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Facile electrochemical polymerization of polypyrrole film applied as cathode material in dual rotating disk photo fuel cell

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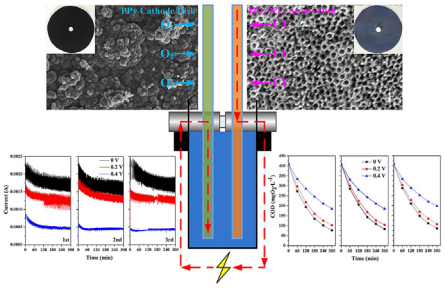
HIGHLIGHTS

- A PPy film was synthesized on Ti substrate through electrochemical methods.
- The film was applied as cathode material in TiO_2 NTs-PPy dual rotating disk PFC.
- Stable current and COD removal were obtained at different output voltage.
- PPy is a promising Pt alternative cathode material in dual rotating disk PFC.
- Rotating speed and pH affected the electricity generation and COD removal in PFC.

GRAPHICAL ABSTRACT



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ABSTRACT

Polypyrrole (PPy) film is synthesized on Ti substrate through electrochemical polymerization method and is applied as cathode material in a TiO_2 NTs-PPy dual rotating disk photo fuel cell (PFC). The optimized PPy electrochemical polymerization is carried out using linear sweep voltammetry from 0 V to 1.2 V (*vs.* SCE) with scan rate of 0.1 V s^{-1}, 100 circles. Sixty milliliter real textile wastewater with the initial COD and conductivity of 408 ± 6 mgO_2 L^{-1} and 20180 μS cm^{-1} is treated in this PFC under UV irradiation. About 0.46 V open-circuit voltage (V_{OC}) and 1.8–2.2 mA short-circuit current (J_{SC}) are obtained. Due to the effective electron-hole separation effect, the COD removal rate is as high as 0.0055 min^{-1}. Stable current and COD removal can be obtained at different output voltage. Two influence factors including rotating speed and pH are investigated. Better electricity generation performance and COD removal activity are achieved at high rotating speed and in acidic condition. In comparison with platinized cathode, though V_{OC} is lower, similar J_{SC} is measured. Considering the high cost of Pt, PPy is a promising alternative cathode material in PFC that can also generate electricity efficiently and stably.

1. Introduction

Industrial wastewater advanced treatment and pollutants resource utilization have gained more and more attention in recent years. Photocatalytic (PC) oxidation is an emerging technique in advanced treatment for refractory industrial wastewater because of

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the high, non-selective oxidation activity and the use of stable and nontoxic materials [1–5]. With the development of new PC reactor, the application of PC technique in industrial wastewater advanced treatment is becoming reasonable [6–8]. A rotating disk PC reactor was early established by us [9]. Several kinds of textile wastewaters were successfully advanced treated in this reactor with high performance and low energy consumption. When it is rotating, the upper part of the TiO_2/Ti disk is coated with a thin aqueous film. UV light can penetrate this thin film, irradiates on TiO_2 directly, which significantly reduces the light loss caused by solution absorption and enhances light utilization efficiency [10–13].

In order to further utilize the chemical energy existing in organic pollutants, photo fuel cell (PFC), as a separate class of photoelectrochemical cells, is recently being studied by using a Pt or Pt/C as cathode in connection with photoanode [14–19]. With light irradiation, a potential difference forms between photoanode and cathode, transferring photo generated electrons from photoanode to cathode through external circuit. In this process, besides electricity is generated, the potential difference is also benefit for electron-hole separation, resulting in an improved PC degradation activity. In our former research, a TiO_2/Ti-Pt PFC was established with a platinized Ti plate as cathode to advanced treat two kinds of real textile wastewaters [20]. Stable electricity generation performance and COD removal activity were observed during long time operation. These refractory wastewaters are difficult to be biodegraded and always with high salinity, but they are reasonable fuels for PFC not only because the high activity of PC oxidation, but also no more electrolyte needs.

In a PFC system, cathode plays very important role and behaves as an oxygen reduction electrode to form H_2O as the following reaction:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O\ (+1.23\ V,\ \text{at pH } 0) \quad (1)$$

However, oxygen reduction rate at cathode is much slower than oxidation rate or electron generation rate at photoanode in PFC. Pt-based catalyst is still the most widely used cathode material in PFC due to its high oxygen reduction reaction (ORR) activity. Considering the limited availability and high cost, Pt is too expensive for realistic large-scale application. Lianos et al. have reported that a buckypaper bearing NiO cathode could very well compete with a standard Pt/carbon-black/carbon-cloth cathode in a PFC [21]. Very recently, Feng et al. have presented a biocathode coupled PFC, which achieved similar methyl orange (MO) decoloration rate and maximum power density to the brush cathode PFC with 50 mg Pt/C loading [22]. However, in comparison with photoanode, there are still very few researches focusing on low cost cathode material in PFC.

