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RAPID COMMUNICATION

High performance ethanol/air biofuel cells with both the visible-light driven anode and cathode

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Abstract
A membrane-less ethanol/air biofuel cell (BFC) with both the anode and cathode driven by visible light has been assembled. Simply upon a light source illumination, the BFC generates the maximum power density of 0.27 mW cm^{-2} with an open circuit voltage of 1.13 V, realizing the dual route energy conversion of light energy and chemical energy to electricity, improving the energy utilization efficiency.

Introduction

The oncoming depletion of fossil-fuel has already given rise to the global energy crisis, and sustainable energy has been actively pursued in the last several decades. Biofuel cells (BFCs), a kind of sustainable and renewable energy conversion technology, attract growing attention due to their moderate operation condition, environmentally benign and low expenditure [1-3]. However, the uni-directional energy conversion pathway from chemical energy to electricity hinders the further improvement of BFC performances [4,5]. Solar energy is the most abundant renewable resource available on earth, but the utilization efficiency is less than 1% by activities on earth such as natural photosynthesis [6,7]. To gain more access to such huge amount of energy, tremendous efforts have been devoted to the researches on solar energy extraction, such as photovoltaics [8,9], and photocatalysis[10,11]. Tailoring sunlight harnessing components to BFCs to achieve dual-directional energy conversion (*i.e.* light and chemical energy to electricity) may open exciting new opportunities for BFCs and provide the guidelines for the future multiple routes of energy conversion.

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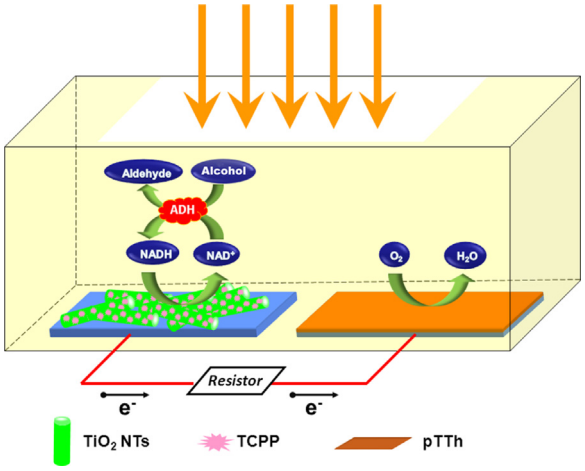
Natural photosynthesis is the most common and effective model for solar energy utilization and mimicking such processes is a fascinating route to improve the conversion efficiency for solar energy [7]. Gust's group has made efforts in the field of photochemical BFCs [12-15]. As early as 2003, they assembled a hybrid BFC with an artificial photosynthetic unit as the photoanode, realizing the coupling of dye-sensitized solar cells with BFCs [12]. After that, they employed [FeFe]-hydrogenase as the cathode catalyst for photochemical H_2 production [14]. In 2012, Willner et al. reported integrated photo-bioelectrochemical cells, generating electrical power during the water-O_2-water recycle without any substrate addition [16]. Very recently, our group developed a visible light enhanced miniature glucose/air BFC employing a photo-responsive cathodic catalyst, representing another proof-of-concept advance in dual-directional energy conversion [17]. Despite the remarkable achievements, these reported BFCs with single photo-responsive electrode are still inadequate for improving light utilization efficiency. Thus, exploring more efficient photon-to-electron approaches for further improvements in energy conversion efficiency has been expected.

Herein, we have assembled a membrane-less ethanol/air BFC composed of both the visible light excited bioanode and cathode, leading to a double enhancement compared to the previous reported BFCs with photo-driven single electrode. Hydrothermal prepared TiO_2 nanotubes (TiO_2 NTs) bearing meso-tetrakis(4-carboxyphenyl)porphyrin (TCPP) act as the substrate to confine alcohol dehydrogenase (ADH) for the visible light driven ethanol oxidation at the bioanode, and electropolymerized 2,2′:5′,2″-terthiophene (TTh) was employed at the cathode for visible light enhanced oxygen reduction (Scheme 1). Compared to the previous studies, large improvements in BFC performances have been achieved, which could be attributed to higher light energy utilization efficiency as well as good electrical contacting of the immobilized enzymes with the electrode surface.



Scheme 1 Schematic presentation of visible-light driven ethanol/air BFC.

Experimental section

Reagents and instruments

TiO_2 powder P25 (Degussa AG, Germany), NaOH and HCl were used to prepare TiO_2 NTs, meso-tetrakis(4-carboxyphenyl)porphyrin was purchased from Aladdin (Shanghai, China), Alcohol Dehydrogenase from *Saccharomyces cerevisiae* (E.C.1.1.1.1, 300 U mg^{-1}) and Nafion (5 wt% in methanol) were obtained from Sigma. NAD^+ and NADH were purchased from Dingguo Reagent Company (Beijing, China). 2,2′:5′,2″-terthiophene (TTh, J&K Scientific Ltd., China) in acetonitrile was used to prepare the cathode catalyst. All other reagents were of analytical grade and used as received. 0.25 M trishydroxylaminomethane (Tris)-HCl buffer solution (pH 8.0) containing 0.1 M KCl was used as the supporting electrolyte. Millipore Milli-Q water was used throughout unless otherwise stated and all of the experiments were carried out at room temperature (22 ± 2 °C).

Morphology and structure characterizations were obtained with a XL30 ESEM field-emission scanning electron microscope (SEM) at an accelerating voltage of 15 kV and a TECNAI G_2 transmission electron microscope (TEM) operating at 200 kV. UV/vis absorption measurements were performed on a Cary 50 UV-vis spectrometer (Varian). X-ray diffraction (XRD) profiles were investigated by a D8 ADVANCE (Germany) with Cu K (λ=1.5406 Å) radiation. A Xe lamp (GE, Japan G4T5) equipped with monochromator and a home-made portable light source (the UV component was filtered) were used as irradiation sources. The light intensity detected at the electrode surface is 30 mW cm^{-2} and 5 mW cm^{-2}, respectively. Electrochemical impedance measurements were conducted on a Zahner Zennium electrochemical workstation (Kronach, Gemany) under an oscillation potential of 5 mV over the frequency range between 0.1 Hz and 1 MHz in the solution of 5 mM $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ containing 0.1 M KCl. Other electrochemical measurements were performed at an electrochemical workstation CHI 832B (Shanghai Chenhua Instrument Corporation, China). Except for the BFC assembly, a conventional three-electrode cell with indium-doped tin oxide (ITO) glass slices as working electrode, Ag/AgCl electrode (saturated KCl) as reference electrode and Platinum wire as counter electrode was used.

Electrode preparation and BFC assembly

TiO_2 NTs were synthesized according to the literature [18] with a little modification: 0.375 g commercial P25 powder was dispersed in 30 mL of 10 M NaOH solution, and then the mixture was transferred into an autoclave reactor and heated at 130 °C for 24 h. The resulted mixture was washed with 0.1 M HCl and distilled water subsequently until the pH of the supernatant reached 7. After that the precipitate was dried at 110 °C and tubular nanostructure was obtained. 20 μL of the as-prepared TiO_2 NTs colloid solution (2 mg/mL in water) was spread onto ITO electrode (scotch tapes were used to control the electrode area) and then calcined at 500 °C in air for 1 h, denoted as TiO_2 NTs electrode. Subsequently, the TiO_2 NTs electrode was immersed into 5 mM TCPP overnight and then rinsed to remove the loose TCPP, denoted as TCPP/TiO_2 NTs electrode. Finally, 10 μL ADH