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A highly efficient immobilized ZnO/Zn photoanode for degradation of azo dye Reactive Green 19 in a photocatalytic fuel cell

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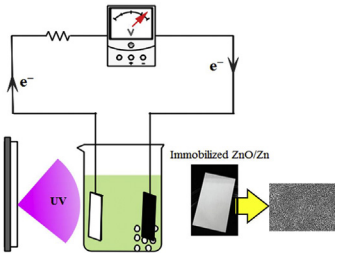
HIGHLIGHTS

- A sustainable photocatalytic fuel cell in the absence of supporting electrolyte.
- An efficient immobilized ZnO/Zn photoanode was fabricated.
- Close circuit gave higher degradation than opened circuit photocatalytic fuel cell.
- Conductivity of the dye solution increased with increase of intermediate products.

GRAPHICAL ABSTRACT



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ABSTRACT

Photocatalytic fuel cell (PFC) is a potential wastewater treatment technology that can generate electricity from the conversion of chemical energy of organic pollutants. An immobilized ZnO/Zn fabricated by sonication and heat attachment method was applied as the photoanode and Pt/C plate was used as the cathode of the PFC in this study. Factors that affect the decolorization efficiency and electricity generation of the PFC such as different initial dye concentrations and pH were investigated. Results revealed that the degradation of Reactive Green 19 (RG19) was enhanced in a closed circuit PFC compared with that of a opened circuit PFC. Almost 100% decolorization could be achieved in 8 h when 250 mL of 30 mg L^{-1} of RG19 was treated in a PFC without any supporting electrolyte. The highest short circuit current of 0.0427 mA cm^{-2} and maximum power density of 0.0102 mW cm^{-2} was obtained by PFC using 30 mg L^{-1} of RG19. The correlation between dye degradation, conductivity and voltage output were also investigated and discussed.

1. Introduction

Recently, photocatalytic fuel cell (PFC) has attracted worldwide interest due to its ability to treat organic wastewater and generate electricity simultaneously (Antoniadou et al., 2010; Li et al., 2013a,b; Wu et al., 2015). Generally, a PFC comprises a photoanode loaded with semiconductor photocatalyst, a cathode that carries the electrocatalyst and liquid electrolyte. Upon illumination, the photocatalyst undergoes photoexcitation and generates electron-hole pairs. The photogenerated electrons will be excited

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from valence band (VB) to the conduction band (CB) of the photoanode and flow to the cathode through an external circuit, resulting in electricity generation. Meanwhile, the photogenerated holes of the photoanode will oxidize and degrade the organic pollutants, or react with OH^- or H_2O to form •OH radicals through H_2O oxidation. The produced hydroxyl radicals (•OH) have a very high oxidation potential (2.80 V) that can oxidize the organic pollutants to the mineral end-products (Konstantinou and Albanis, 2004). Under aerobic condition, the cathode functions as an oxygen electrode.

A PFC using TiO_2 nanotube array (TNA) as photoanode has been studied by several researchers recently due to its high performance in PFC (Liu et al., 2009b, 2011a, b; Li et al., 2013a,b). The well aligned TNA fabricated via anodizing process in HF electrolytes forms a natural Schottky-type contact between TiO_2 and Ti substrate and provides a unidirectional channel to ease the transport of photogenerated electrons. There are also a handful of publications on PFC comprised of TiO_2 photoanode which fabricated by different methods (Kaneko et al., 2006; Antoniadou et al., 2010). Researchers (Liu et al., 2009a, b; Li et al., 2013a,b) found that the structural properties of the photoanode such as the specific surface area and the thickness of photoanode loaded can affect the light harvesting capability and the transport resistance of the photogenerated electrons. A short TiO_2 nanotube array (STNA) photoanode (~280 nm) can enhance the electrons transfer properties and reduce the recombination rate of photogenerated electrons; however, it is not favorable for incident light absorption. This also revealed that the specific surface area of the photoanode plays an important role in photocatalytic oxidation process in the PFC.

