



# Hybridization of photoanode and bioanode to enhance the current production of bioelectrochemical systems

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## ABSTRACT

Bacterial extracellular electron transfer is one of the main bottlenecks in determining the efficiency of bioelectrochemical systems. Here, we report a photobioanode that combines carbon material with a photocatalyst ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), utilizing visible light to accelerate biofilm formation and extracellular electron transfer in bioelectrochemical systems. Cyclic voltammetric studies of this photobioanode revealed active electron transfer at the anode/biofilm interface. The charge-transfer resistance of the anode/biofilm was ca. 46.6  $\Omega$ , which is half that of the unmodified anode. In addition, the results of confocal laser scanning microscopy and bacterial community analysis indicate that the photobioanode and light can accelerate biofilm formation and enrich exoelectrogens. When equipped in photo-bioelectrochemical systems, the start-up time was shortened from about 2.5 days to 1.1 days. The maximum current density of photo-bioelectrochemical systems was almost twice that of a control bioelectrochemical system. In addition, the current density of the photo-bio-electrochemical cell (PBEC) showed almost no decrease after being subjected to 40 d of illumination. This photobioanode is therefore a cost-effective, energy-clean, environment-friendly anode with high electrocatalytic activity and long-term stability, which has broad prospects in various processes, including wastewater treatment, bioelectricity generation, bioelectricity synthesis, and hydrogen production.

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## 1. Introduction

Bioelectrochemical systems (BESs) are appealing for capturing energy from organic wastewater (Logan and Rabaey, 2012; Pant et al., 2013). Bacteria oxidize organic substrates and deliver the released electrons from bacterial cells to the anode, and the electrons are then transported to the cathode through an external circuit (Pant et al., 2013). The current output is mainly based on electron transfer rate between microbes and an electrode surface (Logan, 2009). Therefore, bacterial extracellular electron transfer (EET) is one of the main causes determines the efficiency of BESs (Zhou et al., 2011). To transfer electrons from microbes to an anode efficiently and spontaneously, additional electrical or chemical

energy must be used to overcome the thermodynamic barrier (Logan, 2009). To date, to minimize operational costs, researchers have attempted to couple multiple natural energy sources with BES technologies to enable high power outputs (Chae et al., 2009; Wang et al., 2013; Qian et al., 2014; Liu et al., 2014; Du et al., 2014).

Photo-electrochemical cells have attracted great interest as a novel way of converting sunlight into electrical energy, which is a clean alternative to fossil fuels (Zang et al., 2014; Liu et al., 2015a,b). In the original version of the photoelectric effect, one photon displaces one electron, thereby leaving behind one electron hole (the edge of valence band) (Liu et al., 2015a,b). What is noteworthy is that the electron holes are appealing to free electrons. It would be quite attractive if the anode, comprised of a photoelectrocatalytic material, could produce a large number of electron holes that are able pull electrons from the bacteria, thereby increasing the EET efficiency.

Based on this idea, so far only one report demonstrated that a single solar BES device which employs a hematite photoanode to

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interface with a microbial system could only give a low level current density and the electrogenesis capacity of photoanode was sharp decreasing (Qian et al., 2014). Thus, as semiconductors, the photo-anode still present challenges for use in BESs, including high electrical resistance, poor chemical stability, and poor biocompatibility (Turner, 2004; Liu et al., 2015a,b). In contrast, common carbon electrodes have been extensively used for BES reactors because of their relative low price, good stability, and high biocompatibility (Shi et al., 2012; Guo et al., 2013; Tang et al., 2011; Wang et al., 2011; Machala et al., 2011; Li et al., 2007). It is therefore attractive to combine a carbon material with a photocatalyst to design a composite electrode with high electrocatalytic activity, long-term stability, and biocompatibility.

In this paper, we report a new composite photobioanode and an efficient photo-bio-electrochemical cell (PBEC). The photobioanode represents a combination of photocatalyst-graphite-microorganisms, and the PBEC is composed of the photobioanode and an abiotic cathode. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is chosen as the photocatalyst because of its low price and small band gap (2.2 eV) which is favorable for efficient absorption in the ultraviolet and visible light regions (Fu et al., 2014; Mao et al., 2011; Morrish et al., 2011; Mu et al., 2012). The results may be useful for designing new systems for increasing the efficiency of bio-electrochemical cells (BECs) for long-term electricity generation from solar energy.

## 2. Experimental sections

### 2.1. Synthesis of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> film on the electrode

Graphite plates (diameter 40 mm, thickness 5 mm) were used as anodes. Before modification, the electrodes were ultrasonically cleaned in acetone, ethanol, and deionized (DI) water for 30 min at each solution sequentially. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> film was synthesized on one side of the electrode following the method described in an earlier report (Fu et al., 2014) and the procedure was briefly described in Fig. 1a. Firstly, the electrode was immersed in 0.5 M FeSO<sub>4</sub> solution (ethylene glycol/H<sub>2</sub>O = 1:8, pH = 4.1, adjusted using 1 M HCl). Secondly, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) film was synthesized on the electrode surface by electrochemical deposition. The anodization was performed in a standard three-electrode setup with a graphite electrode as the working electrode and another graphite electrode as the counter electrode. The counter electrodes were ultrasonically cleaned in acetone, ethanol, and deionized (DI) water for 30 min at each solution sequentially. All potentials in this work are quoted relative to the standard hydrogen electrode (SHE). The anodization potential was held at 1.4 V for 15 min using an electrochemical workstation (Autolab302, Metrohm, Switzerland). After the deposition, the resulting electrodes were immersed into DI water for 10 min to remove the impurities. Then the thoroughly rinsed electrodes were sintered in a furnace at 500 °C for 2 h and cooled naturally to room temperature.

