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Metal-based anode for high performance bioelectrochemical systems through photo-electrochemical interaction

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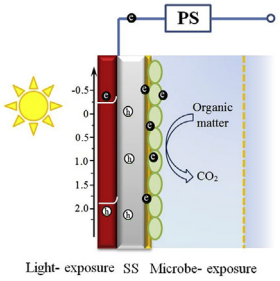
HIGHLIGHTS

- Photo-electrochemical interactions enhance availability of metal-based bioanode.
- High current density and short start-up time were achieved on PSS.
- The photocatalyst-SS anode (PSS) accelerates biofilm formation.
- Increased working life of stainless steel bioanode was achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper introduces a novel composite anode that uses light to enhance current generation and accelerate biofilm formation in bioelectrochemical systems. The composite anode is composed of 316L stainless steel substrate and a nanostructured α-Fe_2O_3 photocatalyst (PSS). The electrode properties, current generation, and biofilm properties of the anode are investigated. In terms of photocurrent, the optimal deposition and heat-treatment times are found to be 30 min and 2 min, respectively, which result in a maximum photocurrent of 0.6 A m^{-2}. The start-up time of the PSS is 1.2 days and the maximum current density is 2.8 A m^{-2}, twice and 25 times that of unmodified anode, respectively. The current density of the PSS remains stable during 20 days of illumination. Confocal laser scanning microscope images show that the PSS could benefit biofilm formation, while electrochemical impedance spectroscopy indicates that the PSS reduce the charge-transfer resistance of the anode. Our findings show that photo-electrochemical interaction is a promising way to enhance the biocompatibility of metal anodes for bioelectrochemical systems.

1. Introduction

Bioelectrochemical systems (BESs) are able to generate energy from organic waste through the direct use of microbes as catalysts to drive oxidation reactions on electrodes [1–3]. The core engine of a BES comprises electrodes and microorganisms. The electrodes act as both electron acceptor/donor and carrier for the bacteria.

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Therefore, the discovery and design of cheap, stable, and high performance electrode materials for BESs have drawn increasing interest and attention. In the past, many materials such as the different structures of carbon [4], metal-based materials [5], metal oxide semiconductors [6], conductive polymer films [7], and nano-materials [8] have been successfully made into anodes for BESs.

However, the high capital costs and low current densities of such electrodes remain the main obstacles to its practical application [9]. Although carbon-based electrodes have been the most extensively used, they have unfortunately limited practical applicability because of their poor ductility and high cost [10]. Metal oxide semiconductors and conductive polymer films are both limited by poor stability and low electrical conductivity, while nano-materials are limited by extremely high capital costs [11].

316L stainless steel (SS) is a common industrial material that has excellent mechanical properties, sufficiently high electric conductivity, and long-term resistance to corrosion, as well as being commercially available [12,13]. However, its poor biocompatibility limits its direct use as an anode for BESs [11]. To resolve this flaw, many modification methods have been investigated to enhance the biocompatibility of SS electrodes, such as heat treatment [14], natural gas flame treatment [15], and surface coating with carbon materials [16]. However, the increases in current density achieved through the above mentioned methods are still considered unsatisfactory.

Recently, several types of solar-assisted BES device prototypes have attracted great interest for exploiting sunlight as a driver to increase power output and reduce operational cost [17–20]. Especially, one previous study introduced a single solar BES device which employs a hematite photo-anode to interface with a microbial system. The photo-anode can benefit biofilms formation and enhance current production by exploiting the attraction of electron holes from the anode toward electrons from microbes [6]. However, the semiconductors still present challenges for being used as anode because of its high electrical resistance, poor chemical stability [19]. In contrast, SS is a kind of excellent electrode material that has great conductivity, but not suitable for biofilm formation. Therefore, it would be attractive to combine SS with a photocatalyst to design a composite electrode.

Herein, we aimed to design a new composite photocatalyst-SS anode (PSS) and an efficient photo-bio-electrochemical cell (PBEC). This kind of photo-bio-anode may have further potential of wide application in wastewater treatments with long working life, because it does not directly contact with the microbes or solution. Hematite (α-Fe_2O_3) was chosen as the photocatalyst because of its small band gap (2.2 eV), which is favorable for efficient absorption in the visible light region [21]. The obtained results may be useful for designing new bioelectrochemical systems that exhibit enhanced metal anode biocompatibility.

