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Enhancement of methyl orange degradation and power generation in a photoelectrocatalytic microbial fuel cell

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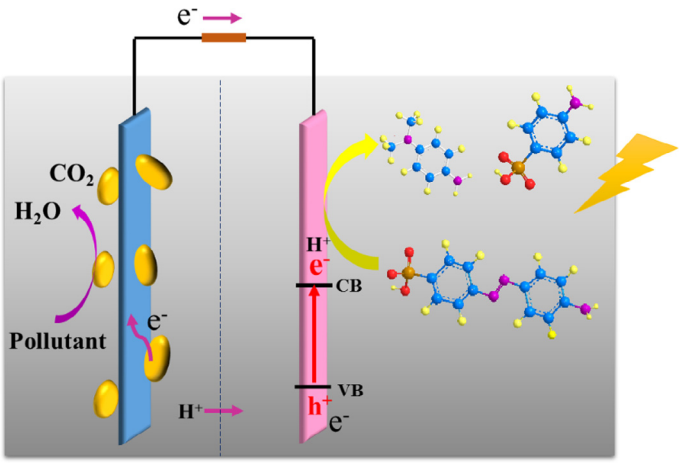
HIGHLIGHTS

- A photo-MFC was built for MO reduction.
- The Pd-SiNW photocathode enhanced the MO reduction reactivity in the photo-MFC.
- The power generation was enhanced in the Pd-SiNW photo-MFC under illumination.
- The mechanism of enhanced MO removal in the photo-MFC was investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

It is of significant importance to develop renewable and environmentally friendly technologies for sustainable wastewater treatment and energy recovery. Microbial fuel cell (MFC), a bioelectrochemical system, has attracted more and more attention because it can treat wastewater and harvest energy simultaneously. However, the practical applications of MFC are often limited by its high cathodic overpotential, relatively slow pollutant degradation rate, and low power output. In this study, a photoelectrocatalytic microbial fuel cell (photo-MFC), consisting of a Pd nanoparticle-modified p-type Si nanowire photocathode and an electricigen-colonized bioanode, was used to degrade a model azo dye, methyl orange (MO), and to generate electricity simultaneously. Results show that the introduction of photocathode enhanced the MO reduction reactivity through reducing the thermodynamic barrier and overpotential of the reduction reaction. Under visible-light illumination, the photo-MFC presented a MO removal efficiency of 84.5% and maximum output power density of 0.119 W/m^2 within 36 h, which were double of those of the conventional MFC with a carbon paper cathode. This observation could be attributed to the synergistic effect of photocathode and bioanode in photo-MFC, which significantly enhanced MO reduction and electricity generation. The new findings reported in this work could provide a new technique for wastewater treatment, and spur interest in using the photo-MFC for treating azo dye wastewater and harvesting energy simultaneously.

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1. Introduction

Energy crisis and environmental pollution are regarded as one of the major global issues in the 21st century. As a promising, renewable and environmentally friendly technology, microbial fuel cell (MFC) has attracted more and more attention in the past decades [1–9]. It can use electricigens as catalysts to oxidize organic and inorganic pollutants, and generate electricity simultaneously [10–12]. In an MFC, the electrons produced by the anodic electricigens are transferred to the anode, and then flow to the cathode through the external circuit. On the cathode surface, the electron acceptors react with the electrons and the protons diffuse from the anode. In this way, the electricity is produced coupled with the degradation of pollutants. However, the high overpotential of cathodic reduction reaction is often the major limiting factor of MFC performance [12–14]. Therefore, it is crucial to improve the cathodic performance for the practical application of MFC.

To promote the practical application of MFC in wastewater treatment, photocatalysts can be introduced into MFC and used as the cathodic catalyst. Photocatalysts can utilize solar energy to activate the cathodic reactions [15]. Under illumination, the photocatalysts can absorb photons to generate photoelectrons, which are excellent reductants and can be used for oxygen reduction. The introduction of photocathode into MFC may enhance the cathodic reactivity through reducing the thermodynamic barrier and overpotential of the reduction reaction due to the activation of photoelectrons [16,17]. However, up to date, very limited research exists on pollutant removal in a MFC system with a photocatalytic cathode. Previous researches have shown that hexavalent chromium and MO can be reduced in a MFC system with TiO_2 cathode [18,19]. However, as an n-type semiconductor, the widely-used TiO_2 is often only responsive to UV light and used as photoanode rather than photocathode in a MFC system [20]. It is hypothesized that the efficient reduction of pollutants and power output could be enhanced in a photoelectrocatalytic microbial fuel cell (photo-MFC) with a p-type and visible light-responsive semiconductor as photocathode, which have not yet been reported.

In this paper, a photo-MFC consisting of an electricigen-colonized anode and a Pd-modified silicon nanowire (Pd-SiNW) photocathode, was constructed to reduce a model aromatic azo dye methyl orange (MO) at the cathode. As a p-type semiconductor with a band gap of 1.12 eV, silicon is well-matched to the solar spectrum and can transit negatively charged photoelectrons more easily [21,22]. Therefore, the p-type silicon is chosen as the photocathode material. The MO reduction efficiency and power output were investigated in a photo-MFC with Pd-SiNW photocathode under various conditions. The synergistic function of the photocathode and bioanode in the photo-MFC for enhanced MO reduction and power generation was discussed and the underlying mechanism was explored. The results will be useful to develop an efficient MFC technique for azo dye-containing wastewater treatment and inspire the development of MFC in the future.