To make the electrodes waterproof, paraffin was impregnated into the micro holes of graphite plates (Fig. 1b). Firstly, the unmodified side (e.g. the side without  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> film) of the electrodes was immersed into light liquid paraffin for 10 min. Secondly, the same side of the electrodes was soaked into surfactant (0.2% 2-phenylphenol) solution for another 10 min to remove the redundant paraffin. After that, the electrodes were rinsed with DI water and dried in air. Then the electrodes were ready to be tested. The unmodified electrodes were treated in the same way of modified electrodes except the anodization step.

### 2.2. Characterization of the anode electrodes

*X-ray Photoelectron Spectroscopy (XPS).* XPS was used to

determine the elemental composition of the electrode surfaces. XPS spectra were collected using an EscaLab 250Xi spectrometer with a monochromated Al K $\alpha$  source (Thermo, England). Spectra were calibrated on the 710.8 eV (Fe2p) and 531.7 eV (O1s) and analyzed using XPSPEAK41 software.

*Photoelectrochemical Characterization.* Photoelectrochemical activities were investigated in the custom-built reactor with the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> film modified electrode as the working electrode, a clean graphite electrode as the counter electrode. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> side of the modified electrode was faced the simulated light. A xenon lamp with an intensity of 10 mW/cm<sup>2</sup> which measured by light intensity detector (Radiometer, FA-A, China) was used as the solar simulator (25 W). The modified electrode was immersed into the 0.1 M Na<sub>2</sub>SO<sub>4</sub> and 0.1 M Na<sub>2</sub>SO<sub>3</sub> mixed solution to measure the *I-t* properties when the potential of the working electrode was set at 0.2 V.

### 2.3. Reactor construction and operation

The reactors used in this study were cubic and dual-chamber Perspex reactors. Fig. 2 and Fig. S1 shows the schematic and the photo of the reactor setup, respectively. The cathode (50 mL) and anode (50 mL) chambers were cylindrical with a cross-sectional area of 12.5 cm<sup>2</sup>. A piece of Nafion 117 cation exchange membrane (CEM, DuPont, USA) was used to separate the two chambers. In PBEC reactor, The anode was a piece of the modified graphite plate with the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> coated side facing the outside air and the other side exposing to the anolyte (projected surface area 12.5 cm<sup>2</sup>). A xenon lamp (12 V–35W, Shenlei, China) was used to illuminate the outside of the anode. The cathode was a piece of graphite felt (4 cm diameter and 0.4 cm thickness) which was immersed in the catholyte. Reference electrode was placed in the anodic chamber and next to the anode. The structure of BEC reactor was completely consistent with PBEC except the unmodified electrode. In BEC, one side of the unmodified electrode faced the outside air without illumination and the other side exposed to the anolyte. Photo-electrochemical cell (PEC) and electrochemical cell (EC) were abiotic controlled reactor and structurally identical to PBEC and BEC, respectively.

Working volume for both anolyte and catholyte was 40 mL. The anolyte consisted of CH<sub>3</sub>COONa (2 g/L), M9 solution (NH<sub>4</sub>Cl, 0.1 g/L; NaCl, 0.5 g/L; KH<sub>2</sub>PO<sub>4</sub>, 4.4 g/L; K<sub>2</sub>HPO<sub>4</sub>, 3.4 g/L; MgSO<sub>4</sub>, 0.1 g/L; NaHCO<sub>3</sub>, 2 g/L) and trace elements (FeSO<sub>4</sub>·7H<sub>2</sub>O, 1.0 mg/L; CuSO<sub>4</sub>·5H<sub>2</sub>O, 0.02 mg/L; H<sub>3</sub>BO<sub>3</sub>, 0.014 mg/L; MnSO<sub>4</sub>·4H<sub>2</sub>O, 0.10 mg/L; ZnSO<sub>4</sub>·7H<sub>2</sub>O, 0.10 mg/L; Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, 0.02 mg/L; CoCl<sub>2</sub>·6H<sub>2</sub>O, 0.02 mg/L). The catholyte was only M9 solution. The anolyte was flushed with high-purity nitrogen gas for 10 min and inoculated with (10 mL) fresh anodic effluent (OD<sub>600</sub> was about 1) of an existing acetate-fed BE reactor in the lab that had been continuously running for five months. The anode potential was controlled at 0 V and current generation was recorded using a potentiostat (CHI 1040c, Chenhua, Shanghai). The three-electrode system could avoid the cathodic limitation such as cathodic alkalization and low cathode surface area.

All of the reactors were firstly run in fed-batch mode, because of the small amount of bacteria and poor stability of biofilm on the anode surface. After 7 cycles (a cycle is about one day), the reactors were switched to continuous mode (5 mL/45 mL h<sup>-1</sup>) in order to increase the mass transfer rate, thus enhancing the performance of current generation. During day 21–25, light On/Off experiment was carried out to test the response of the anodic biofilms to light. The On/Off illumination cycles were controlled by a piece of black paper which could cover the outside of the photobioanode. For PBEC and BEC system we used four parallel reactors.

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