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In-situ utilization of generated electricity in a photocatalytic fuel cell to enhance pollutant degradation

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ABSTRACT

How to lower recombination of photogenerated electons and holes for efficient pollutant degradation remains a critical challenge for widespread application of photocatalytic fuel cell (PFC). Herein, a PFC based on in-situ utilization of generated electricity for strengthening pollutant removal efficiency was developed. The system was operated in alternate charging and discharging (ACD) mode using a capacitor-based circuit. With the increase of switch time (T_s) from 1 min to 10 min, the rhodamine B (RhB) decolourization rate decreased from 0.05931 min^{-1} to 0.03879 min^{-1} with current densities decreasing from $2.58 \pm 0.08\ A\ m^{-2}$ to $1.86 \pm 0.02\ A\ m^{-2}$, which were 133–223% higher than that obtained in continuous energy harvesting (CEH) mode ($0.80 \pm 0.02\ A\ m^{-2}$). However, the average power densities increased from $22.2 \pm 1.9\ mW\ m^{-2}$ to $110.3 \pm 3.7\ mW\ m^{-2}$, which were lower than that in CEH mode ($154.0 \pm 16.7\ mW\ m^{-2}$). This improvement of current output at the expense of power output was beneficial to minimize the recombination of photogenerated charge carriers and improve RhB decolourization, suggesting the enhancement effect of ACD mode on pollutant degradation compared with CEH mode. This work demonstrates that the electricity produced by PFC could be reused to improve system performance, which also provided a promising avenue of PFC operation for better pollutants removal.

1. Introduction

Photocatalytic fuel cell (PFC) has been widely studied in the past several years and much understanding of its reactor architecture, electrochemistry, and photocatalytic material has been obtained through intensive research [1–3]. PFC is attractive as an integration of photocatalysis and fuel cell technology. This new type of technology could convert energy contained in wastewater organics directly to electricity, especially for those nonbiodegradable substances [4,5]. In a typical PFC system, substrate in the wastewater is oxidized to biodegradable organics by the holes created upon illumination. Photogenerated electrons are transported from photoanode to external circuit and then finally accepted at cathode to form H_2O [6,7]. Thus, PFC overcomes the fuel limitation in traditional fuel cells such as microbial fuel cell and hydrogen fuel cell [8,9], which possesses advantage of wider application fields.

However, high recombination rate between the photogenerated electrons and holes remains as a major obstacle for high-efficiency operation of PFC [10,11]. In respect of decreasing recombination, most of previous efforts have been focused on reducing the affinity between electrons and holes by employing modified photocatalytic material including element doping [12–14] and semiconductors coating [15,16]. Various immobilization methods were also used to enhance the photocatalytic performance of photocatalyst [17,18]. And most of such modifications put emphasis on forming a well Schottky-type contact or creating a unidirectional electrical channel for efficient transport of photogenerated electrons. Apart from the material modification, the recombination rate of electron-hole pairs was also affected by the operational parameters such as fuel types, fuel concentration, electrolyte properties and external circuit design. For example, alkaline electrolyte was more favorable compared with neural or acid aqueous, as OH^- played as efficient hole scavenger, thus preventing electron-hole recombination [7,19]. A small resistor could also be beneficial to high current output and promote the separation of the electrons and holes [20]. Especially, extra electric

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field was applied to improve anode potential to trigger photogenerated electrons to move to electrode surface and minimize the recombination of photogenerated charge carriers [8,21,22]. These previous studies were all healthy attempts to reduce the adverse effect of recombination of electron-hole pairs and increase the electricity output to facilitate substrate degradation. But almost all those PFC systems focused on cell design or required extra energy input, with little consideration given to electricity utilization. Thus, it would be exciting if the seemly useless electricity offers the option of energy self-sufficient enhancement on separation of photogenerated electrons and holes.

Capacitor is an ideal power management device and has been widely used in microbial fuel cell (MFC). Electrical energy produced by MFC was firstly stored in capacitor, and then the energy was discharged to particular load. In this charging and discharging process, capacitor acted as a "metronome" to regulate the quantity and rate of electrical energy generation or export. Liang et al. for the first time, designed a capacitor-based circuit (alternate charging and discharging mode, ACD) to achieve higher electricity generation performance, successfully increasing the average current production by 22% compared with intermittent charging mode in MFC [23]. Dewan et al. reported the 111% increase of power in comparison with the constant energy recovery mode using resistor in MFC [24]. As a specific power conditioning device, ACD circuit has been demonstrated capable of obtaining more current from microbial fuel cell. From a thermodynamic point of view, a large number of free electrons exist inside the semiconductor, if the surface potential of the semiconductor could be sufficiently-sustainable positive, the potential-driven directional photogenerated electrons move from inside to surface of semiconductor would be expected. As a consequence, it could mitigate the problems of electron-hole recombination, in favor of photocatalytic activity.

