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# Porous carbon with defined pore size as anode of microbial fuel cell

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ABSTRACT

This paper reported a novel anode material, porous carbon with a defined pore size (DPC) matching bacteria, for microbial fuel cell (MFC). The DPC was prepared by using silica spheres as templates and sucrose as carbon precursor. The structure and morphology of the as-prepared DPC were characterized with X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM), and its performance as anode of MFC based on *Escherichia coli* (*E. coli*) was evaluated with chronoamperometry, cyclic voltammetry (CV) and polarization curve measurement. The result from SEM demonstrates that pores in the as-prepared DPC are well defined with an average diameter of 400 nm, which is a little larger than that of *E. coli*, and the polarization curve measurement shows that the as-prepared DPC exhibits superior performance as anode material loaded on carbon felt, delivering a power output of 1606 mW $m^{-2}$, compared to the 402 mW $m^{-2}$ of naked carbon felt anode, in the solution containing 2 g/L glucose. The excellent performance of the as-prepared DPC is attributed to its suitable pore size for accommodating *E. coli* strain, which facilitates the formation of bacterial biofilm and the electron transfer between bacteria and anode.



## 1. Introduction

Microbial fuel cell (MFC) converts chemical energy into electrical energy by the catalytic activity of microorganisms and has potential applications in many areas including energy recovery from wastewater, marine sediment and human excrement in space (Xie et al., 2011; Oliveirab et al., 2013; Zhang et al., 2014). However, currently available MFCs yield low power outputs and research progress needs to be made for their applications in large scale (Bullen et al., 2006). Anode materials play a vital role in power output because electricity generation in a MFC mainly depends on the biofilm formed on anode (Mekawy et al., 2013). Carbon materials as anodes of MFC have attracted much attention because they are conductive electronically, stable chemically and most importantly low cost (Gutiérrez et al., 2007; Guo et al., 2010; Hutchinson et al., 2011; Higgins et al., 2011; Lanas et al., 2014; Wei et al., 2011). Unfortunately, the biocompatibility of carbon materials cannot meet the requirement of higher power output. During the past decade, many efforts have been devoted to the modification of carbon anode for its biocompatibility improvement (Chen et al., 2011, 2013; Kim et al., 2004; Rabaey et al., 2004; Liu et al., 2008; Cheng and Logan, 2007).

Apparently, the biocompatibility of carbon materials is highly related to their surface nature. It has been known that increasing the specific surface area of carbon materials enhances the power output of MFCs (Logan et al., 2007; Chaudhuri and Lovley, 2003; Lorenzo et al., 2010). Some researchers ascribed this enhanced MFC performance to the oxygen-containing groups on carbon surface, which were believed to be able to adsorb bacteria via the physical contact between carbon and electrolyte (Zhu et al., 2011; Tang et al., 2011; Stams et al., 2006; Crittenden et al., 2006). The carbon surface with oxygen-containing groups is wettable for the electrolyte solution containing bacteria and thus provides the physical contact sites for bacteria. However, this physical contact cannot ensure that a biofilm suitable for electron transfer between bacteria and carbon anode is formed.

An ideal biofilm should be one that can be attached firmly on carbon surface and provide electron transfer paths to anode. In fact, rough anode surface not only provides proper sites to accommodate bacteria but also stimulates bacteria to produce their nanowires (pili) that help bacteria to firmly bond each other and provide the electron transfer bridges (Wang et al., 2014; Cui et al., 2014). Therefore, surface morphology of carbon anode plays a more important role than its oxygen-containing group in the formation of a biofilm that is suitable for electron transfer between bacteria and anode. Several reports have confirmed the significance of carbon anode morphology controlling for the performance improvement of MFC. Carbon brush anode based MFC

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yielded a power density of 1430 mW $m^{-2}$ due to its open structure which not only immobilized the microbe but also avoid biofouling (Logan et al., 2007). A sponge anode, owing to its open three-dimensional (3D) structure, facilitated microbial colonization and attachment and provided MFC with a power density of 1240 mW $m^{-2}$ (Xie et al., 2012). Reticulated carbon foam established a robust microbial film through its open-pore and exhibited an enhanced power density (Lepage et al., 2012). All the anodic carbons in these reports are porous but the pore size is not defined. It is reasonable to assume that the carbon anodes will provide MFC with better performance if the carbon has uniform pores with their sizes suitable for microbial colonization.

With this assumption, we prepared porous carbon with defined pore size (DPC) by using silica spheres as templates. The performance of the as-prepared DPC as anode of a MFC was evaluated with *Escherichia coli* (*E. coli*), an easily available exoelectrogenic bacterium (Qiao et al., 2008; Zhang et al., 2007). The pore size of the DPC was designed a little larger than that of *E. coli* to provide suitable accommodation for the colonization of *E. coli*.

