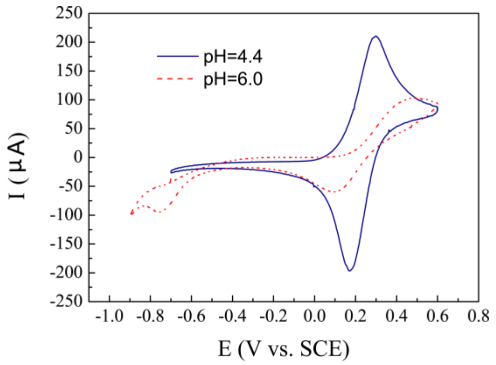

Fig.2 Cyclic voltammograms of the functionalized electrode at different electrolyte pH.

As another important component of the optical switching system, the electrode with pH sensitive interface was fabricated by grafting the pH sensitive polymer, P4VP, on the ITO single-side conducting glass. The functionalized ITO electrode was evaluated in a standard potentiostatically controlled three-electrode system with cyclic voltammetry (CV) method. The electrolyte (without the photoacid) pH was artificially adjusted by HCl solution or NaOH solution. When the electrolyte was at pH=6.0, a small reduction peak (I_{max}=-65 μA) was shown in the cyclic voltammograms (Fig.2). When the electrolyte was at pH=4.4, the height of the reduction peak dramatically increased (I_{max}=-196 μA). These changes were attributed to the morphological change of the polymer interface caused by the solution pH value variation. Specifically, when the pH of the electrolyte was around 6.1, the tethered P4VP chains collapsed on the ITO glass, thus the shrunken hydrophobic polymer prevented the permeation of the potassium ferricyanide ions to the ITO conducting base.[17] When the pH of the electrolyte was around 4.4, the pyridine functional groups on the polymer chains were ionized into the positive charged hydrophilic state. This resulted in the swelling polymer layer and the ITO conductive surface became accessible. Therefore the $[Fe(CN)_6]^{3-}$ ions were able to be attracted to the ITO surface and were reduced on the surface. Theoretically, no reduction peak can be observed in the cyclic voltammograms at pH=6.1. However, there was still a minor $[Fe(CN)_6]^{3-}$ reduction peak in the cyclic voltammograms (about -65 μA), which might be owning to the grafting defects on the electrode surface. Although the electrode was not perfect, the low level current at OFF state was still acceptable compared to the current signal at ON state (the ratio of ON/OFF current, *i.e.*, the ratio of the reduction peak height at the ON state to that at the OFF state, was around 3). The current in OFF state was about 65 μA, which indicated the functionalized interface was not completely shrunken. This allowed bacteria respire with the anode in MFC mode when the cathode of the MFC was in “OFF” state.

The reproducibility is another important factor for evaluating the reliability of the functionalized electrode. Therefore, the electrode was switched between ON and OFF states repeatedly for 5 cycles. The peak heights at pH=4.4 and 6.1 were both recorded. The ratio of ON/OFF current was stable (around 3), which indicated that the functionalized electrode was reliable for multiple switches.

After being tested separately, the photoacid and the functionalized electrode were integrated to be an optical switching system. The most important three indexes representing the overall performance of the optical switching system are the ratio of ON/OFF current, response time and reproducibility. The larger the ratio of ON/OFF current is, the better ON and OFF states are defined. We repeatedly switched the system for 15 cycles and the ratio obtained from CV measurements was stabilized around 1.7 (Fig.3). While, the ratio obtained from chronoamperometry (CA) measurements was 1.34±0.03 (averaged from three cycles). The difference was because the results obtained from CV were instantaneous values and the ratios deduced from CA were 5 minutes averaged values. Katz *et al.* built a similar optical switching system based on photoisomerizable nitrospiropyran/nitromerocyanine monolayer modified Au electrodes. The ratios of the electrical responses at ON and OFF states vary from 1.90 to 2.20, which are higher than our results.[23] However, our system is more versatile.

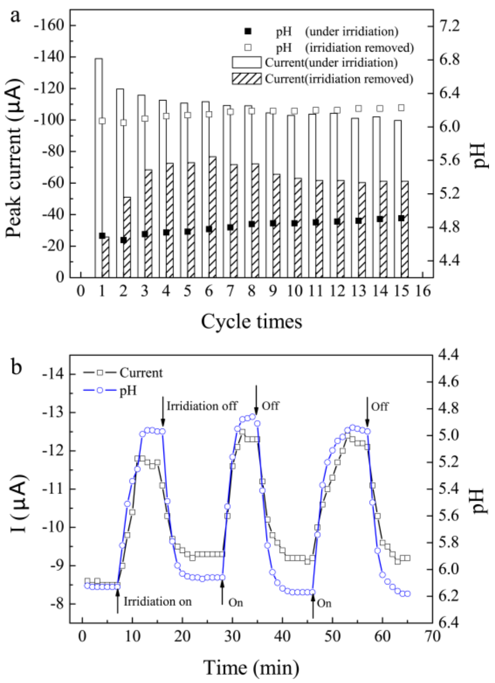

Fig.3 (a) The reduction peak current in cyclic voltammograms in ON and OFF states and pH variations in 15 cycles; (b) Chronoamperometric current and pH variation controlled by an optical signal.

