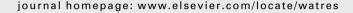


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Efficient electricity production and simultaneously wastewater treatment via a high-performance photocatalytic fuel cell

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ABSTRACT

A great quantity of wastewater were discharged into water body, causing serious environmental pollution. Meanwhile, the organic compounds in wastewater are important sources of energy. In this work, a high-performance short TiO2 nanotube array (STNA) electrode was applied as photoanode material in a novel photocatalytic fuel cell (PFC) system for electricity production and simultaneously wastewater treatment. The results of current work demonstrate that various model compounds as well as real wastewater samples can be used as substrates for the PFC system. As a representative of model compounds, the acetic acid solution produces the highest cell performance with shortcircuit current density 1.42 mA cm⁻², open-circuit voltage 1.48 V and maximum power density output 0.67 mW cm⁻². The STNA photoanode reveals obviously enhanced cell performance compared with TiO2 nanoparticulate film electrode or other long nanotubes electrode. Moreover, the photoanode material, electrolyte concentration, pH of the initial solution, and cathode material were found to be important factors influencing the system performance of PFC. Therefore, the proposed fuel cell system provides a novel way of energy conversion and effective disposal mode of organics and serves well as a promising technology for wastewater treatment.

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1. Introduction

With the rapid increase in population and fast development of industries in recent years, large amounts of organic waste discharged into water bodies have caused serious environmental pollution. In 2009, the total discharge amount of wastewater in China was ~58.92 billion tons and the relevant amount of chemical oxygen demand (COD) reached ~12.77 million tons. Meanwhile, the organic compounds in wastewater are

important sources of energy (Feng et al., 2010; Kaneko et al., 2010; Liu et al., 2010; Strataki et al., 2010). According to the statistics (Japan Energy Society, 2002), the energy of the biowaste in the environment has reached 130 EJ y^{-1} , corresponding to a third of the global energy demand of 450 EJ y^{-1} . Therefore, finding methods for efficient recovery of the chemical energy and rapid decomposition of the organic matters in wastewater comprise the highest priority for future wastewater treatment technologies.

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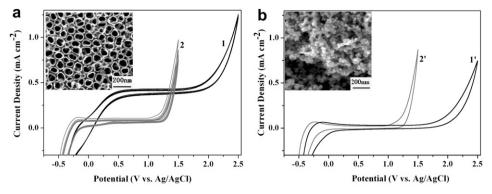


Fig. 1 – Continuous cyclic voltammograms (CV) of STNA electrode (curve 1 and 1') and TiO_2 nanoparticulate film electrode (curve 2 and 2') over five cycles in 0.1 mol L^{-1} Na₂SO₄ (a) under UV illumination and (b) in the dark, respectively. The inset is the SEM image of typical STNA (a) and conventional TiO_2 nanoparticulate film (b), respectively.

Microbial fuel cell (MFC) was once considered the best proposal for wastewater treatment, which can use bacteria as the catalysts to produce electricity and oxidize organic matters (Logan et al., 2006; Wang et al., 2009). The greatest potential of MFC lies in the use of wastewater as a substrate (fuel), which breaks the traditional concept of sewage treatment and allows combining wastewater treatment with power generation. However, the electron transfer process within MFC devices involves complicated mechanism among different cells or cell systems, which directly lead to poor cell performance (Qian et al., 2010). Furthermore, MFC also possess disadvantages such as complex operation, bacteria cultivation, long start-up time, and stringent working conditions (Logan et al., 2006).

 ${
m TiO_2}$ -based photocatalytic oxidation is a promising and efficient process that can be used to degrade various recalcitrant organic pollutants (Fujishima et al., 2008; Kim and Choi, 2010; Zhang et al., 2008). Upon UV illumination, the electrons are excited from the valence band to the conduction band of ${
m TiO_2}$, generating electron/hole pairs. The positive holes are powerful oxidants for degrading organic compounds into ${
m CO_2}$ and ${
m H_2O}$, and the negative electrons are powerful reductants (Choi et al., 2010).

By substituting the slow and complex biochemical electron transfer process in traditional MFC with the fast and direct transportation process of photogenerated electrons in photocatalysis (i.e. substituting the microbial anode of MFC with the TiO2 photoanode), the TiO2 photocatalytic process may degrade organic matter and produce photogenerated electrons that pass through the conductive substrate to the cathode. In turn, this forms a TiO2-based photocatalytic fuel cell (PFC) system and the chemical energy of organics can be transformed into electricity accompanied with organic compounds degradation at the expense of incident light. Different from traditional MFC, the generation of electrons in the PFC system comes from photoexcitation, which is a much fast and direct process. It is, therefore, possible to generate electricity and simultaneous decomposition of organic compounds via the PFC system. However, the research on PFC system was in its infancy, there are still many problems need to be solved or improved and the most crucial factor was remaining the photoanode material.

The properties of functional materials are highly dependent on their microstructure. Recently, the highly ordered TiO2 nanotube array (TNA) fabricated by anodization of titanium in HF or [F-]-based electrolyte has attracted much attention for its peculiar architecture and remarkable properties (Grimes, 2007; Mor et al., 2006). Within nanotubular microstructures, vertically oriented TiO2 nanotubes directly grown on the electrically conductive Ti substrate, forms a natural Schottky-type contact and provides an unidirectional channel for the rapid transport of photogenerated electrons. Lots of work can be found regarding the photocatalytic applications of TNA into organic compounds degradation (Liu et al., 2008; Xu et al., 2006). Nevertheless, most studies have mainly focused on the efficiency and the extent of mineralization. An equally important aspect of photocatalysis, energy recovery, has not received much attention.

Preparation by sonoelectrochemical anodization of a short, robust, and highly ordered ${\rm TiO_2}$ nanotube array (STNA) with superior electron transfer performance and excellent mechanical stability has been reported (Liu et al., 2009). In this work, the high-performance STNA electrode was applied as a photoanode material in the novel fuel cell system for electricity yield and simultaneously wastewater treatment. Various model compounds and actual wastewater were investigated using the fuel cell system. The results of current work demonstrate that

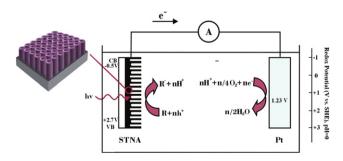


Fig. 2 – Schematic diagram of working principle of the STNA-based PFC system. The photogenerated electrons flow from the conduction band of TiO₂ nanotubes and the holes move toward the surface to generate proton. CB and VB refer to the energy levels of the conduction and valence band of TiO₂.

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