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Fast and sensitive water quality assessment: A μL-scale microbial fuel cell-based biosensor integrated with an air-bubble trap and electrochemical sensing functionality

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ABSTRACT

This work describes the development and operation of a microliter-sized microbial fuel cell-based biosensor for monitoring toxic substances in water. The biosensor features the integration of (i) a three-electrode configuration to provide electrochemical sensing functionality for improving sensitivity and reliability in water quality testing and (ii) an air-bubble trap to prevent all unwanted bubbles from entering the sensing surface for maximizing bacterial growth and their subsequent electron transfer. The miniaturization of the biosensor produced favorable conditions for (i) reducing measurement time with high probability of cell attachment/biofilm formation in the micro-sized chamber and (ii) enhancing the reaction sensitivity with large surface area-to-volume ratio and increased reaction kinetics. When formaldehyde was introduced as a toxic component, the rapid and sensitive current responses were obtained over a concentration range from 0.001% to 0.1% in the biosensor with 0.2 V (versus solid-state thin film Ag/AgCl reference electrode) applied on the anode.

1. Introduction

Recently, the National Academy of Engineering (NAE) has identified "provide access to clean water" as one of fourteen "grand challenges" for engineering in the 21 century. Securing clean and safe water is a significant challenge in developing countries: one in six global residents lacks access to clean drinking water; one in three lacks adequate sanitation, increasing vulnerability to diseases like dysentery. Developed countries are not immune: the American Society of Civil Engineers (ASCE) assigned the United States (US) water and wastewater infrastructure a "D+," and predicts astronomical costs to meet the country's basic wastewater needs in coming decades. Therefore, the monitoring of water quality is critical for providing safe and clean drinking water to the public [1]. Accurate and sensitive detection of various toxic compounds in water quality monitoring are conventionally detected using physiochemical analysis [1,2]. However, the techniques used require various instruments, are cumbersome, and time-consuming. In addition, these techniques do not allow for the understanding of the interactions associated with biological and chemical mixtures [3]. A relatively new approach for water quality monitoring includes biologically based biosensing such as using daphnids, bivalves, protozoans, algae, and fish [4,5]. While this technique allows for a wide range of toxic elements to be detected by monitoring changes in the survival, growth, behavior, or physiological conditions in those water organisms, it yields enormous amounts of information from continuously monitored organisms that require further analysis [1]. Therefore, there is an urgent need to develop a fast, simple, sensitive, and generic toxicity biosensor for real-world applications.

Microbial fuel cells (MFCs) can potentially be utilized as a biosensor for water quality monitoring because a broad range of toxic components can inhibit bacterial metabolic activity [2,6,27]. MFCs are bioelectrochemical systems that utilize bacterial metabolism to generate an electrical current [7,8]. A change in current generation in a MFC is based on various environmental factors including dissolved oxygen, pH, organic compounds, and biochemical oxygen demand (BOD). Therefore, MFCs may be used to measure water quality since the bacterial metabolism and growth will be impacted by the toxic components in water, such as formaldehyde, benzene, hexane, toluene, and heavy metals. For instance, when a drop in current is measured from a MFC-based

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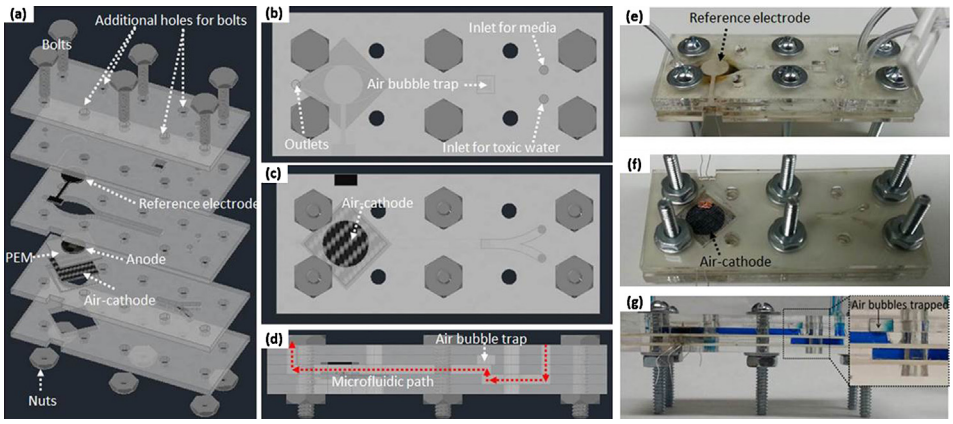

Fig. 1. Schematic diagram of (a) the individual layers of the MFC biosensor, (b) top view, (c) bottom view, and (d) side view of the assembled device. Photo-images of the assembled MFC biosensor; (e) top and (f) bottom view. (g) Photo-image of the device showing the microfluidic path and air bubbles trapped in a designed space.