The integration of the photoacid and the functionalized electrode provides a way for a quick ON/OFF switch. The response time for switching from OFF state to ON state was 4.33±1.73 minutes and 5.67±0.57 minutes for switching from ON state to OFF state (averaged from three cycles). Compared to enzymatic reactions based pH switching system, our photoisomerizable reaction based optical switching system has a shorter response time. For example, Tam *et al.* developed a dual enzyme controlled interface to enable and reset a glucose biosensor, the enable time was around 5 minutes and the reset time was about 20 minutes, which was 4 times longer than our optical signal switching system.[11] Another advantage of our system compared to those enzymatic reactions based switching system is the input to the system is an optical signal, which is non-contact. A non-contact input signal can minimize the impact on MFCs comparing to contacting signals (*e.g.*, dosing chemicals). Our optical switching system offers a possibility that utilizing visible light or sunlight as an input signal to control microbial fuel cells. With the help of the long-distance transmission property of laser, this system could also possibly realize remote control with laser. From the aspect of practical applications, our optical switching system can be in employed to achieve *in situ* and real-time control of marine sediment MFCs with laser.

To evaluate the reproducibility of the system, we repeatedly switched the system with an optical signal. Even after being switched for 15 times, the ratios of ON/OFF current were still relatively stable (Fig. 3a). This indicated our optical switching system is reliable. However, compared to the performance of the photoacid and the functionalized electrode tested separately, both the pH variation range and the ratio of ON/OFF current were diminished. This may be due to the equilibrium among MEH, ME and SP+ state of the photoacid was disturbed by the ionization of the modified polymer on the ITO base. To improve the performance, future work should focus on developing some alternatives for the photoacid or the polymer layer to eliminate the interference.

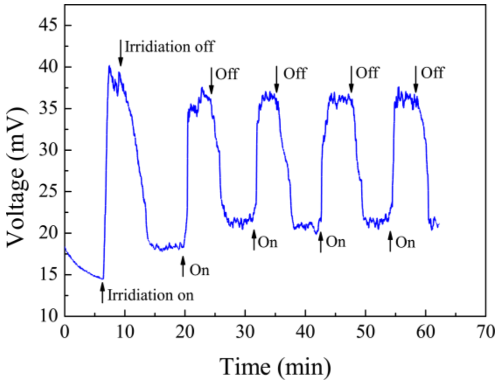

Fig.4 Optical signal controlled voltage production of the MFC.

At last, we integrated the optical switching system into the cathode chamber of a dual-chambered MFC, to achieve the goal of controlling a MFC between ON and OFF states with light. The two chambers were separated by PEM, and an external resistance of 1000Ω. was connected between the anode and the cathode. The anode chamber was inoculated with electrochemically active bacteria and the bacteria would not contact with the photoacid solution. The voltage produced by the MFC was chosen as the output signal and a laser was used as the input signal. As shown in Fig.4, the voltage of the MFC increased dramatically once the cathode chamber was exposed to the illumination. When the illumination was removed, the voltage dropped immediately to the initial level (1.55±0.27 minutes to turn it on and 3.09±0.16 minutes to reset). The ratio of ON/OFF current was around 1.68±0.02 (averaged from four cycles). Therefore, the optical switching system could be employed to achieve fast and reliable switching of a MFC. Nowadays, MFC based biosensors become a very promising technology in different fields. Our system can provide two potential applications in this area: 1) reversibly switching the biosensor between ON and OFF state with optical signal; 2) our optical switching system can adjust the measuring range of a biosensor with laser.

Conclusions

An optical switching system was developed. The two components of the system are a photoacid and a P4VP modified electrode. Firstly, we successfully synthesized the photoacid and fabricated the functionalized electrode. Then the switching system was tested in a potentiostatically controlled three-electrode system. The ratio of ON/OFF current was stabilized around 1.7, and the response time for switching from OFF state to ON state was 4.33±1.73 minutes and 5.67±0.57 minutes for the reverse process. In addition, we repeated the optical switch for 15 cycles and the ratio of ON/OFF current and the response time were both stable. This indicated the optical switching system was reliable and fast response. At last, we successfully used our system to control a MFC. The voltage of MFC was reversibly switched between high and low levels for multiple cycles. Based on this result, this optical switching system would provide a new idea for controlling MFCs.

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Footnotes

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