Journal of Photochemistry and Photobiology A: Chemistry 300 (2015) 38–43

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Effect of light irradiation on the photoelectricity performance of microbial fuel cell with a copper oxide nanowire photocathode

Zhe Sun [a], Ruixue Cao [b], Manhong Huang [a,*], Donghui Chen [c,*], Wei Zheng [a], Li Lin [a]

[a] College of Environmental Science and Engineering, State Environmental Protection Engineering Center for Pollution Treatment and Control in Textile Industry, Donghua University, Shanghai 201620, China
[b] Zhengzhou Research Institute of Aluminum Corporation of China, Zhengzhou 450041, China
[c] School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 200235, China

ARTICLE INFO

Article history:
Received 23 August 2014
Received in revised form 25 November 2014
Accepted 3 December 2014
Available online 4 December 2014

Keywords:
Microbial fuel cell
Photocatalysis
Electrochemistry
Energy
Anaerobic

ABSTRACT

A new way to enhance the performance of a microbial fuel cell (MFC) using photoelectricity was studied. The effect of light irradiation on the photoelectricity performance of a MFC with CuO nanowire-arrayed photocathode was investigated. The MFC produced a maximum power density of 46.44 mW m^{-2} under light irradiation, 125% increase compared to 36.99 mW m^{-2} in the dark. The open circuit voltage (Vocv) of the MFC was 466 mV under light irradiation, which increased by 113% compared to 412 mV in the dark. The linear sweep voltammogram (LSV) of the MFC cathode proved that the CuO cathode current was higher under light illumination than in the dark. The electrochemical impedance spectrum of the CuO cathode was lower under light irradiation conditions than in the dark. The results show that the R_{ct} and R_{Ω} of the CuO cathode under light irradiation decreased from 179.9 and 7.92 Ω to 138.6 and 2.04 Ω, respectively. The resistance of the photoelectrode decreased and the cathode potential increased, thus increasing the MFC power. The cathodes made of semiconductor materials such as copper oxide nanowires were used for the first time in MFC, which cooperated with the solar and biomass energy in MFC. The study provided a new insight into the biological energy coupling with solar energy and provided exciting opportunities for the unique study in semiconductor and MFC.

1. Introduction

Microbial fuel cells (MFCs) can convert the chemical energy in wastewater into electrical energy [1–3]. The performance of a MFC is affected by many factors, such as MFC configuration [4], microbial species [5], electrode material, and cathode. Among them, cathode plays an important role in achieving excellent performance [6]. The decrease in the activation energy of cathodic reactions and increase in the reaction kinetics at the cathode can enhance the performance of MFC. Many types of catalysts have been used as the cathode catalysts such as modified carbon materials [7], metal oxides [8], and Fe and Co heterocycles [9].

A new way to enhance the properties of MFC is to combine with other power sources. Semiconductors under light irradiation or photoexcitation promote electrons from the valence band to the conduction band of semiconductors, leaving behind highly oxidizing photogenerated holes. Based on this principle, photoelectrochemical cells (PECs) convert light energy into electrical energy. The photogenerated holes in the valence band have a strong tendency to accept electrons, while the photogenerated electrons in the conduction band reduce electron acceptors. Qian et al. successfully demonstrated substantial current generation from a microbial photoelectrochemical solar cell (MPSC) device based on the synergistic effect of bioanode and semiconductor Cu_2O nanowire photocathode at zero bias [10]. Lu et al. investigated the photocatalysis on the cathodic side of an MFC using semiconductor rutile as the cathode catalyst [6]. Wang et al. demonstrated a new device coupling solar water splitting and microbial electrohydrogenesis in a photoelectrochemical cell-microbial fuel cell (PEC-MFC) that could self-sustained hydrogen gas [11]. He et al. also constructed a microbial photoelectrochemical cell system which used TiO_2(P25) photocathode for hydrogen production under ultraviolet (UV) light [12]. But these similar photocathodes had not photoresponse under visible light.