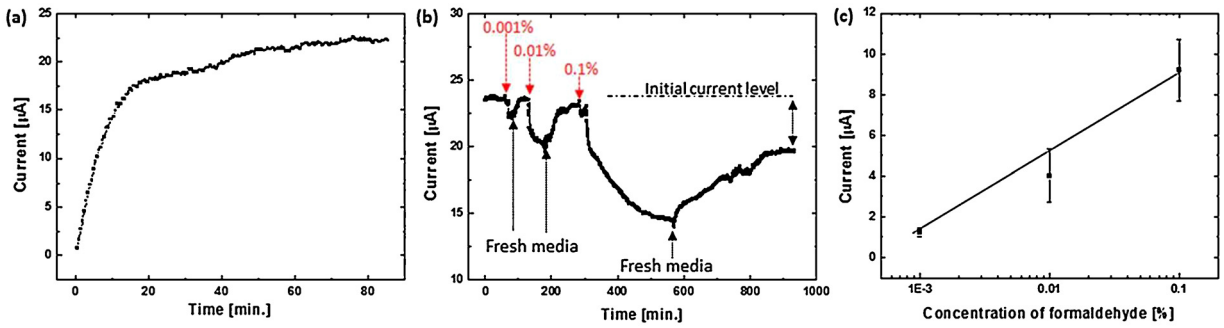

Fig. 2. (a) Stabilized baseline current. Stable current generation was obtained when the anodic potential was poised at 0.2 V versus Ag/AgCl reference, (b) current responses to toxic substances. Real-time toxicity measurement response obtained with different concentration of the formaldehyde. (c) Calibration curve of the MFC biosensor for the formaldehyde.

biosensor, an alarm can be triggered so that proper procedures can be taken to protect our waterways from pollution [9]. As a biosensor, MFCs have several distinct advantages for monitoring of water quality: (i) long-term online monitoring is enabled due to the self-repairing and self-sustainable nature of MFCs, (ii) MFCs do not require external transducing techniques/instruments and power sources because the current generated from the MFC can be used as a quantitative indicator for the presence of toxic substances in water, (iii) microorganisms/biofilms in MFCs are fast to respond to changes in toxic elements, (iv) the operation and fabrication of MFCs are cost-effective, and (v) polymicrobial communities can respond to a broad range of toxins. While macro-sized MFCs have been conceptually validated for the use as biosensors, only a small number of research groups have attempted to miniaturize standard macro-sized MFCs for biosensing applications [10–12]. Although miniaturization allows for inherently advantageous features such as short electrode distance, large surface area-to-volume ratio, and a fast response time, there are significant limitations present in miniaturizing biosensing MFCs; these include (i) stabilizing the baseline current with conventional two-electrode configurations and (ii) interferences resulting from unwanted microbubbles in the chamber. First, two-electrode MFCs are rarely reproducible due to changes in the growth, evolution, and metabolism of the consortium of microbes [13]. Furthermore, they can be limited by the electrode materials and substances in the electrolyte that are not electrochemically inert and may themselves generate currents in the potential range of the experiment in question. In addition, recent findings suggest that bacteria may use different electron transfer systems when the anode is set to different potentials, and significant current enhancement may be achieved by optimizing the anode potential [14,26]. Second limitation comes with the potential invasion of air bubbles in the microliter-sized MFCs, which will be directly related to the current generation as the bubbles normally occupy significant chamber volume and likely interfere with bacterial growth and subsequently their electron transfer [15].

In this work, two novel technologies were integrated into the microliter-sized MFC-based biosensor. First, the solid-state thin film Ag/AgCl reference electrode was implemented into the biosensor to avoid unwanted system perturbations and to provide more reliable and accurate information for a quantitative monitoring of the toxic substances in water [13,16]. Second, a microscale air bubble trap was integrated into the device. While macro-sized MFCs are not vulnerable to invading bubbles, micro-sized MFCs become sensitive to even tiny air bubbles [15]. This is because the size of the air bubble becomes comparable to that of the chambers/channels and a small number of bacteria on the miniaturized anodic surface are more susceptible to bubbles. Moreover, they are difficult to be removed due to the slow flow rate of solutions. The proposed platform provides a dramatic increase in the detection speed and sensitivity.

2. Materials and methods

2.1. Device fabrication

Fig. 1 shows photo images and schematic diagrams of the micro-sized MFC biosensor (3 cm × 7 cm). The three-electrode