Several researchers have reported that the addition of supporting electrolytes can enhance the performance of PFC (Antoniadou et al., 2010; Wang et al., 2014; Yang et al., 2014; Li et al., 2015; Wu et al., 2015). Sodium sulfate (Na_2SO_4) is the most commonly used electrolyte in the PFC systems. The presence of supporting electrolyte can increase the conductivity of the solution and reduce the internal resistance of the PFC. The decrease in internal resistance can led to greater potential difference on both electrodes and promote the flow of electrons to the cathode, leaving strongly oxidizing holes at photoanode. Therefore, most of the researchers applied the supporting electrolytes into the PFC to enhance the degradation efficiency and electricity generation of PFC.

So far, there is not much work reported on the application of ZnO as a functional photoanode in PFC systems. In our previous study, we have reported the performance of PFC based on an anodized ZnO/Zn as photoanode using NaCl as supporting electrolyte (Lee et al., 2016). In this paper, we applied an immobilized ZnO/Zn photoanode in a PFC without any supporting electrolyte. The effect of some operating parameter such as open and closed circuit; initial dye concentration and pH on dye degradation and electricity generation were investigated. The objective of this study is to evaluate the degradation efficiency and power output of the fabricated immobilized ZnO/Zn photoanode in a PFC system free of supporting electrolyte.

2. Material and methods

2.1. Materials

A commercial ZnO powder (HmbG Chemical) was used as the photocatalyst in this study. A synthetic dye, Reactive Green 19 (RG19), with molecular formula $C_{40}H_{23}Cl_2N_{15}Na_6O_{19}S_6$ from Acros Organic was used as the organic pollutant in this research.

2.2. Preparation of the photoanode

The fabrication of ZnO/Zn photoanode was prepared according to the heat attachment method (Behnajady et al., 2009) with some modifications. A Zn foil (thickness 0.3 mm, purity 99.999%) with dimensions 5.0 cm × 3.0 cm was used as the substrate for the immobilized ZnO/Zn photoanode. First, Zn foil was ultrasonically cleaned in ethanol solution and rinsed with distilled water. A ZnO suspension was prepared by dissolving 1.0 g of commercial ZnO powders in 100 mL distilled water. Next, the Zn foil was immersed in the ZnO suspension and ultrasonicated for 1 h. Then, the Zn foil was taken out from the ZnO suspension and allowed to dry in oven at 90 °C for 24 h. Finally, the Zn foil was annealed at 300 °C in furnace for 2 h. The immobilized ZnO/Zn photoanode was dipped in distilled water for few seconds to eliminate any weakly attached ZnO powders before application in the PFC. The immobilized ZnO/Zn photoanode was characterized by X-ray diffraction XRD (Shimadzu XRD-6000) and scanning electron microscopy (SEM) from JEOL (Model: JSM 6460 LA).

2.3. Construction of the PFC

A PFC based on immobilized ZnO/Zn photoanode and Pt/C cathode was constructed. The distance between the two electrodes was set at 5 cm. An ultraviolet A (UVA) lamp (Philips, 7.7 W, 350–400 nm) was used as the light source, and the distance between the lamp and the ZnO/Zn photoanode was fixed at 15 cm. Aeration was provided at the cathode side, and the study was conducted at room temperature.

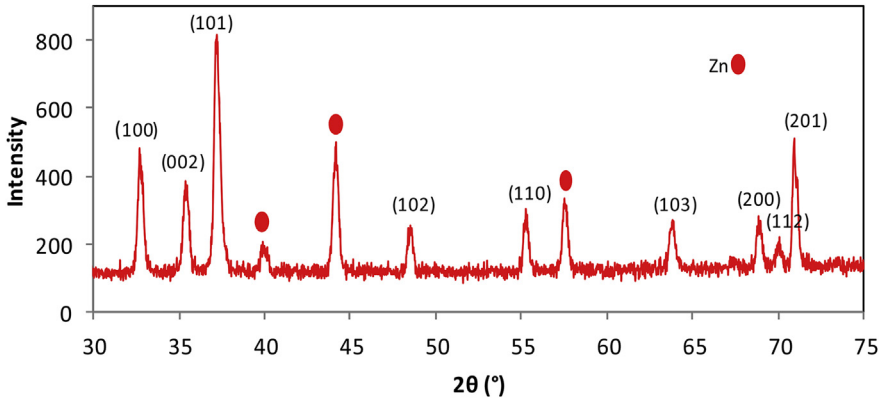

Fig. 1. XRD diffraction pattern of ZnO/Zn photoanode after annealed at 300 °C for 2 h.