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## Carbon materials derived from waste tires as high-performance anodes in microbial fuel cells

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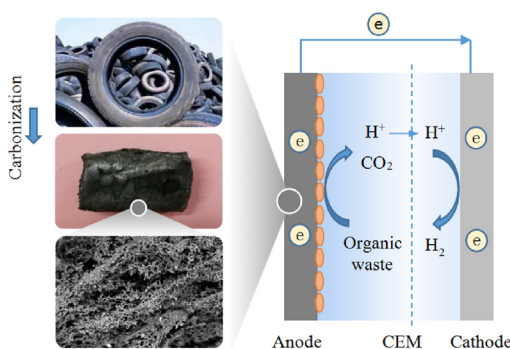
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### HIGHLIGHTS

- A carbonized waste tire anode achieved a high current density ( $24.3 \text{ A m}^{-2}$ ).
- Carbon with a special reticular structure was obtained at  $800 \text{ }^\circ\text{C}$ .
- This method provides an environmentally friendly treatment of common solid wastes.

### GRAPHICAL ABSTRACT



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### ABSTRACT

In this study, carbonized waste tires were directly used as a high-performance anode material in microbial fuel cells (MFCs). The effect of the pyrolysis temperature used for waste tire carbonization on the current output performance was investigated to determine the optimal pyrolysis temperature. Thermal gravimetric analysis/differential scanning calorimetry showed that tire carbonization started at  $200 \text{ }^\circ\text{C}$  and ended at about  $500 \text{ }^\circ\text{C}$ ; the weight loss was about 64%. When used in an MFC, the electrode obtained from waste tires carbonized at  $800 \text{ }^\circ\text{C}$  gave a current density of  $23.1 \pm 1.4 \text{ A m}^{-2}$ , which is much higher than that achieved with traditional graphite felt anodes ( $5.5 \pm 0.1 \text{ A m}^{-2}$ ). The results of this study will be useful in optimizing the design of carbonized waste tire anodes for enhancing MFC performances and will alleviate the environmental problems caused by waste tires.

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### 1. Introduction

In the last few years, with the rapid development of the global economy, the automobile-manufacturing industry has also developed rapidly. The increase in the automotive market is accompanied by increased

production of waste tires. It is estimated that about 1.5 billion rubber tires are produced globally each year and >50% of waste tires are discarded without any treatment (Thomas and Gupta, 2016; Shen et al., 2013). Once discarded, these waste tires are dangerous to the environment and human health. This is because leakage of various chemicals leads to soil pollution and air pollution when waste tires are exposed to sunshine and rainwater (Shu and Huang, 2014; Constantinescu, 2012). At present, the methods for disposal of waste tires are restricted to traditional solid waste treatment methods such

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as direct landfill and burning (Eiras et al., 2014; Bhadra et al., 2003). Landfilling is becoming unacceptable because the availability of waste disposal sites is rapidly decreasing. Direct burning in the open air is also no longer allowed because it is wasteful and violates air pollution regulations (Bhadra et al., 2003). The traditional methods used to treat solid wastes are therefore unsuitable for waste tire treatment.

For economic and environmental reasons, material recycling is desirable. The components of waste tires are rubber (~41%), carbon black (29% to 31%), textiles, antioxidants, and other organic and inorganic substances (Bhadra et al., 2003; Amari et al., 1999). Recently, some methods have been developed for regeneration of carbon black from waste tires. For example, Bhadra et al. (2003) successfully achieved regeneration of carbon black with a high surface area from waste tires. Banar et al. (2015) studied the solid products such as carbon black obtained from tire-derived fuel pyrolysis. However, further multi-step treatment is necessary after pyrolysis to eliminate impurities such as carbonaceous particles, and other inorganic materials and ashes, which could cause severe secondary pollution (Bhadra et al., 2003; Rafat et al., 2004; Alamo-Nole et al., 2011; Abdul-Raouf et al., 2010; Banar et al., 2015). It is therefore necessary to develop economical and environmentally friendly methods to treat and recycle waste tires.

Microbial fuel cells (MFCs) are an emerging bio-energy technology with tremendous potential for capturing energy from organic wastewater using electrochemically active microorganisms as catalysts. The interactions between microorganisms and anode materials are crucial to the anode performance and therefore to the overall power output of an MFC (Logan and Rabaey, 2012; Feng et al., 2016). Over the past few decades, a large number of anode materials have been developed to substantially increase the anode power performance. The canonical examples of efficient microbial bioanode materials are carbon-based anode materials (carbon paper, carbon felt, carbon cloth, and graphite) because they have good electrical conductivity, chemical stability, and strong biocompatibility. However, at present, practical applications of traditional carbon-based materials are limited by high capital costs (25–75 k\$ m<sup>-3</sup>), which represent more than half the costs of the cloth,  $0.6 \pm 0.1 \text{ A m}^{-2}$  (Feng et al., 2016; Karthikeyan et al., 2015; Frackowiak and Béguin, 2001; Ma et al., 2016). The development of low-cost, high-current-output, carbon-rich anode materials from waste tires for use in MFCs would therefore be significant. The aim of this work was to use carbonized waste tires as anode materials in MFCs, not only to avoid the secondary pollution caused by waste tires, but also to provide a new source of anode materials for engineering applications of MFCs.