2. Materials and methods

2.1. Photocathode preparation and reactor setup

A 5.0 cm^2 commercial Si wafer was obtained from Tianjin Guike Co., China and pretreated following the procedure described below [17]. The Si wafer was immersed in a solution containing 0.2 M $AgNO_3$ and 5.6 M HF at 30 °C for 1 h and then immersed in dilute HNO_3 (1:1 v/v) at 30 °C for 30 min. Afterwards, the silicon nanowire was dried with N_2 and immersed into a 0.1% HF solution to remove the residual oxidation layer. The prepared silicon nanowire was immersed into a Na_2PdCl_4 solution (11 mM in 1% HF solution). After 15 min of reaction, the Pd-modified electrode was thoroughly rinsed with distilled water and used as the photocathode.

The structure of the photo-MFC in the experiment consisted of two cylindrical 400 mL glass and quartz chambers separated by a 7.0 cm^2 proton exchange membrane (Ultrex AMI7001, Membranes International Inc., US). The anode was made of 16 cm^2 carbon felt (Beijing Sanye Carbon Co., China), and the remaining space in the anode chamber was filled with granular graphite. During the MFC startup stage, the carbon felt was also used as the cathode. All the carbon felts were boiled in distilled water for 1 h and washed by 1 M HCl and distilled water 3 times each before use. The anode and cathode electrodes were connected by a 1000 Ω external resistor and the distance between the electrodes was 10 cm.

During the startup of the photo-MFC, a mixed anaerobic sludge harvested from a pilot UASB was injected into the anode, and N_2 was purged to remove residual O_2 to ensure anaerobic conditions. Artificial wastewater was used as the anode substrate, which contained (per liter) $CH_3COONa{\cdot}3H_2O$, 1400 mg; $NaH_2PO_4{\cdot}12H_2O$, 6981 mg; $Na_2HPO_4{\cdot}2H_2O$, 4758 mg; NH_4Cl, 310 mg; KCl, 130 mg; $CaCl_2$, 10 mg; $MgCl_2{\cdot}6H_2O$, 20 mg; NaCl, 2 mg; $FeCl_2$, 5 mg; $CoCl_2{\cdot}2H_2O$, 1 mg; $MnCl_2{\cdot}4H_2O$, 1 mg; $AlCl_3$, 0.5 mg; $(NH_4)_6Mo_7O_{24}$, 3 mg; H_3BO_3, 1 mg; $NiCl_2{\cdot}6H_2O$, 0.1 mg; $CuSO_4{\cdot}5H_2O$, 1 mg; and $ZnCl_2$, 1 mg. The anode camber was continuously fed with the substrate at a flow rate of 25 mL/h. The cathodic solution volume was 260 mL and contained (per liter) $NaH_2PO_4{\cdot}12H_2O$, 6981 mg; $Na_2HPO_4{\cdot}2H_2O$, 4758 mg; NH_4Cl, 310 mg; and KCl, 2370 mg, and air was purged in the cathode. Oxygen was used as the electron acceptor during the startup period.

2.2. Photoelectrocatalytic degradation experiments

After the MFC output voltage increased to 400 mV and remained stable, the carbon felt cathode was replaced by the Pd-SiNW photoelectrode or the 5.0 cm^2 carbon paper electrode (control). In this study, MO was used as the model pollutant for degradation in the photo-MFC. The experimental conditions are listed in Table 1. Initially, 260 mL 25 mg/L MO solutions at various pH were injected in the cathode chamber, and then N_2 was purged into the cathode chamber for 15 min to ensure no oxygen was present. After that, the cathode solution was irradiated by a visible-light source (Xe lamp, 350 W, PLS-SXE-300UV, Beijing Trusttech Co., China) with a 420 nm cut-off filter. The distance between the cathode electrode and the light source was kept at 6 cm. The anode and cathode were connected by a 20 Ω external resistor for voltage monitoring. During the degradation process, the cathodic solution and gas in the headspace were extracted every 6 h for analysis of the MO concentration and H_2 content.

2.3. Electrochemical measurement

All electrochemical measurements to evaluate the performance of the photocathode and photo-MFC were carried out using a CHI

Table 1
The various experimental conditions of photo-MFC for MO reduction.

Experimental set	Cathode	Light	Circuit	pH
A	Silicon nanowire	ON	CLOSE	1
B	Silicon nanowire	OFF	CLOSE	1
C	Carbon paper	ON	CLOSE	1
D	Carbon paper	OFF	CLOSE	1
E	Silicon nanowire	ON	OPEN	1
F	Silicon nanowire	OFF	OPEN	1
G	Silicon nanowire	ON	CLOSE	3
H	Silicon nanowire	ON	CLOSE	5
I	Silicon nanowire	ON	CLOSE	7