Conductive polymers such as polypyrrole (PPy), polyaniline (PANI) and polythiophen (PTh) have been investigated for application towards ORR catalysis due to their low cost, high electronic conductivity and distinct redox properties. A class of (non-precious metal)/(heteroatomic polymer) catalysts have been synthesized and used as cathode catalysts in H_2–O_2 fuel cells in the past few years [23–27]. In our former research, we have found that PPy-functionalized Ni foam cathode exhibited similar H_2 evolution rate with Pt black coated Ni foam cathode in a photoelectrochemical H_2 generation system [28]. Then, whether the PPy can also be applied as cathode material in PFC to generate electricity and PC advanced treat industrial wastewater efficiently. In this research, we have synthesized an immobilized PPy film on Ti substrate through facile electrochemical polymerization method. Electrochemical polymerization conditions were optimized carefully. The film was applied as cathode material in a TiO_2 nanotube arrays (TiO_2 NTs)-PPy dual rotating disk PFC to advanced treat real textile wastewater. The rotation of photoanode disk can reduce light loss caused by solution absorption, while the rotation of cathode disk is more benefit for O_2 mass transfer [29]. Electricity generation performance and PC degradation activity were intensively studied. The result was compared with that obtained by using platinized cathode. The aim of this study is to investigate whether the PPy film prepared through electrochemical polymerization is a kind of promising cathode material for PFC.

2. Materials and methods

2.1. Materials and reagents

Titanium plate (99.6% purity, thickness 0.5 mm) purchased from Shanghai Hongtai Metal Production Co. Ltd. (Shanghai, China) was employed as substrate for photoanode and cathode. The plate was polished with 1000 grit sandpaper and then immersed into acetone under ultrasonic vibration for 15 min to degrease before the use. Platinized titanium plate was purchased from Suzhou Borui Industrial Material Science & Technology Co. Ltd. (Jiangsu, China). The Pt content was 2.163, 4.326 and 6.489 mg cm^{-2} for the plate with the Pt thickness of 1, 2 and 3 μm, respectively. All chemical reagents purchased from Shanghai Chemical Reagent Co. (Shanghai, China) were in analytical grade without further purifications. The real textile wastewater after secondary bio-chemical treatment was collected from a textile plant located in Shaoxing (Zhejiang, China). The wastewater was stored at 4 °C before use. The initial COD was 408 ± 6 mgO_2 L^{-1}, the conductivity was 20180 μS cm^{-1}, the concentration of SO_4^{2-}, Cl^- and NO_3^- was 3418, 1056 and 1233 mg L^{-1}, respectively.

2.2. Preparation of TiO_2 NTs/Ti photoanode and PPy/Ti cathode

TiO_2 NTs/Ti photoanode was prepared by an electrochemical anodization method in 300 ml ethylene glycol electrolyte with addition of 0.5 wt% NH_4F and 10 vol% DI water. Anodizing was performed at 40 V for 13 h using a Ti disk (diameter 75 mm) as anode and a graphite plate (80 mm × 80 mm) as cathode. After anodization the photoanode was cleaned by ethanol, and finally calcined at 450 °C for 2 h with a heating rate of 5 °C per minute. The obtained anatase TiO_2 NTs was 0.25 μm in diameter and 8 μm in length (Fig. S1).

The PPy/Ti cathode was prepared by one-step electrochemical linear sweep voltammetry using Ti disk (diameter 75 mm) as working electrode, Ti plate (80 mm × 80 mm) and saturated calomel electrode (SCE) as auxiliary and reference electrode. The polymerization precursor was 300 ml 0.5 vol% pyrrole solution with 0.1 mol L^{-1} KNO_3 and 0.1 mol L^{-1} HNO_3. The start potential was set as 0 V (*vs.* SCE), the end potential was optimized from 0.8 V to 1.4 V (*vs.* SCE), the number of scan circles was optimized from 20 to 200 circles, the scan rate was optimized from 0.05 to 0.2 V s^{-1}.

2.3. Structure of simple photoelectrochemical cell

The optimization of PPy film electrochemical polymerization condition was operated in a simple photoelectrochemical cell with the size of 45 mm × 25 mm × 60 mm (length × width × height) (Fig. 1a). Both the size of TiO_2 NTs/Ti photoanode and PPy/Ti cathode was 40 mm × 40 mm in optimization experiments. An 11 W mercury lamp (Philips, 254 nm) was used as UV source and the irradiance maintained constantly at 3 mW cm^{-2}, measured using a UV radiometer (UV-B, Beijing Normal University Electric Light Instrument Factory, Beijing, China). Sixty milliliter 0.05 mol L^{-1} Na_2SO_4 solution containing different organic compounds was used as fuel to investigate the electricity generation performance of the