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Photocatalytic removal organic matter and bacteria simultaneously from real WWTP effluent with power generation concomitantly: Using an Er—Al—ZnO photo-anode

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ABSTRACT

Wastewater treatment plant (WWTP) effluent is one of the most bulk water body that carries organic matters which is promising for energy catching, but it also contains complex un-degradable organic matters with low concentrations. Integration of advanced treatment of Wastewater treatment plant (WWTP) effluent and electricity generation is an attractive method but rarely reported. We innovatively applied a photocatalytic fuel cell (PFC) with a highly efficient Er-Al co-doped ZnO photo-anode to treat the WWTP effluent, which realized simultaneous advanced organic matters removal, bacteria disinfection, and considerable electricity generation. In the constructed visible light-driven PFC system, the chemical oxygen demand (COD) and dissolved organic carbon (DOC) removal efficiencies achieved 69.7% and 53.0%, respectively. The soluble microbial products decreased significantly. Both of the total bacteria cell and *Escherichia coli* (*E. coli*) cell accounts showed a ~99% disinfection efficiency. Advanced electricity generation capability was simultaneously observed, in which the open-circuit voltage, short-current density, and maximum power density were 0.55 V, 9.13 μA cm^{-2} and 1.83 μW cm^{-2}, respectively, with the fill factor as high as 0.36. In summary, the proposed PFC open up more opportunities for WWTP effluent reusing and clean energy generation.

1. Introduction

Domestic, industrial and animal wastewater together was assumed to contain ~1.5 × 10^{11} kilowatt-hour (kWh) of potential energy (~17 GW of power) in the United States alone [1]. Capturing this energy is very attractive as the contradiction between water crisis and energy crisis is more and more serious in nowadays. Microbial fuel cell (MFC) and photocatalytic fuel cell (PFC) are promising technologies to achieve this goal, by using bacteria and metal-oxide-semiconductors basted photocatalyst, respectively, to decompose organic pollutants and produce power simultaneously [2,3].

Wastewater treatment plant (WWTP) effluent is one of the most bulk water body that carries organic matters among all the wastewater. The actual capacity of WWTP sewage was about 21.031 billion tons every year in China. Moreover, the advanced treatment of wastewater for reusing has become very urgent to effectively cope with the current global water shortage [4,5]. Thus, combining advanced treatment of WWTP effluent with energy recovery is very promising. However, organic matters in WWTP effluent are usually very complex but in low concentrations (20–60 mg L^{-1} in chemical oxygen demand) [6]. This so-called effluent organic matter (EfOM) is composed of refractory components, residual degradable substrate, intermediates and soluble microbial products (SMPs) [7]. Most of above components were difficult-to-degrade organic matters, even usually in low concentrations but in high total quantities. They were considered to be very harmful to the aquatic environment and the downstream reusing treatment process [8–11]. The release of EfOM could bring biotoxicity and genotoxicity to the aquatic organisms [10,11]. Yu et. al. [11] indicated that the WWTPs effluent is a significant source of antibiotic resistance genes released into the environment, which is seriously threatening the health of humans and animals. Additionally, SMPs are a major contributor to membrane fouling in membrane bioreactors (MBR) and constrain the application of this promising technology [9]. So far, under the pressure of the strict governmental regulations on WWTP effluent quality, the

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prolonged hydraulic retention time of the biological treatment plant further aggravate the un-degradability of the EfOM [8,12]. In this context, Using MFC is not feasible for advanced treatment of WWTP effluent, because anode respiring bacteria (ARB) are very sensitive to toxic residuals and the electricity generation relies on high organics concentrations [2,13]. Furthermore, MFC is also incapable to remove microorganisms which is normally necessary to be removed before re-using WWTP effluent [14].

In contrast, photocatalytic fuel cells (PFC) are theoretically suitable for further polishing WWTP effluent due to their unselective oxidation for almost all organic substances, easy operation with direct electron transfer processes and flexible working conditions [15]. In a typical PFC process, the valence band (VB) of the photocatalysts is inspired by the light photons, and the photoelectrons are transferred to the conduction band (CB), generating electron-hole pair [16,17]. Then, the photo-generated electrons can be transported to a cathode through an external circuit because of the difference of potential between the photo-anode and cathode and thereby generate current. Besides, the positive holes are strong oxidizer for degradation of organic matters. Therefore, we hypothesized that the PFC could satisfy the simultaneous organic matters removal and disinfection of WWTP effluent with concomitant electricity generation. However, PFC is mostly concerned on specific toxic chemical removal, such as tetracycline hydrochloride and dye [16,18], but rarely used to target real complex wastewater treatment, like EfOM in this present work.

The performance and efficiency of the PFC is mainly determined by the characteristics of the anode, where the positive holes generated. Most existing PFC systems use semiconductors as photo-anodes such as TiO_2, ZnO and WO_3 [3,19,20]. Among these, ZnO photo-anodes have been extensively investigated due to their high photocatalytic activity and chemical stability. Nevertheless, the significant limitation of the ZnO photo-anode is that it could only be driven by UV light (< 387.5 nm), which accounts for less than 3–7% of the sunlight. Accordingly, many studies have been conducted to accomplish the modification of ZnO [21–25]. Among these, co-doping of Er and Al into ZnO could significantly improve its visible light photocatalytic activity according to our previous study [26].