## 2. Experimental

### 2.1. DPC preparation

DPC was prepared by using $SiO_2$ spheres as templates. $SiO_2$ templates were synthesized by hydrolyzing tetraethoxyorthosilicate (TEOS) (Bogush et al., 1988). TEOS was dissolved in ethanol and performed hydrolyzing by adding aqueous ammonium hydroxide solution for forming $SiO_2$. The resulting $SiO_2$ was transferred into an aqueous $H_2SO_4$ solution containing sucrose. The mixture was heated for 6 h at 100 °C and another 6 h at 160 °C in air. Then, the residue was carbonized at 850 °C for 2 h in $N_2$. Finally, the DPC was obtained by etching the $SiO_2$ templates with 10% HF (Lei et al., 2001). The particle size of DPC duplicated that of the template, which was controlled by changing the proportion of TEOS, ethanol and aqueous ammonium hydroxide.

### 2.2. Materials characterization

The X-ray diffraction (XRD) pattern was obtained on a D8 Advance X-ray diffractometer using Cu Kα radiation. The infrared spectrum was collected by Fourier transform infrared spectroscope (BRUKER TENSOR27). The scanning electron microscopy (SEM) images were obtained by field-emission-type scanning electron microscopy (ZESISS ULTRA 55). The specific

surface area of the materials was determined using Brunauer–Emmett–Teller (BET) method on the Carlo Erba Sorptometer, in which $N_2$ adsorption at 77 K was applied.

### 2.3. Bacterial culture

Luria-Bertani medium, containing 10 g peptone, 5 g yeast extract and 10 g sodium chloride per liter, was used to cultivate *E. coli* (DH5$\alpha$). The cultivation was performed aerobically at 37 °C for 12 h and then the cultivated *E. coli* was suspended in phosphate-buffered basal medium (PBBM) with 2 g/L glucose (Wang et al., 2013). For a comparison, 2 g/L starch or sucrose was also used as the substrate.

### 2.4. Electrode preparation and MFC assembly

The working electrode was prepared by pasting the DPC dispersed in 1 wt% poly (tetrafluoroethylene) solution on carbon felt (3.0 cm × 3.0 cm). For a comparison, the naked carbon felt without loading DPC was also used as the working electrode. MFC was assembled with the working electrode as anode and a membrane cathode assembly (MCA) that was prepared by using platinum as catalyst as our previous report (Zeng et al., 2011). The anode chamber was made of polymethyl methacrylate with its size of 5.0 cm × 4.0 cm × 5.0 cm. Anodic solution was PBBM with 2 g/L glucose as electron donor unless specified. To initiate the MFC experiment, 10 mL cell suspension in a constant temperature incubator (HPG-280H, China) at 37 °C was inoculated in anode chamber.

### 2.5. Electrochemical measurements

Electrochemical measurements were carried out on Solartron 1480. Polarization curves were obtained by linear sweep voltammetry (scan rate 1 mV $s^{-1}$) from the open circuit potential to 0 V. Before the measurement, the cell was kept quiescent for three days until a constant voltage output was achieved. Power density was calculated according to $P=IU/A$, in which $I$ is the current, $U$ is the voltage between the working electrode and air cathode and $A$ is the apparent area of the working electrode (9.0 $cm^2$). The chronoamperometry and cyclic voltammetry were performed with the air cathode as the counter electrode and Ag/AgCl (saturated with KCl) as the reference electrode. Cyclic voltammetry was also used to determine if the dead biofilm contributed to the electron transfer. The electrode was first inoculated with the *E. coli* cell for 48 h for the formation of biofilm, then sterilized under ultraviolet lamp for 30 min and performed with cyclic voltammetry in the fresh phosphate-buffered basal medium (PBBM) with 2 g/L glucose.

## 3. Results and discussion

### 3.1. Physical characterization of DPC

The morphology of the template and the resulting DPC was observed by SEM. The obtained results are presented in Fig. 1. Fig. 1$A_1$ and $A_2$ shows the SEM images of $SiO_2$ templates. It can be seen that $SiO_2$ particles are spherical with uniform diameter of about 400 nm. As shown in Fig. 1$B_1$ and $B_2$, porous carbon with uniform pore size, which is well-defined by the $SiO_2$ templates, has successfully been obtained.

XRD was used to confirm the accomplished conversion of sucrose precursor to carbon and the complete removal of $SiO_2$ template. Fig. 2A presents the XRD pattern of the resulting DPC, Two broad diffraction peaks are observed at 22° and 44°, which are corresponding to the (002) and (100) reflections of carbon, respectively, and characteristic of single-layer carbon sheets that are not stacked in a parallel fashion (Yi et al., 2011; Lee et al., 2005; Wang et al., 2003). No impurity phase is observed, indicating that the precursor has been converted into carbon and the template has been removed completely.

FTIR was used to identify the surface oxygen-containing group on DPC. Fig. 2B shows the FTIR spectra of the resulting DPC. The band centered at 1140 $cm^{-1}$ is assigned to the stretching mode of C–O groups (Liu et al., 2010; Vinu et al., 2007; Bahr et al., 2001) and the vibrational band at 3468 $cm^{-1}$ corresponds to the stretching vibration of O–H in water molecules (Yi et al., 2011), which are attributed to the adsorbed water. The peak at around 1600 $cm^{-1}$ is associated with a stretching vibrations of aromatics (C=C) (Yue et al., 1999; Tian et al., 2008), which results from the single-layer carbon sheets. A trace of C=O groups in aldehyde, ketone or lactone could not be found in this spectra, suggesting that few oxygen-containing groups exists on the surface of the resulting DPC.