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Invited feature article

A biocathode-driven photocatalytic fuel cell using an Ag-doped TiO_2/Ti mesh photoanode for electricity generation and pollutant degradation

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ABSTRACT

A biocathode-drived photocatalytic fuel cell (bio-PFC) was established for simultaneous refractory wastewater treatment and electricity generation. The successful doping of Ag nanoparticles into the three-dimensional arrays of TiO_2 nanotubes formed on Ti mesh was found to effectively reduce recombination of the photogenerated carriers and extend the light absorption properties of TiO_2. The biocathode provided the sustainable oxygen-reducing reaction in cathode, which eliminated the persistent kinetic limitations using abiotic cathode and ensured the stable operation of photoanode. The bio-PFC using Ag/TiO_2 photoanode achieved higher RhB degradation efficiency of 99.5% with the k of 0.0451 min^{-1}, compared to that using TiO_2 photoanode (degradation efficiency of 97.3% with the k of 0.0301 min^{-1}). A maximum power density of 318.19 $mW\,m^{-2}$ at a current density of 1.26 $mA\,m^{-2}$ was obtained. Pyrosequencing revealed that the cathodic microbial community was dominated by electrographic microorganisms including *Acinetobacter* sp., *Shewanella* sp., and nitrifiers (*Nitrospira* sp., *Nitrobacter* sp., *Nitrosococcus* sp.). Little differences in cathodic microbial structures were observed between the bio-PFCs using Ag/TiO_2 and TiO_2 photoanodes, indicating the improvement of system performance was mainly attributed to the effective modification of TiO_2 by Ag doping.

1. Introduction

Photocatalytic fuel cell (PFC), as an emerging technology which offers simultaneous refractory wastewater treatment and electricity generation, has drawn great attention in recent years [1,2]. Compared with traditional photocatalytic technologies, PFC exhibits excellent capability of improved oxidation activity and low cost [3]. PFC systems using TiO_2 as anodic photocatalyst have been proven to work extremely well due to its high light quantum yield and chemical stability [4]. However, a high degree of recombination between the photogenerated electrons and holes remains as a major obstacle for wider application of PFC [5]. Besides, the photogenerated electrons could only move from TiO_2 to cathode under UV irradiation [6,7], which impedes the PFC for real industrial application with solar energy. So it is necessary to find appropriate ways to improve electrons and holes separation and enhance the visible-light-induced photocatalytic performance. Modification of the TiO_2 might be the feasible approach to overcome these limitations.

In respect of modification of TiO_2 photocatalyst, most previous efforts have been focused on element doping and optimizing fabrication methods [8,9]. Among these studies, TiO_2 surface modified with metal nanoparticles displayed great potentials in improving the photoelectric properties and photocatalytic activity [10,11]. On the one hand, such modification could effectively reduce the recombination of photogenerated carriers and extend the service lifetime because of the capture of these photogenerated carriers by noble metals [12]. On the other hand, the noble metal was found to extend the light absorption properties of TiO_2 due to the special optical property of the noble metal [13,14], especially in visible light region [15–17]. For example, Ag-doped TiO_2 prepared on a titanium plate exhibited a higher photocatalytic activity than the undoped one [18]. Recently, TiO_2 nanotubes formed on Ti mesh were proved to show a significant improvement in stability and reliability, which ensured a fast degradation of refractory organics [19]. So, it would be exciting if an Ag-doped TiO_2 photocatalyst could be prepared using Ti mesh as matrix. Such Ag/TiO_2 photocatalyst tapping special structure of Ti mesh would possess

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a more compact 3D nanotube arrays and behave with higher pollutant degradation efficiency.

The cathodic reaction in a PFC system is usually oxygen reduction, which is crucial to anode performance and electricity generation [3,20]. Metal-based catalysts such as Pt and Cu have been commonly used in many types of PFC systems [3,21]. However, persistent kinetic limitations for cathodic oxygen reduction reaction using these metal-based catalysts remain a major challenge for stable operation of the PFC systems [22]. Microbial catalysts of biocathode which takes huge advantage in long-term sustainability have gained growing attentions in microbial fuel cell (MFC) researches compared with the abiotic cathode [23]. Besides, affinity to environment is also a typical feature of biocathode [24]. In spite of these potential advantages, there still remain several issues to be elucidated for comprehensive assessment of its application in PFC system: (a) Confirming electrographic microorganisms in biocathode in PFC system is needed when taking the system differences between PFC and MFC into account; (b) The photocatalytic performance of photoanode depends not only on photocatalyst itself, but also on cathode performance in a PFC system. Therefore, it is necessary to determine the differences in cathode performance so as to provide a more accurate comparison of different photoanodes.

In this work, a novel biocathode-drived PFC (bio-PFC) with an Ag-doped TiO_2 photoanode and microbial-catalyzed biocathode was constructed. The Ag nanoparticles were deposited on the surface of the TiO_2 nanotubes formed on Ti mesh by photoreduction. The physical and electrochemical techniques including X-ray diffration (XRD), X-ray photoelectron spectroscopy (XPS), UV–vis absorption spectrum and photoluminescence specturm were employed to analyze the morphological characteristics of prepared Ag/TiO_2 electrode. In the bio-PFC tests, the system performance was evaluated by electricity generation and rhodamine B (RhB) degradation, which were compared to that using TiO_2 photoanode without Ag doping. The electrochemical activity of the two biocathodes under various photoanodes was analyzed to determine if the difference in photoanode performance was caused by biocathode.