Cupric oxide (CuO) has been widely studied in the field of electrochemical energy storage because it is inexpensive, easy to synthesize, and environmentally friendly [13–15]. As a semiconductor with a narrow band gap (1.2 eV) [16,17] and excellent photoconductive and photochemical properties, CuO is a promising material for fabricating solar cells [18]. Therefore, well-defined

* Corresponding author. Tel.: +86 21 67792546.
E-mail addresses: chendh@dhu.edu.cn, egghmh@163.com (D. Chen).

http://dx.doi.org/10.1016/j.jphotochem.2014.12.003
1010-6030/

CuO nanostructures with various morphologies have been fabricated [19].

In this study, CuO nanowire arrays were used as the photocathode for the first time, and output voltage, cathode potential, power density (PD), linear sweep voltammogram (LSV), and electrochemical impedance spectroscopy (EIS) were studied. The electrochemical performance and mechanism of the photo-electrochemical MFC were also analyzed for CuO photocathode MFC.

2. Materials and methods

2.1. MFC configuration and anode pretreatments

The MFC used in this study is known as H-type MFC, consisting of two column chambers made of glass, with a volume of 250 mL. The chambers were separated by a cation exchange membrane (CEM, Beijing Anketech Membrane Separation Engineering & Technology Co., Ltd., China) with an area of ~20 cm^2. The distance between the electrodes was ~14 cm. The anode was made of a carbon fiber brush (Jilin Carbon Plant, China, carbon fiber coverage length: 80 mm, carbon fiber coverage diameter: 30 mm), constructed as described by Logan et al. [20], with a two-wire Ti core that served as the current collector. All the carbon brushes were first cleaned by soaking them in pure acetone for 12 h, and then heat treated in a muffle furnace at 450 °C for 30 min [21]. The electrode was connected to a pure titanium wire (0.5 mm in diameter). The anode chamber was filled with a medium containing the following substances: 2.42 g L^{-1} of NaOAc, 0.13 g L^{-1} of KCl, 0.31 g L^{-1} of NH_4Cl, 6.571 g L^{-1} of $K_2HPO_4{\cdot}3H_2O$, 2.883 g L^{-1} of KH_2PO_4, and 12.5 mL L^{-1} mineral salt. The mineral salt contained 0.1 g L^{-1} $CaCl_2{\cdot}H_2O$, 0.01 g L^{-1} $CuSO_4{\cdot}5H_2O$, 0.1 g L^{-1} $FeSO_4{\cdot}7H_2O$, 0.01 g L^{-1} H_3BO_3, 0.5 g L^{-1} $MgSO_4{\cdot}H_2O$, 0.13 g L^{-1} $ZnCl_2$, 0.1 g L^{-1} $CoCl_2{\cdot}6H_2O$, and 1 g L^{-1} NaCl. The operation mode of the anode chamber was batch operation. The cathode chamber contained 0.5 M Na_2SO_4 solution, which was used to maintain conductivity. Air was continuously sparged into the cathode chamber to maintain the aerobic conditions (>8 mg L^{-1} dissolved oxygen (DO)). The DO concentrations were measured using a DO meter (Oxi 330i/SET, WTW GmbH, Germany). All the reagents used in this study were of analytical grade and used as received without further purification. The anode anaerobic sludge was collected from another MFC anode chamber. Anaerobic condition was maintained in the anode chamber by bubbling filtered N_2 for 30 min to remove the residual oxygen during the initial setup, and then the cell was sealed. For the acclimation of electrochemically active microorganisms, the MFC was operated with 1000 Ω external load for three months. The anode potential and cathode potential were measured by saturated Ag/AgCl electrode when the MFC was open circuit. Then, the anode potential was stabilized at approximately −260 mV (vs. NHE) before the experiment.

2.2. Cation exchange membrane pretreatment and cathode fabrication

The CEM was pretreated before the MFC was assembled by rinsing with water and kept in a NaCl solution (1 M) for 24 h [22]. CuO nanowires were prepared by the thermal annealing of Cu $(OH)_2$ nanowire array in air [23]. A piece of Cu foil (99.96%) (20 × 70 mm^2) was successively sonicated with acetone, ethanol, and distilled water and then immersed into an aqueous solution containing 2.5 M NaOH and 0.125 M $(NH_4)_2S_2O_8$ [10]. After 45 min, the Cu foil that turned blue was removed from the solution, rinsed with distilled water, and dried under air. Finally, the Cu foil was roasted in a muffle furnace in air at 450 °C for 1 h. For photoelectricity performance comparison, the data of output voltage were gathered under light irradiation and in the dark when Cu and CuO were used as cathode.