2. Experimental

2.1. Preparation of PSS

316L stainless steel discs (diameter 40 mm, thickness 5 mm) were used as anodes. Before modification, the electrodes were first ultrasonically cleaned for 30 min using acetone, ethanol, and deionized (DI) water in turn. The nanostructured α-Fe_2O_3 film was synthesized on one side of the electrode following the simple procedure briefly described in Fig. 1. The electrode was immersed in a 10 g L^{-1} nanostructured α-Fe_2O_3 suspension that had been dispersed for 10 min in advance using an ultrasound cleaner. Thereafter, the immersed electrode was horizontally oscillated at 130 rpm and 30 °C for a certain time using a shaking table. After the deposition, the obtained electrodes were immersed in DI water for 10 min to remove impurities. The thoroughly rinsed electrodes were sintered in a furnace at 500 °C for certain time and then allowed to cool naturally to ambient temperature in air.

2.2. Electrode surface characterization

The elemental composition of the surface of the electrodes was examined by X-ray photoelectron spectroscopy (XPS) using an EscaLab 250Xi spectrometer with a monochromated Al Kα source (Thermo, England). The obtained spectra were calibrated using the O1s and Fe2p peaks and the results were analyzed using XPSPEAK41 software. The XPS could provide an integrated sampling depth of about 10 nm. The surface morphology of the PSS and SS samples were observed with a field emission scanning electron microscope (FESEM; SU-70, Hitachi, Japan).

All photoelectrochemical activity measurements were carried out using a three-electrode cell with the anode as the working electrode, the cathode as the counter electrode, and an Ag/AgCl electrode (CHI 111, Chenhua, China) as the reference electrode. All potentials in this work are quoted relative to the Ag/AgCl (3.5 M KCl) reference electrode. The illumination-side of the nanostructured α-Fe_2O_3 film-modified electrode was placed facing solar simulated light from a xenon lamp (12 V–35 W, Shenlei, China) at a light intensity of 10 mW cm^{-2}. The transient current responses to ON–OFF cycles of illumination on PSS properties of the modified electrodes were measured by *I-t* curve and *linear sweep voltammetry* (LSV) in a mixed solution of 0.1 M Na_2SO_4 and 0.1 M Na_2SO_3. The applied potential of *I-t* curve was 0.01 V. The LSV was conducted within a potential window of −0.5 V to 0.1 V at a scan rate of 1 mV s^{-1}. The corrosion characteristics of the samples were measured using Tafel polarization curve recorded with linear sweep voltammetry (LSV). The potential window was −0.6 V to 0.4 V, and the scan rate was 0.1 mV s^{-1}.

2.3. Biofilm characterization

The current-generation experiments were terminated on day 20, and the electrochemical characteristics of the generated biofilms were then analyzed by electrochemical impedance spectroscopy (EIS) using an electrochemical workstation (Biologic VSP, Claix, France). The EIS measurements were carried out at open circuit potential, amplitude of 10 mV, and a frequency range of 10 kHz to 0.005 Hz. The EIS results were fitted based on the equivalent electrical circuit using EC-Lab software.

Biofilm samples were subjected to the LIVE/DEAD BacLight bacterial viability test (LIVE/DEAD® BacLight™ Bacterial Viability Kit, Molecular Probes, USA) according to the manufacturer's instructions. Labeled cells were visualized and z-stacks were captured using a confocal laser scanning microscope (CLSM, LSM 780, Zeiss, Germany). The three-dimensional (3D) biofilm images were processed using ZEN 2010 software.

2.4. Reactor construction and operation

In this study, a sealed rectangular Perspex dual chamber was used for the experiments. The compartments were separated by a Nafion 117 proton-exchange membrane (DuPont, USA), which was pretreated by immersion in 5% NaCl solution for 24 h. Both the anode and cathode chambers were 4 cm in diameter and 4 cm in length, and the total active volume of the reactor was 40 mL. The anode chamber was equipped with the following different anodes (exposed surface area of 12.5 cm^2): (a) PBEC: the α-Fe_2O_3 film-modified side of the PSS which was pointing outwards to receive light from the xenon lamp. The other side (in contact with the solution) was used for the immobilization of the microbes (Fig. S1);