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A micro photocatalytic fuel cell with an air-breathing, membraneless and monolithic design

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Abstract In this study, a membraneless, monolithic micro photocatalytic fuel cell with an air-breathing cathode was developed for simultaneous wastewater treatment and electricity generation. In this newly-developed micro photocatalytic fuel cell, the photoanode and cathode were arranged with a shoulder-to-shoulder design, forming two planar electrodes. Such design offers several advantages of enhanced mass transfer, uniform light distribution, short light transfer path, membrane elimination and easy fabrication, integration, and compatibility with other microdevices. The performance of this type fuel cell was evaluated by using methanol as a model pollutant under the alkaline condition. Experimental results indicated the developed micro photocatalytic fuel cell was able to show good photo-response to the illumination and satisfactory performance as well as durability. Parametric study on the cell performance was also performed. It was found that increasing the light intensity, methanol concentration and KOH concentration could improve the cell performance. But for the effect of the liquid flow rate, it was shown that the cell performance firstly increased with increasing the liquid flow rate and then decreased with further increasing the liquid flow rate. This study not only opens a new avenue for the design of the micro photocatalytic fuel cell but also is helpful for the optimization of the operating conditions.

Keywords Photocatalytic fuel cell · Membraneless and monolithic design · Air-breathing cathode · Photo-response · Cell performance

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1 Introduction

With the economic development, people become more concerned about the environmental problems all over the world. In particular, every year a huge amount of wastewater is discharged to natural ecosystem, which greatly threatens aquatic life and human health [1–3]. Hence, the wastewater treatment has become an issue of global concern, especially in developing countries [4]. To resolve this issue, several approaches have been developed, including the biodegradation [5–7], adsorption [8, 9], chemical oxidation [10] and so on [11, 12]. On the other hand, it should be recognized that although the discharge of wastewater causes a severe environmental problem [13], wastewater contains numerous organics [12, 14], which is an available energy source. However, the above-mentioned conventional wastewater treatment technologies usually aim at the efficient degradation of these organics. The chemical energy stored in wastewater is not efficiently utilized, leading to the energy loss. Therefore, recovering the energy released from organic pollutants in wastewater during the treatment is promising to address the environmental and energy problems simultaneously [15, 16], but still challenging.

Photocatalytic fuel cell (PFC), which is an integration of the photocatalysis and fuel cell technologies, is one of ideal solutions to simultaneously address the wastewater and energy recovery issues. Unlike conventional fuel cells, in which noble metals are usually employed to oxidize the simple organic compounds, the PFCs use the abundant materials of semiconductors [17] as the catalysts to form the photoanode, which greatly lowers the capital cost. Upon illumination, the absorbed photons ensure the electron-hole pairs to be generated in the semiconductors. The photo-generated holes can firstly oxidize OH^- to hydroxyl radicals (•OH), which are powerful oxidants [18, 19] and then degrade the organic compounds into CO_2 and H_2O. The photo-generated electrons spontaneously flow to the cathode through an external circuit to form the electricity. As a result, the PFCs enable simultaneous wastewater treatment and electricity production [20–24]. Moreover, PFCs can degrade most organic compounds such that the fuel type limitation in conventional fuel cells can be avoided [8]. Because of these advantages, the PFC has received ever-increasing attention.

Since the performance of the PFC mainly depends on the photocatalysts, extensive efforts have been devoted to the development of materials over the past decade [25–29]. These works mainly aimed to promote the photoelectrochemical oxidation rate and reduce charge transport resistance. Besides, the photon and mass transport also play important roles in the PFC performance, which is inherently associated with the cell design. However, the design of the PFC has not been widely explored. Most existing PFCs have large dimensions. Such design usually has the problem of low specific surface area and mass transfer rate. The ion exchange membrane is also typically required to separate the PFC into two compartments of the anode and cathode, respectively [22, 30]. The use of the ion exchange membrane definitely increase the capital cost of the PFC. Moreover, conventional PFCs usually adopt the mode of the oxygen-dissolved electrolyte at the cathode. Because of the low solubility of oxygen, the cathode performance of the PFC is restricted. All these disadvantages arising from the conventional PFC design with large scale dimension limit its performance improvement.

Recently, the incorporation of microfluidics into the photocatalytic technologies opens a new avenue for enhancing the performance of the PFC. Owing to its intrinsic merits of large surface-to-area ratio, fine flow control and enhanced heat and mass transfer, the microfluidic platform has been successfully applied to water splitting [31], wastewater treatment [32] and so on [33, 34]. In particular, the microfluidics enables uniform light distribution and short light transfer path. Under such circumstance, along with enhanced mass transfer by the microfluidic platform, the photocatalytic reaction rate can be greatly improved. Inspired by this idea, a membraneless monolithic micro PFC (μPFC) with an air-breathing cathode was developed in this study. Unlike the previously-reported membraneless micro PFC with an air-breathing cathode [32], in which the photoanode and cathode were face-to-face, the photoanode and cathode were arranged with a shoulder-to-shoulder design in this study, forming two planar electrodes. In addition to the above-mentioned advantages, this new design also offers the following advantages. First, the membrane elimination not only reduces the capital cost but also makes the membrane-related issues such as membrane fouling disappear. Second, the air-breathing design can greatly enhance the oxygen transport as compared to the oxygen-dissolved mode and simplify the cell system. Third, this simple design benefits for the fabrication (e.g., replication), integration, and compatibility with other microdevices [35, 36]. To demonstrate the feasibility of this new design of μPFC, methanol was used as a model fuel to examine the performance of the developed μPFC in an alkaline environment under the UV illumination. The photo-response and its durability were studied, as well as the effects of the methanol concentration, KOH concentration, light intensity and liquid flow rate on the cell performance.

2 Materials and methods

2.1 Design of μPFC and working principle

As sketched in Fig. 1, the μPFC developed in this work mainly consisted of a cover, a photoanode, a cathode and a baseplate. The cover was made of Polydimethylsiloxane (PDMS). In this cover, there were two microchambers for the photoanode and cathode, respectively. Each microchamber had one inlet and one outlet. A FTO glass with the dimension of 30 mm × 50 mm (resistance 10 Ω per square, Xinyan Technology Co., China) was chosen to fabricate the photoanode. In the middle, the conducting layer with a width of 1.0 mm was removed by the etching method to separate the photoanode and cathode and avoid the short circuit. On one side of this line, the photoanode was fabricated by coating TiO_2 on the FTO glass with the dimension of 24 mm × 4.5 mm. A rectangular shape hole with the dimension of 10 mm × 24 mm was drilled on the other side of this line for positioning the cathode and breathing oxygen from air. A commercial cathode of the Pt coated carbon paper (DMFC Cathode, Alfa Aesar, UK) was chosen as the air-breathing cathode, which was tailored into T shape. As

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