2. Materials and methods

2.1. Preparations of Ag/TiO_2 photoanode and biocathode

TiO_2 electrode as reported in our previous study was prepared [25] before synthesis of Ag/TiO_2 electrode. To fabricate Ag/TiO_2 electrode, silver nitrate ($AgNO_3$) was dissolved in solution consisting of ethanol and water with a volume ratio of 1:4, then purged with nitrogen. The photodeposition of Ag was carried out by submerging the TiO_2 electrode into the well-prepared $AgNO_3$ solution in a cylindrical quartz container (inner diameter: 30 mm, wall thickness: 2 mm) under UV irradiation. This photodeposition process lasted 30 min in the nitrogen-saturation solution. The Ag^+ in the solution would be reduced to Ag nanoparticles depositing on the surface of TiO_2 under UV irradiation. As-prepared Ag/TiO_2 nanotube array was annealed in muffle furnace under nitrogen atmosphere at 500 °C for 2 h at heating and cooling rates of 1 $°C\,min^{-1}$, then rinsed with deionized water and dried in air.

The biocathode was made of carbon fiber brushes (Φ: 3 cm × H: 3 cm, Toray, 3 K carbon fiber). It was well-cultured in a two-chamber microbial fuel cell using a cation exchange membrane (CEM) as separator before installing into the bio-PFC system. The anodic chamber of that MFC was initially inoculated with a mixture consisting of 20% domestic wastewater and 80% acetate medium as previously reported [26]. The cathodic chamber was inoculated with domestic wastewater (50%, v/v), and the medium contained $NaHCO_3$ (1.0 $g\,L^{-1}$) and NH_4Cl (0.3 $g\,L^{-1}$) during the startup period. The phosphate buffered solution (KCl 0.13 $g\,L^{-1}$, $NaH_2PO_4·2H_2O$, 3.32 $g\,L^{-1}$, $Na_2HPO_4·12H_2O$, 10.32 $g\,L^{-1}$), tracer minerals (12.5 mL L^{-1}) and vitamins (5 $mL\,L^{-1}$) were added in the medium solution. The culture condition was the same as previously reported until the stable voltage was obtained [27].

2.2. Bio-PFC configuration and operation

PFC reactor was made of plexiglass consisting of two cylindrical chambers with the same cross-section dimension (3 cm in diameter). The working volume of the anodic chamber was 15 mL, and corresponding value for cathodic chamber was 20 mL. The anodic chamber was equipped with a quartz window to facilitate light transmission. The two chambers were separated by a cation exchange membrane (CEM, Ultrex CMI7000, Membrane International) with a cross-sectional area of 7 cm^2. Two circular holes of 1 cm in diameter were drilled on the top of anodic chamber for sampling and inserting electrode. Another two circular holes were drilled on the top of cathodic chamber for pumping air and sampling. An air diffuser was located at the bottom of cathodic chamber to inject air at a rate of 4 $mL\,min^{-1}$ (dissolved oxygen concentration at 5–6 $mg\,L^{-1}$). Titanium wires were used to connect the electrodes to an external resistance (1000 Ω, except as noted). All the chambers were clamped together by stainless steel fasteners and silica gel plates were inserted between CEM and the chambers to prevent water leakage.

A 150 W xenon lamp (GY-10A, Toupu Co. Ltd., China) was used as light source and installed 15 cm away from the anode. RhB (30 $mg\,L^{-1}$) was used as model pollutant dissolved in 0.05 M Na_2SO_4 solution in anodic chamber. A magnetic bar stirred in it to shorten the time needed for the photoanode to reach the optimum condition. The substrate for biocathode was the same with the MFC for biocathode culture. Prior to the experiment, the bio-PFC was operated on an open-circuit condition in dark during the first half hour to achieve adsorption/desorption equilibrium. In degradation experiment, the RhB concentration was measured by a UV–vis spectrophotometer (UV-722S, PuXiTongYong, China) at the wavelength of 552 nm every 20 min.

2.3. Structural and electrochemical characterization

The microstructure of the Ag/TiO_2 electrode was observed by a field-emission scanning electron microscope (SEM, FEI Quanta 200F) coupled with energy-dispersive X-ray (EDX) analysis. Surface images of the biocathodes after biofilm acclimation were also captured by SEM. The presence of Ag nanoparticles was further confirmed by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM, H-7650, Hitachi Ltd.). The X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (D8 Advance, Bruker, Germany). The constituent elements for Ag/TiO_2 nanotubes were evaluated by X-ray photoelectron spectroscopy (XPS) with employing a monochromatic Al Kα radiation at 800 eV (XPS, PH1-5700 ESCA system, US). The absorption spectrum of Ag/TiO_2 nantubes was analyzed using UV–vis spectrophotometry (UV-2550, Shimadzu, Japan). Photoluminescence (PL) spectrum was recorded using Hitachi F-4600 fluorescence spectrophotometer at an excitation wavelength of 290 nm.

The electrochemical activity of photoanode was tested in an abiotic electrochemical reactor which was filled with 0.05 M Na_2SO_4 solution. The abiotic electrochemical system was composed of prepared photoanode (working electrode), Pt sheet (counter electrode), and saturated calomel referenced electrode (SCE, +241 mV versus standard hydrogen electrode; SHE). Linear sweep voltammetry (LSV) was scanned at a rate of 1 $mV\,s^{-1}$ from −0.5 V to 0.5 V. The electrochemical analysis of biocathode was