



## Research Paper

# A visible-light responsive micro photocatalytic fuel cell with laterally arranged electrodes



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## HIGHLIGHTS

- A visible light responsive  $\mu$ PFC with laterally arranged electrodes is developed.
- The  $\text{TiO}_2$  photoanode is photosensitized by CdS-ZnS to broaden the spectra.
- The developed  $\mu$ PFC is evaluated under various operating conditions.

## ARTICLE INFO

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## ABSTRACT

A micro photocatalytic fuel cell with a visible-light responsive photoanode and the lateral arrangement of the electrodes at the same plane was developed to enable simultaneous organics degradation and electricity generation. The developed micro photocatalytic fuel cell was assessed by using methanol as a representative organic compound in the alkaline environment. It is shown that good visible-light response was achieved. The effects of the light intensity, methanol concentration, KOH concentration and liquid flow rate were also explored. Experimental results showed that when the light intensity was increased, the cell performance was improved due to more photo-excited electron-hole pairs. Upgrading the KOH concentration led to the increased performance due to more efficient capture of the holes and enhanced cathodic reaction and ion transport. The increase of the methanol concentration in the testing range led to the improved performance as a result of the enhanced mass transport. The discharging performance was firstly increased and then decreased with increasing the liquid flow rate due to the competition of enhanced mass transfer and decreased residence time and increased methanol crossover.

## 1. Introduction

Directly discharging wastewater into natural water body not only threatens the human health but also triggers unwanted ecological effects. Therefore, the environmental problem of water pollution has become one of the critical issues facing our planet [1–3]. For this reason, many methods have been developed, such as biodegradation [4,5], adsorption [6,7] and chemical oxidation [8]. However, traditional wastewater treatment methods are usually concerned with how to rapidly and efficiently degrade pollutants contained in the wastewater. Actually, these pollutants also contains plenty of chemical energy, which almost meets 1/3 demand of the global energy

consumption per year [2]. Unfortunately, the above-mentioned technologies are unable to efficiently utilize plentiful chemical energy contained in the wastewater, resulting in the energy loss. In this case, it is urgent to seek for new and efficient methods to simultaneously remove pollutants and recover the chemical energy stored in the wastewater.

The photocatalytic fuel cell (PFC) is one of promising technologies to meet the above demand, in which the abundant semiconductors are employed to function as the photoanode. As a result, the capital cost of the PFC can be much lower than that of conventional fuel cell [9]. During the PFC working process, the electron/hole pairs are photo-excited in the semiconductors upon illumination [10,11]. The photo-

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excited holes can oxidize most organic compounds [12–15], while the photo-excited electrons go through the external circuit to the cathode to complete the oxygen reduction reaction. Since most organic compounds can be degraded photocatalytically, not only the wastewater can be efficiently purified but also the electricity can be generated simultaneously by using solar energy. Therefore, the PFC technology has been regarded as a promising method to treat wastewater and generate clear energy simultaneously [16–18].

In the past, the development of highly active photocatalysts has received numerous attention towards the improvement in the PFC performance [19–21]. For instance, Antoniadou et al. used CdS to functionalize commercial nanocrystalline titania [22]. Shu et al. developed BiOI-based photoanode to generate electricity by using organic compounds [23]. Li et al. developed a photocatalytic fuel cell with a BiOCl/Ti photoanode and a Pt cathode for the dye degradation and electricity generation [24]. Li et al. developed a dual-photoelectrode photocatalytic fuel cell with a TiO<sub>2</sub>/Ti photoanode and a Cu<sub>2</sub>O/Cu photocathode for hazardous organics treatment with simultaneous electricity generation [25]. In addition to the photocatalysts, the PFC performance is also dependent of its cell structure design due to its effect on the photon and mass transport. Currently, most existing PFCs are referred to as bulk reactors [8–10]. Besides, Seger et al. [26,27] developed a photoelectrochemical cell with a membrane electrode assembly design. Tang et al. [28] proposed a photocatalytic fuel cell with an aqueous-film rotating disk for the generation of hydrogen and electricity. However, conventional PFCs usually have large dimensions, which is not beneficial for the photon and mass transport. For this reason, microfluidics that has the advantages of enhanced mass transfer due to high surface-to-volume ratio [29,30], has been incorporated into the photocatalytic technologies to improve the performance, such as wastewater treatment [17] and CO<sub>2</sub> photoreduction [31,32]. Recently, Xia et al. [33] developed a micro membraneless and monolithic photocatalytic fuel cell with the bare TiO<sub>2</sub> photoanode and an air-breathing cathode, in which two electrodes were laterally arranged at the same plane. In this design, not only the ion exchange membrane was eliminated to reduce the cost and the issues associated with the membranes, but also the oxygen transport could be enhanced to improve the cell performance as compared to the oxygen-dissolved cathode. Moreover, this design allowed it to be easily fabricated and integrated with other microdevices [34,35]. Besides, the lateral arrangement of the electrodes makes it possible to use the photocathode without two-side illumination. However, bare TiO<sub>2</sub> photoanode was employed in this work, which could only respond to the UV light. The UV light only accounts for 3–5% sunlight. Under such a circumstance, the solar energy could not be efficiently utilized. Therefore, the development of a visible-light responsive photoanode for this new type of PFC is needed, by which the cell performance and solar energy utilization efficiency can be further improved. Aiming at this target, a visible-light responsive micro photocatalytic fuel cell ( $\mu$ PFC) with the lateral arrangement of two electrodes at the same plane was developed in this study. The developed  $\mu$ PFC was assessed by using methanol as a representative organics pollutant in an alkaline environment.