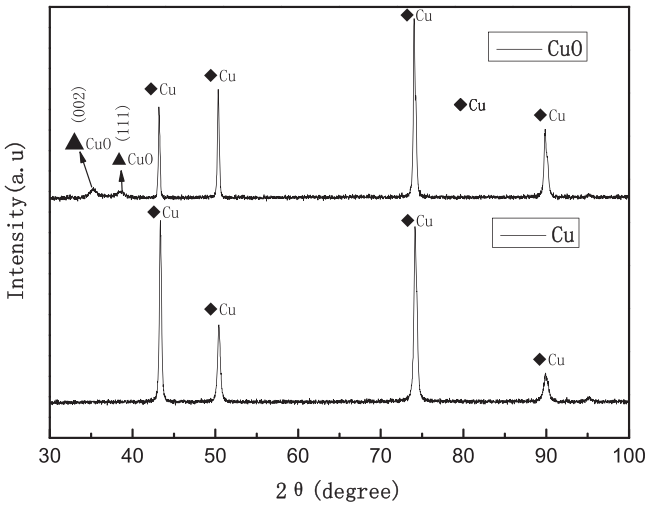

Fig. 1. X-ray diffraction patterns of a copper foil (Cu) and CuO nanowires (CuO).

2.3. Data collection and analysis

The voltage across the 1000 Ω external resistor was continuously measured using a Land series batteries testing system (Land CT2001A, Wuhan LAND Electronics Co., Ltd., China) at 1 min interval. The cathodic polarization and PD curves were obtained by measuring the voltages at different external resistances from 5000 to 20 Ω. The resistance between the electrodes was lowered stepwise, pausing at each resistance. The values were recorded when the voltage reading stabilized, lasted ~4–5 min. The current (I), power (P), and PD were calculated as described by Logan et al. [1]. The PD of the MFC was expressed in mW m^{-2} (normalized by the cathode electrode projected area) to compare the performance under light and darkness conditions.

The cathode half-cell electrochemical experiments were carried out in air-saturated 0.5 M Na_2SO_4 solution; the DO concentration was >8 mg L^{-1}. LSV and EIS were tested using a conventional three-electrode system (Parstat 2273 Advanced Electrochemical System, Princeton Applied Research, USA). The CuO cathode served as the working electrode, and a Pt wire served as the counter electrode. The reference electrode was connected to a saturated Ag/AgCl electrode, which was placed close to the working electrode. LSV was collected from the CuO cathode at a scan rate of 10 mV s^{-1} and

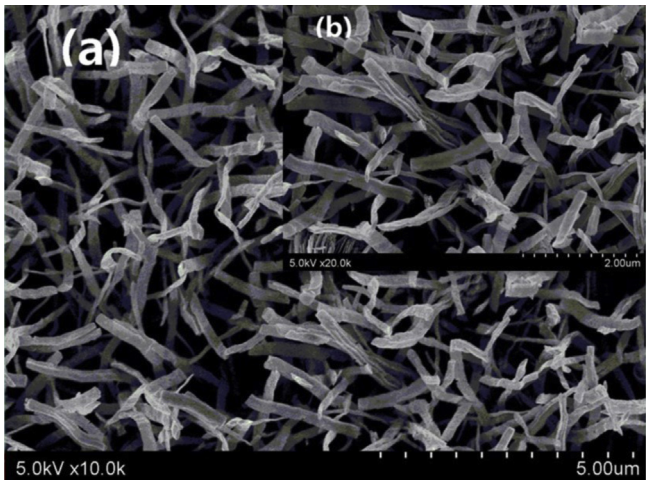

Fig. 2. SEM image of CuO nanowires grown on a copper foil, (a) 5.0 kV × 10.0 k and (b) 5.0 kV × 20.0 k.