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# Electricity generation from banana peels in an alkaline fuel cell with a $Cu_2O$-Cu modified activated carbon cathode

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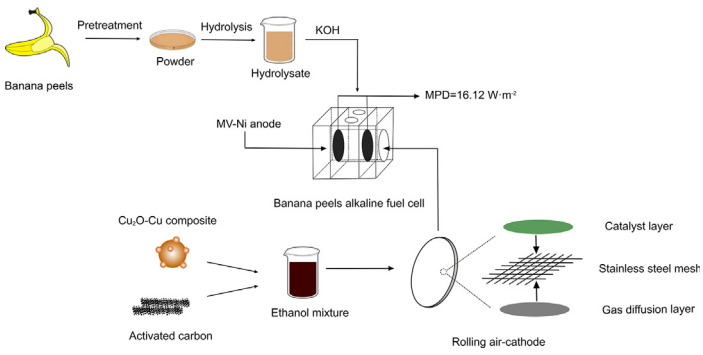
## HIGHLIGHTS

- Chemical energy stored in biomass waste was converted into useful electricity.
- Maximum power density of 16.12 W $m^{-2}$ was achieved under ambient conditions.
- Activated carbon doped with $Cu_2O$-Cu composite was used as air-cathode catalyst.
- Main oxidation products in the alkaline fuel cell were small organic acids.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Low-cost and highly active catalyst for oxygen reduction reaction is of great importance in the design of alkaline fuel cells. In this work, $Cu_2O$-Cu composite catalyst has been fabricated by a facile laser-irradiation method. The addition of $Cu_2O$-Cu composite in activated carbon air-cathode greatly improves the performance of the cathode. Our results indicate the enhanced performance is likely attributed to the synergistic effect of high conductivity of Cu and the catalytic activity of $Cu_2O$ towards the oxygen reduction reaction. Furthermore, an alkaline fuel cell equipped with the composite air-cathode has been built to turn banana peels into electricity. Peak power density of 16.12 W $m^{-2}$ is obtained under the condition of 3 M KOH and 22.04 g $L^{-1}$ reducing sugar, which is higher than other reported low-temperature direct biomass alkaline fuel cells. HPLC results indicate the main oxidation products in the alkaline fuel cell were small organic acids.



## 1. Introduction

Low temperature direct biomass alkaline fuel cells (AFC) have recently received increasing attention for their benign operation conditions and low environmental impacts (Gao et al., 2018; Liu et al., 2018; Zhao et al., 2017). A large number of substrates have been explored as fuel, such as glucose, papaya fruits, algae, and so on (Basu and Basu, 2010; Chen et al., 2012; Provera et al., 2016; Rashid et al., 2013). However, the low power generation still hampers their practical application.

The oxygen reduction reaction (ORR) on the cathode is considered as one of main limiting steps for electricity production in AFCs (Santoro et al., 2017). The strong O═O bond (489 kJ $mol^{-1}$) with very

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sluggish oxygen reduction reaction rate at the alkaline fuel cell cathode needs the use of catalysts (Gewirth and Thorum, 2010). In general, the ORR catalyst materials are Pt or Pt-transition metal alloys. Because of Pt's high cost and low catalytic stability due to poisoning, searching for low-cost non-Pt catalysts for ORR has been a key scientific issue in the development of high performance fuel cells. In the past few years, considerable research effort has been devoted to develop non-precious electrocatalysts (Zhang et al., 2017; Zhao et al., 2015; Zhao et al., 2017). Kruusenberg et al. synthesized Co and Fe phthalocyanine catalyst for a hydrogen oxygen fuel cell using multi-walled carbon nanotubes as support materials (Kruusenberg et al., 2012). Serov et al. developed a chemically reduced Pd/three Dimensions-Graphene nanosheets (3D-GNS) catalyst for the electrochemical oxidation of ethanol and methanol in alkaline media (Serov et al., 2015). Geng et al. conducted a study on nitrogen-doped carbon nanotubes as catalysts for oxygen reduction reaction in both alkaline and acid solutions (Geng et al., 2011). Park et al. used $La_{0.8}Sr_{0.2}MnO_{3+\delta}$ as cathode electrocatalyst in an anion exchange membrane fuel cell (Park et al., 2016). Although these non-noble catalysts exhibited comparable catalytic activity to Pt, their fabrication cost remains high.

Copper is widely used in the electronics industry and its oxide has been considered to be a promising alternative catalyst to Pt (Zhou et al., 2014). The use of copper materials as catalysts in fuel cells has been reported. Priya et al. used CuO microspheres to modify glassy carbon electrode, which exhibited high stability and good catalytic performance in the fuel cells (Priya and Berchmans, 2012). Yan et al. prepared cuprous oxide nanoparticles dispersing on reduced graphene oxide and showed preeminent catalytic ability (Yan et al., 2012). However, more efficient copper based catalyst should be further explored to enhance the practical applications of fuel cell technology.

Banana, a tropical fruit, is an important fruit crop cultivated over 130 countries worldwide. Globally, its product is the second largest amount compared with other fruits. It is characterized by rapid growth and high biomass (Oberoi et al., 2011). The peels of banana represent 30–40% of the total weight of fresh banana. It contains large amount of carbohydrates, proteins, and fibers, and can be converted into glucose, then ferments into ethanol (Emaga et al., 2008; Hammond et al., 1996). However, these materials have long been treated as solid waste and end up in open dumps or drainage systems, which threaten both surface water quality and causes serious environmental and health problems. The open burning of these wastes, spontaneous combustion in landfills and incinerating plants can cause air pollution (Oberoi et al., 2012). Thus, finding an approach for the efficient use of these biomass wastes is of great importance for the sustainable development.