## 2. Experimental

### 2.1. Design and fabrication of $\mu$ PFC with the laterally arranged electrodes

The design of the developed  $\mu$ PFC with the lateral arrangement was similar to the previous work, which was consisting of a cover, a photoanode, a cathode and a baseplate [33], as shown in Fig. 1a. The polydimethylsiloxane (PDMS) was used to fabricate the cover and the baseplate. The photoanode was made by coating TiO<sub>2</sub> nanoparticles (Aeroxide P25, Acros, Belgium) on the fluorine-doped SnO<sub>2</sub> (FTO) conducting glass (resistance 10  $\Omega$  per square, Xinyan Technology Co., China). Commercially-available carbon paper coated with Pt (DMFC Cathode, Alfa Aesar, Great Britain) was cut into the T-shape to function

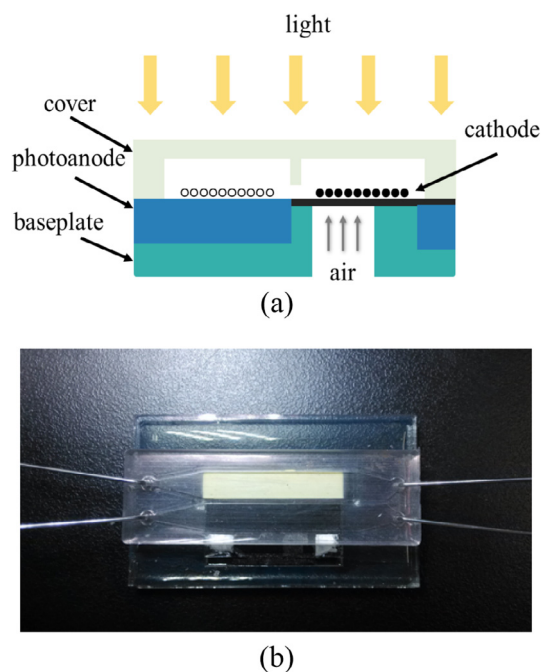


Fig. 1. Illustration of (a) design and (b) picture of the developed  $\mu$ PFC.

as the cathode. Each part was briefly introduced as follows. The cover with the built-in micro chambers functioned as the reaction chambers for both the electrodes. In this study, methanol was used as a representative organics pollutant to function as the fuel for the PFC. Hence, methanol and electrolyte mixture was supplied into the photoanode chamber from the triangular-shape inlet and discharged out from the triangular-shape outlet, while the electrolyte was supplied into the cathode chamber. Depth of both the chambers was 0.9 mm. There existed a line-shape convex in the middle at the cover plate. The convex had the depth of 0.4 mm. Due to the existences of the line-shape convex and triangular-shape inlets and outlets, the uniform supply of methanol and electrolyte, and the reduced organics crossover from the photoanode to the cathode could be ensured. For the photoanode, the FTO conducting glass with the dimension of 50 mm in length, 30 mm in width and 2.2 mm in thickness was employed. The conducting layer with 1 mm  $\times$  50 mm in the middle was removed to form an insulating region. The photocatalysts were coated on one side of the FTO conducting glass and a rectangular hole with 10 mm  $\times$  24 mm was drilled at the other side, which could be used to hold the cathode and breathe air. For the cathode, the straight region of the T-shaped Pt coated carbon paper was used for oxygen reduction reaction with the dimension of 24 mm  $\times$  4.5 mm and the remaining region was used to collect the current. For the baseplate, it had the same dimension of 50 mm  $\times$  30 mm as the FTO conducting glass. Corresponding to the rectangular hole, a platform on the baseplate with the same size and location as the hole in the FTO conducting glass was designed, whose function was to hold the cathode and keep it at the same level with the photoanode. A rectangular hole with 20 mm in length and 3 mm in width was also designed to provide the oxygen transport path from the ambient air. Fig. 1b gives the picture of the fabricated  $\mu$ PFC.

### 2.2. Photoanode

The preparation of the visible-light responsive photoanode had four steps, including the laser drilling, etching, spraying and SILAR cycles. First, a 10 mm  $\times$  24 mm hole was drilled in the FTO conducting glass by laser. Second, a 50 mm  $\times$  1 mm conduction layer in the middle of the FTO conducting glass was removed by the etching process, which could avoid the short circuit between the photoanode and cathode.

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