Herein, we report for the first time the capacitor-based circuit applied in PFC system to lower recombination of photogenerated carriers. The capacitor was firstly charged by PFC and then it performed as a power supply discharging to the PFC itself. During this charging and discharging process, the photocatalytic system switched between PFC mode and PEC mode. The effect of charge and discharge frequency on performance of PFC was investigated. Based on the circuit analysis and energy calculation, the possible mechanisms for the acceleration of RhB decolourization were also discussed.

2. Experimental section

2.1. PFC design and construction

The PFC used in this study consisted of two polymethylmethacrylate compartments, with a liquid volume of 32 mL (anode) and 17 mL (cathode) (Fig. S1). The anodic compartment was equipped with a quartz window to facilitate light transmission. The anode chamber and cathode chamber were separated by a cation exchange membrane (CEM, Ultrex CMI7000, Membrane International) with a cross-sectional area of 7 cm^2. The photoanode was TiO_2 nanotube array in-situ manufactured on titanium mesh (2 × 10 cm, nominal aperture 0.19 mm, wire diameter 0.23 mm, purity >99.6%). It was preconditioned, electrochemically anodized, and annealed before use [25]. The absorption spectrum of prepared TiO_2 photoanode was analyzed using UV–vis spectrophotometer, which showed strong absorption between 250 and 350 nm (Fig. S2). Cathode was made by "rolling-press" method using activated carbon and PTFE [26]. The cathode was clamped by an O-ring from air side to prevent water leakage. In the anodic compartment, 30 mg/L RhB was used as model pollutant dissolved in 0.05 M Na_2SO_4 solution. The anolyte was stirred with a magnetic stirrer to ensure the rapid diffusion of RhB. In the cathodic compartment, 50 mM phosphate buffer solution (PBS) was used as catholyte (pH = 7).

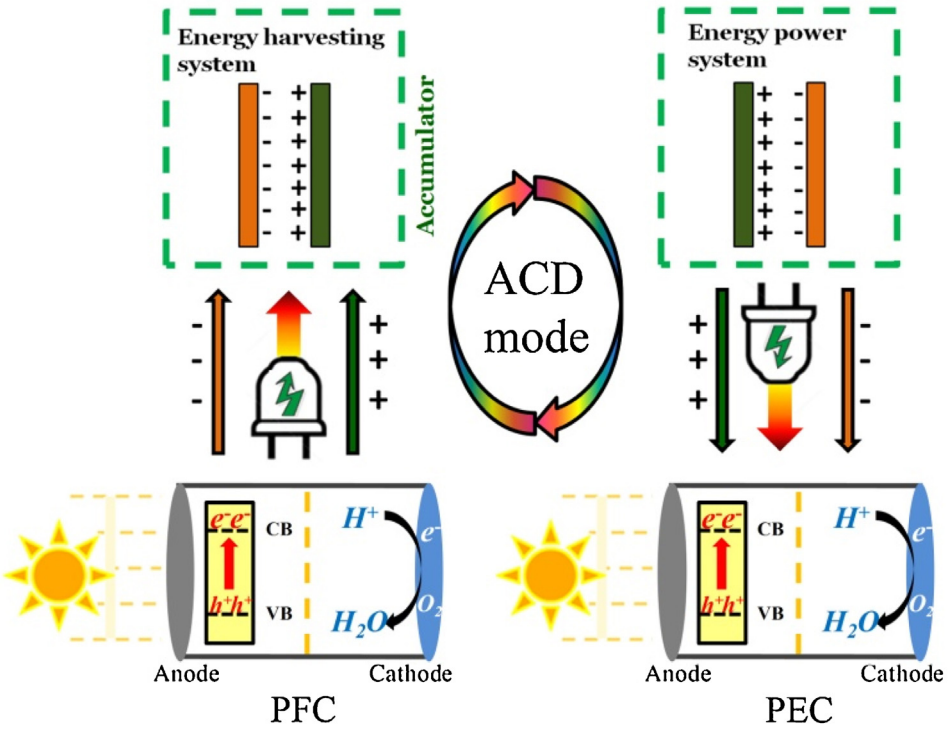

Fig. 1. Schematic diagram of photocatalytic system switching between PFC mode and PEC mode.