There have been many reports on the efficient use of banana peels. Gebregergs et al. conducted a study to utilize banana peels for the production of bioethanol by using yeast *S. cerevisiae* (Gebregergs et al., 2016). Karthikeyan et al. showed the great potential of using banana peels as substrate for the production of citric acid by *A. niger* (Karthikeyan and Sivakumar, 2010). González-Montelongo et al. extracted a substance that had a high antioxidant capacity to scavenge free radicals from banana peels (Gonzalez-Montelongo et al., 2010). However, the large-scale use of banana peels is still hindered by technical and economic problems.

The aim of this study is to (1) develop a high efficient and low-cost air-cathode for direct biomass AFCs; (2) construct a direct biomass AFC without using of noble metals; and (3) explore the possibilities of turning banana peels into electricity. To the best of our knowledge, this is the first study that using low-power laser to fabricate high-efficient catalyst for AFCs. Furthermore, the direct biomass AFC technology studied in this work can convert chemical energy stored in biomass waste into useful electricity directly, which minimizes the environmental impacts and benefits the sustainable development of whole society.

## 2. Material and methods

### 2.1. Preparation of air-cathodes

The $Cu_2O$-Cu composite catalysts were synthesized using a $CO_2$ laser (3020, Xinbang Co. Ltd., China). In a typical synthesis process, 0.5 g $CuSO_4 \cdot 5H_2O$, 20 mL ethylene glycol, and 10 mL deionized water were mixed together in a cylindrical beaker and kept in a 60 °C water bath for 10 min. Then, 10 mL of NaOH solution (5 M) was added. After 5 min, 10 mL of glucose solution (1.1 M) was dropwise added into the above mixture within 30 s. Then, 30 mL of the mixture was transferred into a petri dish and irradiated under the $CO_2$ laser with 10 mA current. Finally, the $Cu_2O$-Cu composite was collected by centrifugation, washed by ethanol and deionized water, and dried in a vacuum oven at 60 °C.

Activated carbon powder (YEC-8A, 2100 $m^2\ g^{-1}$) was obtained from Yihuan Carbon Co. Ltd (Fuzhou, China). 60 wt% PTFE solution was purchased from Heshen Inc. (Shanghai, China). All the air-cathodes were made by rolling-press method, according to previous studies (Dong et al., 2012; Gao et al., 2018; Liu et al., 2016; Zhao et al., 2017). The air cathode has triple layers: a gas diffusion layer, a catalyst layer and a stainless steel mesh as supporting layer. Typically, the catalysts used in the catalyst layer are the pristine activated carbon (AC) or the $Cu_2O$-Cu modified AC composite. The mass fraction of 0.5%, 1%, 2% and 3% of $Cu_2O$-Cu catalysts were doped into AC with polytetrafluoroethylene (PTFE) as the binder and then subjected to a rolling-press process to form a thin film of 0.35 mm, resulting in four samples that were named as AC-0.5, AC-1, AC-2 and AC-3, respectively. The detail procedure was described in Supplemental information and illustrated in Fig. S1. In addition, the air-cathode which only had pristine AC in the catalyst layer was used as a control. All prepared cathodes were dried in an incubator at 30 °C for 12 h.

### 2.2. Characterization and electrochemical analysis

The morphology and microstructure of the fabricated catalysts were characterized by a scanning electron microscopy (SEM, S-4800, Hitachi) with an acceleration voltage of 20 kV. The energy-dispersive X-ray spectroscope (EDS) of catalyst layer was also measured in order to analyze its elemental composition.

The electrochemical measurements were performed on an electrochemical workstation (CHI 660E, Shanghai, China) by using a three-electrode electrochemical cell in the electrolyte of 3 M KOH. The cathode that had a geometric area of 7 $cm^2$ was used as the working electrode and a platinum sheet (1 $cm^2$) was used as counter electrode. The reference electrode was a mercuric oxide electrode and all potentials were referenced to this reference electrode (Sugano et al., 2014). The linear sweep voltammetry (LSV) of all the cathodes was tested at a scan rate of 1 mV $s^{-1}$ from open circuit potential to −0.45 V. Electrochemical impedance spectroscopy (EIS) of all the cathodes was measured at a frequency range of 100 kHz to 10 mHz with amplitude of 5 mV. Tafel plot was recorded by sweeping from over-potential of 0 mV–100 mV at scan rate of 1 mV $s^{-1}$ to determine the intrinsic current (Li et al., 2016b).

The membrane-less alkaline fuel cell was made from polymethylmethacrylate (PMMA) and a schematic of its structure was shown in Fig. 1. It consists of a Methyl viologen/Activated Carbon/Ni (MV/AC/Ni) anode (Liu et al., 2016), a $Cu_2O$-Cu composite air-cathode and a cylindrical internal chamber (14 mL). The performance of the fuel cell was determined by the polarization curve and power density measurement. To obtain the polarization curve and power density, the external resistance was varied from 9000 Ω to 10 Ω.

### 2.3. Banana peel pretreatment and electricity production

Ripe bananas were purchased from the local store (Tianjin, China) and the banana peels were dried in a vacuum oven at 70 °C for 72 h.