## 2. Materials and methods

### 2.1. Preparation of carbonized waste tire electrodes (WTEs)

Waste tires (GitiVan 600, China) were bought and used as precursors for preparing electrode materials. The waste tires were cut into cubes of dimensions  $1.2 \times 3 \times 0.5 \text{ cm}^3$  using a large utility knife, cleaned, and dried naturally at room temperature. The cubes were carbonized in a tube furnace for 2 h at 300, 450, 600, 800, and 1000 °C under N<sub>2</sub> at a flow rate of about 300 mL min<sup>-1</sup>. After calcination was complete, a piece of titanium wire was bonded to the carbonized waste tire mass with a conductive epoxy fixative to form electrical connections, and dried naturally at room temperature. The remaining surfaces of the WTEs were covered with a hot-melt adhesive; WTEs with a projecting surface areas of 1 cm<sup>2</sup> are denoted by WTE-300, WTE-450, WTE-600, WTE-800, and WTE-1000, based on the carbonization temperature (Fig. 1).

### 2.2. Characterization

The surface morphologies of the carbonized waste tires were investigated using scanning electron microscopy (SEM; Phenom Pro, the



Fig. 1. Schematic diagram of WTE fabrication process.

Netherlands). X-ray photoelectron spectroscopy (XPS) was used to determine the elemental compositions; the O1s (528–546 eV) and C1s (281–300 eV) peaks were recorded using an Escalab250Xi spectrometer with a monochromatic Al K $\alpha$  source (Thermo, UK). Thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) was performed using a TA Q600 TG/DSC instrument. The weight losses over the temperature range 0–1400 °C were measured in a N<sub>2</sub> atmosphere. The specific surface areas of the samples were determined using a Quadrasorb SI instrument (Quantachrome Instruments, USA). Biofilm samples were tested using a LIVE/DEAD BacLight bacterial viability kit (Molecular Probes) and labeled cells were visualized and z-stacks were captured using a Zeiss LSM 780 confocal laser scanning microscope. Microbial proteins were deposited on electrodes using an ultrasonic cell disrupter (JY92-IIN, China) and a high-speed freezing centrifuge (D-37520 Osterrode, Germany). The amount of biological protein was determined using an ultraviolet spectrophotometer (UV-2600, Japan) by the Coomassie brilliant blue method.

### 2.3. Electrochemical measurements

All electrochemical tests were performed using a three-electrode system (Biologic, France). Cyclic voltammetry (CV) was performed at a scanning rate of 1 mV s<sup>-1</sup> in the potential window –0.7 V to 0.2 V (vs. Ag/AgCl) in fresh anolyte. Electrochemical impedance spectroscopy (EIS) was performed at the open-circuit potential with an amplitude of 10 mV in sterile solution and a frequency range of 200 kHz to 200 mHz.

### 2.4. MFC start-up and operation

A rectangular sealed double-chamber (anode and cathode) reactor with an anion-exchange membrane (AMI-7001, Membranes International, USA) was constructed. The ion-exchange membrane was soaked in 5% NaCl solution for 24 h before use. The effective volume of the anode and cathode chambers of the reactor was 45 mL. The anolyte solution consisted mainly of sodium acetate (1 g L<sup>-1</sup>) and M9 solution (NH<sub>4</sub>Cl, 0.1 g L<sup>-1</sup>; NaCl, 0.5 g L<sup>-1</sup>; KH<sub>2</sub>PO<sub>4</sub>, 4.4 g L<sup>-1</sup>; K<sub>2</sub>HPO<sub>4</sub>, 3.4 g L<sup>-1</sup>; MgSO<sub>4</sub>, 0.1 g L<sup>-1</sup>; NaHCO<sub>3</sub>, 2 g L<sup>-1</sup>) and trace elements (FeSO<sub>4</sub>·7H<sub>2</sub>O, 1.0 mg L<sup>-1</sup>; CuSO<sub>4</sub>·5H<sub>2</sub>O, 0.02 mg L<sup>-1</sup>; H<sub>3</sub>BO<sub>3</sub>, 0.014 mg L<sup>-1</sup>; MnSO<sub>4</sub>·4H<sub>2</sub>O, 0.10 mg L<sup>-1</sup>; ZnSO<sub>4</sub>·7H<sub>2</sub>O, 0.10 mg L<sup>-1</sup>;

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