In this work, we addressed whether PFC could achieve simultaneous advanced oxidization for residual DOC and bacterial disinfection of real WWTP effluent with concomitant electricity generation. We successfully constructed a PFC with an Er-Al co-doped ZnO anode and examined the DOC, SMPs and bacteria in the effluent. In addition, we characterized the generation of electricity. To the best our knowledge, this is the first work that a PFC with WWTP effluent as anolyte, and we definitely provide a new and feasible clue for WWTP effluent effectively reclamation and power collection.

2. Experimental

2.1. Preparation of Er-Al co-doped ZnO photo-anode

Er-Al co-doped ZnO nanoparticles were prepared by a hydrothermal process according to our previous report [26]. The Fluorine-doped Tin Oxide (FTO) glass (30 × 40 × 1 mm in length × width × depth) was used as the anode support and cleaned in the ultrasonic bath with acetone, dehydrated alcohol, and ultrapure water in sequence for three times before use. 2.0 g of obtained nanoparticle samples were ultrasonically dispersed into anhydrous ethanol to give a 0.1 g mL^{-1} nanoparticle suspension. The resulted suspension was spin-coated (2000 rpm) onto the FTO by using spin coater (KW-4A, IMECAS, China). The photo-anode was obtained after rinsing with deionized water 3 times and drying at 60 °C.

2.2. Physical characterization

The morphology and elemental compositions of the samples were investigated by a scanning electron microscope (SEM, Quanta 200 ESEM, FEI) equipped with energy dispersive X-ray spectroscopy (EDX, Rigaku). The Transmission Electron Microscopy (TEM) and High-Resolution TEM (HRTEM) for the crystal structure of the prepared nanoparticles were characterized via a Transmission Electron Microscope (200 kV FEI-Tecnai F20, USA). The X-ray diffraction (XRD) patterns of the photocatalyst were obtained with a powder X-ray diffraction (XRD, Bruker D8, Germany) equipped with Cu Kα radiation. The surface chemical bonding states were collected by an X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, America) using an Al Kα (h = 1486.6 eV) radiation excitation source. All of the obtained spectra were calibrated against the C 1s signal at BE = 284.6 eV. The UV−Vis diffuse reflection spectra (DRS) spectrum was acquired from a Shimadzu UV-2500 spectrophotometer.

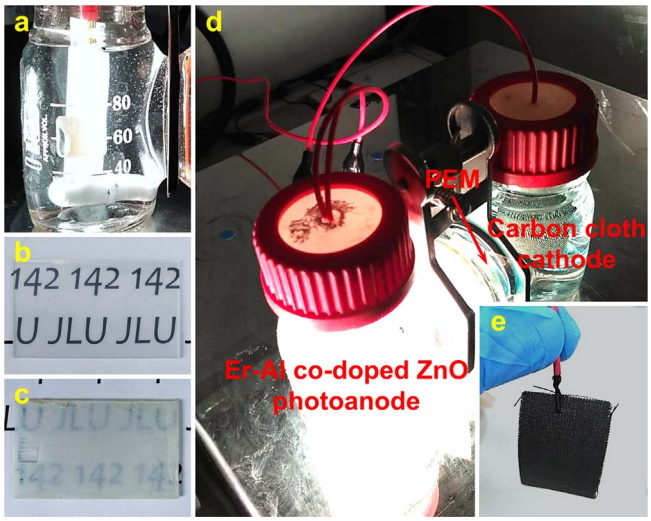

Fig. 1. Layout of the PFC. a, Light delivered Er-Al co-doped ZnO photo-anode. b, Pristine FTO conducting glass. c, Er-Al co-doped ZnO coated anode. d, The assembled PFC. e, Carbon cloth cathode.

2.3. Configuration and operation of PFC

An H-type and double-chamber PFC reactor was used in this study (Fig. 1). A bipolar chamber reactor was used in this study. The prepared photo-anode and cathode (carbon cloth, 3 cm × 4 cm) were connected through an external circuit. A proton exchange membrane (AMI-7001, Membranes International, USA) was mounted between the two chambers. The exposed area of both electrodes was 9 cm^2 and the vessel width between the two electrodes was 10 cm.

In this study, 100 mL of WWTP effluent was used as the anolyte and the same volume of 100 mM Na_2SO_4 was used as the catholyte. The WWTP effluent was collected from a secondary sedimentation tank of a municipal wastewater treatment plant located in Changchun, China. The quality of the effluent was shown in Table S1, and the corresponding analytical methods were given in our previous publication [8]. The anode chamber was stirred using a magnetic stirrer and maintained ~20 °C. For the experiments with photocatalysis, the photo-anode was illuminated by a 126 W LED panel which provided typical visible light characteristics having a wavelength range from 420 to 700 nm (incident light intensity, 43.13 mW cm^{-2}; Hueler, Guangdong, China). This LED lamp illuminates visible light that very similar to the solar light, for both of wavelength and intensity (see detailed description in SI-1). The full spectrum is shown in Fig. S1. The distance between the light source and the photo-anode was 15 cm.

2.4. Photoelectrochemical measurements

All the photoelectrochemical tests were performed in a two-