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In-situ modified carbon cloth with polyaniline/graphene as anode to enhance performance of microbial fuel cell

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ABSTRACT

The microbial fuel cell (MFC) technology has potential in recovering bioelectricity from different types of waste. However, the low power density, closely associated with anode performance, limits its practical application. In this study, polyaniline (PANI) together with graphene was chosen to in-situ modify oxidized carbon cloth (CC) by the aid of secondary bond forces (such as π–π stacking, hydrogen bonds and electrostatic forces). The MFC reactor with PANI/graphene modified CC (PANI+G+CC) anode achieved the highest voltage with 573 ± 37 mV, and produced a peak power density of 884 ± 96 mW/m^2, which was 1.3 and 1.9 times of those with the CC control. Based on cyclic voltammetry (CV) scanning and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) spectra, it was speculated that the weakly acidic microenvironment derived from bio-anode delayed or impeded the deprotonation of PANI and made PANI hold a certain level of conductivity for electron transfer. This study provided a simple and environment-friendly modifying method to enable the prepared PANI+G+CC anode to dramatically promote the performance of MFC.

Introduction

Microbial fuel cell (MFC), being able to directly convert biomass to bioelectricity, has become a research hotspot in recent years. Exoelectrogens are prone to decomposing substrate and directly or indirectly transferring the released electrons towards the anode. The electrons are further transferred to the cathode via the external circuit, wherein ultimately combine with H^+ and electron acceptor (such as O_2) to form water [1–3]. Increasingly more attention has been paid to MFC in the background of energy crisis and huge environmental pressure [4,5]. At present, the low bioelectricity generation is one of the main bottlenecks limiting the practical application of MFC. The anode can directly affect microbial

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attachment and electron transfer, and then further influence electrogenesis [6]. The efficient anode is highly desired.

Polyaniline (PANI), with conductivity, safe environment, low cost and ease of synthesis, has been studied in MFC as the anode modifier. It can switch from an insulator to a conductor by protonic acid doping [7]. Moreover, PANI carries positive charges in neutral environment, and is attractive to adhesion growth of negatively charged bacteria. Graphene is a kind of carbonaceous material possessing the stable chemical properties, anticorrosion, good conductivity and huge specific surface area, which also has been extensively applied in MFC electrode modification [8]. However, PANI presents smaller specific surface area and reluctant conductivity and graphene possesses poor biocompatibility, which resultantly influence the bacterial loading capacity and extracellular electron transfer (EET) efficiency. So, the combined modification by PANI and graphene would make best use of their advantages and bypass shortcomings above, and may be more suitable to serve as the MFC anode. The previous researches about modified anode with PANI and/or graphene in MFC system were summarized in Table 1. The MFC reactor with carbon cloth (CC) anode modified firstly by electrochemically reducing graphene oxide and then coating PANI nano-fibers outputted the maximum power density (P_{max}) of 1390 mW/m^2 [9]. Zhao et al. fabricated a novel MFC anode by electrodepositing PANI networks onto graphene nanoribbons-coated carbon paper (CP/GNRs/PANI), and the maximum power density in MFC reactor equipped with the CP/GNRs/PANI anode was 856 mW/m^2 [10]. Kumar et al. fabricated the graphene/PANI/Pt modified CC as anode of MFC via spray technique by the aid of 1 wt% polytetrafluoroethylene (PTFE) solution, generating the maximum power density of 2059 mW/m^2 [11]. It was worth noting that the higher power densities above-mentioned were produced with ferricyanide served as electron acceptor in cathode chamber. Further, the modification methods above brought about complex procedures, such as needing organic solvent, binder, or electrochemical facilities.

