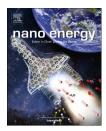


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# Solar-assisted microbial fuel cells for bioelectricity and chemical fuel generation



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#### Abstract

Microbial fuel cell (MFC) is an electrochemical device that uses electrogenic bacteria as biocatalysts to decompose organic matter while simultaneously generating bioelectricity. Besides electricity, the bio-electrons generated in the microbial electrogenesis process at the anode can also be used to produce chemical fuels, such as hydrogen gas. However, microbial electrohydrogenesis process does not occur spontaneously due to the thermodynamic barrier for the conversion from protons to hydrogen gas, and therefore an electrical bias has to be supplied to supplement the energy required for the proton reduction. The requirement of external bias adds to the complexity and cost for hydrogen production, making microbial electrohydrogenesis less attractive as a cost-effective energy solution. Alternatively, the energy required to overcome the barrier can be provided by a renewable energy source such as solar light, which is a promising approach that could fundamentally address this issue. Recently, a number of solar-assisted microbial fuel cells have been demonstrated by coupling the conventional MFC with photosynthetic bacteria, semiconductor photoelectrodes, solar cell or photoelectrochemical cell. In these devices, solar energy was utilized to facilitate bioelectricity or hydrogen generation. The demonstration of these new solar-assisted MFC devices opens up new opportunities in the recovery of chemical energy in wastewater for chemical fuel production. This article highlights the recent accomplishments in the solarassisted MFC technology and discusses the current challenges and future opportunities in the field.

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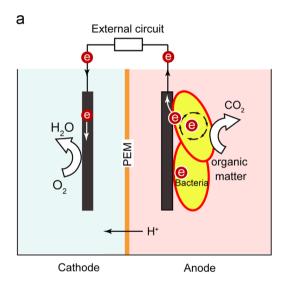
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#### Introduction

The rapid growth of global population leads to the increasing demand for energy and clean water. Microbial fuel cell (MFC) provides a promising solution to address this energy and environmental challenge by recovering chemical energy from organic matter in wastewater for producing bioelectricity. In past few decades, researchers have made extraordinary efforts on the development of MFC technology, which was highlighted as one of the top 50 most important inventions by Time Magazine in 2009 [1]. Figure 1a shows the schematic diagram of a typical dual-chamber MFC device [2-4]. The MFC chambers can be constructed by a number of materials, such as glass, polycarbonate, as well as plexiglass [5,6]. The essential physical components of the MFC are the anode electrode, cathode electrode, and an ion exchange membrane that allows specific ions to diffuse from one chamber to the other. The anode electrode materials must be conductive, bio-compatible, and chemically stable in the bacterial culture. Carbon-based materials such as carbon cloth, carbon paper, graphite, graphite felt and graphite brush are commonly used as anode electrode for MFC [7-10]. The cathode electrodes are typically carbonbased materials as well. For air-cathode, platinum (Pt) or Pt black-catalyst materials are commonly used to suppress the overpotential for oxygen reduction [10-12]. Anode chamber is filled with organic substrates that can be degraded by electrogenic microorganisms. The microorganisms that have been reported for use in MFCs include pure bacterial strains, e.g. Geobacter [13-16], and Shewanella species [17-19]; or the mixed culture, e.g. natural microbial community domestic wastewater, sediment from marine and lake, as well as brewery wastewater [20-22]. The cathode chamber is filled with solution containing an electron acceptor. The anode and the cathode are connected via an external load to complete the circuit. As shown in Figure 1, when the MFC is in operation, protons migrate from the anode to the cathode chamber through proton exchange membrane (PEM). Meanwhile, the microbially generated electrons flow through the external circuit from the anode to the cathode, where they are subsequently used to reduce electron acceptor, such as ferricyanide ( $[Fe(CN)_6]^{3-}$ ) or permanganate  $(MnO_4^-)$ , in the cathode chamber. While these chemical solutions serve as excellent catholytes for MFC devices, they are not sustainable and may cause environmental issues [23,24]. Alternatively, oxygen is a better electron acceptor for MFCs, due to its abundance sustainability and environmental cleanliness [25]. Figure 1b shows the digital image of a real dual-chamber MFC device with an air cathode (blue cap bottle) and a bacteria-colonizing anode (yellow cap bottle). Air was continuously bubbled into the catholyte (water). The anode was inoculated with anaerobic digester sludge from a sewage treatment plant (black solution in the beaker). The microbes in anode oxidized the organic wastes and converted the black wastewater solution into an almost clear solution. Table 1 summarizes a few recently developed MFC devices using different electrogenic microorganisms and system design.

The utilization of MFC as an alternative energy source was limited by its relative low power output for most practical applications. Therefore, significant efforts have been made in improving the current densities and power densities of MFCs, including modification of the architecture of MFC device [26-30], optimization of the microbial activities [31,32], increasing of the effective surface area of both anode [33-36] and cathode [37-39], as well as the incorporation of various oxygen reduction reaction catalysts on cathode electrodes, such as Ni [40,41], Co [42,43] and Au [7,44]. The rapid development of nanostructured electrodes also opens up new opportunities of enhancing the performance of MFCs. For instance, 3D porous materials with extremely large surface area are emerging as a new class of electrode materials for MFCs [19,45-49]. A 3D porous conductive scaffold not only considerably increases the effective surface area for microbial colonization, but also allows efficient electron transfer and mass transport of both nutrients and metabolites. These recent advancements in the MFC technology have been highlighted in the recent reviews [5,50-55].

In addition to bioelectricity, the electrons generated by the microorganisms can also be used to produce various chemical fuels, depending on the electron acceptors used in the catholyte. If protons serve as the electron acceptor, hydrogen gas will be generated at the cathode. This type of MFC device is called microbial electrolysis cell (MEC). Although MEC technology represents an environmental friendly approach for hydrogen generation, major improvements are required since additional energy input is needed to overcome the thermodynamic energy barrier of converting protons to hydrogen gas.





**Figure 1** (a) Schematic illustration and (b) digital picture of a conventional microbial fuel cell device with an air cathode.

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