In this study, some secondary bond forces (such as electrostatic forces, π–π stacking and hydrogen bonds) were utilized to in-situ modify CC with PANI/graphene. Before modification, CC was soaked in 6 mol/L nitric acid for obtaining oxygen-containing groups (such as COOH, C–OH, C=O and C–O–C) [12] to form hydrogen bonds with graphene. Graphene was prepared by redox method and usually contained a few oxygen-containing groups due to incomplete redox [13]. In graphene aqueous solution, there would be a tendency of hydrophobic graphene keeping close to the oxidized CC with nitric acid [14]. When keeping close enough, the CC and graphene would be combined to form graphene modified CC (G+CC) via hydrogen bonds as well as π–π stacking, without the aid of binder or electrochemical method [15]. Then, the G+CC was soaked in aniline monomer solution, and PANI was polymerized on the surface of G+CC when added ammonium persulfate (APS) to obtain PANI/graphene modified CC (PANI+G+CC). The adhesion between PANI and graphene was powerful due to there existing various forces (such as π–π stacking, hydrogen bonds and electrostatic attraction) [16,17]. This modification procedure was characterized by simplicity, ease of operation and friendly environment. Furthermore, the PANI+G+CC anode overmatched the controls in power output, without the need to obtain graphene nanosheets via vacuum desiccation, and free of organic solvent and complex electrochemical apparatus [9–11].

Experimental

Preparation of modified anodes

Before modification, the non-watertight CC (thickness of 0.34 mm, HCP330N, Shanghai Hesen Electric Co., Ltd, China) was soaked in acetone and 1 mol/L HCl solution in turn for 12 h to remove impurities, rinsed with deionized water to neutral, and dried at 60 °C for 12 h. Then, the clean CC was oxidized in 6 mol/L nitric acid at 30 °C for 4 h to obtain oxygen-containing groups [12]. The atomic percentage of oxygen in the oxidized CC by nitric acid reached 3.23% based on the spectra of an energy dispersive X-ray (EDX, Genesis Apollo X/XL, EDAX) (Fig. S1), compared with the pristine CC (1.99%), which indicated that more oxygen-containing groups were introduced into the carbon backbone of CC due to nitric acid oxidation. The spectra of an attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet iS10, Thermo Fisher Scientific spectrophotometer) further demonstrated that some oxygen-containing groups joined into the carbon backbone of CC (Fig. S2). Next, the oxidized CC was immersed into 0.1 mol/L aniline monomer solution (prepared using 1 mol/L HCl) for 6 h till full infiltration, and then dripped with 25 mL pre-cooled 0.4 mol/L APS (prepared using 1 mol/L HCl) at ice-cooled and magnetic stirring conditions (400 r/m), wherein the polymerized PANI would tightly bonded with the oxidized CC by the aid of hydrogen bonds and π–π stacking [19,22]. Six hours later, the oxidized CC with PANI (PANI+CC, green in color) was taken out, rinsed by 1 mol/L HCl solution and deionized water in turn, and air-dried.

For the preparation of G+CC, the aqueous dispersion of graphene was prepared by the method described by Marcano et al. [38]. The oxidized CC was immersed into graphene aqueous solution (2 g/L) for 6 h with stirring (400 r/m) to obtain the G+CC via hydrogen bonds and π–π stacking. For the fabrication of PANI+G+CC, firstly the G+CC was prepared according to the procedure above-mentioned, and then the following process was the same as the PANI+CC.

Setup and operation of MFC reactors

Air–cathode single chamber MFC reactors with an internal volume of 28 mL were used in this study as previously reported [39]. The cathodes were made by applying platinum (7 cm^2, 0.5 mg/cm^2 Pt, Hispec3000, Shanghai Hesen Electric Co., Ltd, China) and four diffusion layers (polytetrafluoroethylene, PTFE) on a 30 wt% wet-proofed CC (thickness of 0.40 mm, HCP330P, Shanghai Hesen Electric Co., Ltd, China) [40]. The MFC reactors were inoculated with effluent from the existing well-running MFC (originally seeded with Taihu Lake sediment, China) and culture medium solution at a ratio of 1:1. The culture medium solution contained 1 g/L NaAc, 2.77 g/L $NaH_2PO_4 \cdot 2H_2O$, 11.40 g/L $Na_2HPO_4 \cdot 12H_2O$, 0.31 g/L NH_4Cl,