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Polydopamine as a new modification material to accelerate startup and promote anode performance in microbial fuel cells

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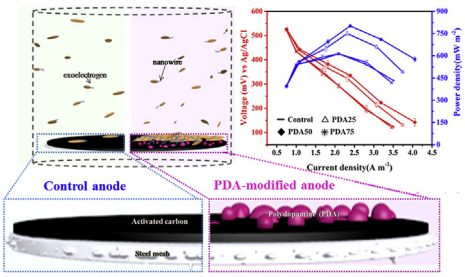
HIGHLIGHTS

- Polydopamine (PDA) modification accelerates the startup of MFC anode.
- 50% PDA content in the anode increases MFC power density by 31%.
- The Coulombic efficiencies also increased from 19% to 48%.
- The increase can be attributed to the abundant functional groups introduced by PDA.
- The superhydrophilic PDA imposed selective pressure on anode microbial community.

GRAPHICAL ABSTRACT



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ABSTRACT

The bacterial anode material is important to the performance of microbial fuel cells (MFCs) because its characteristics affect the biofilm formation and extracellular electron transfer. Here we find that a superhydrophilic semiconductor, polydopamine (PDA), is an effective modification material for the anode to accelerate startup and improve power density. When the activated carbon anode is added with 50% (wt.) PDA, the startup time is 14% shorter than the control (from 88 h to 76 h), with a 31% increase in maximum power density from 613 ± 9 to 803 ± 6 mW m^{-2}, and the Columbic efficiency increases from 19% to 48%. These can be primarily attributed to the abundant functional groups (such as amino group, and catechol functions) introduced by PDA that improve hydrophilicity and extracellular electron transfer. PDA also increases proportions of *Proteobacteria* and *Firmicutes* families, indicating that PDA has a selective effect on anode microbial community. Our findings provide a new approach to accelerate anode biofilm formation and enhance MFC power output by modification of biocompatible PDA.

1. Introduction

Microbial fuel cell (MFC) is a green technology using electroactive microbes as catalysts to degrade organic/inorganic pollutants in wastewater, where chemical energy is directly converted to electrical energy [1–3]. It has been widely recognized that the interface between electrochemically active biofilm and the anode is vital to MFC performance [4–6]. A high performance anode material should be stable, easy for biofilm attachment, and highly conductive to facilitate electron transfer from microbes to the anode. Taking all of these requirements as well as the cost into consideration, the most commonly used anodes are made of carbon

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(carbon fiber brush, carbon cloth, carbon paper and graphite plates etc.) [7]. Among them, activated carbon is widely used as MFC anode material due to its high surface area, relatively good conductivity and low cost. In order to further improve the anode performance, surface modification technologies, such as doping [2], coating [8] and surface functionalization [9] were applied. Modification with hydrophilic (contact angle less than 90°) materials has been demonstrated to enhance bacterial affinity [10], and thus to promote power output. For instance, Chen et al. coated carbon tubes with polyvinyl alcohol, and gained a 98% greater power density of 1.631 W m^{-2} than that with PTFE modification (0.824 W m^{-2}) [11]. Another work showed that CTAB-treated felt anodes produced 23.8% higher current than carbon felt [12]. However, for the future application of modified anode in complex wastewater, the modification material should be bacterial friendly and chemically stable with strong adhesive force to the carbon matrix.

In recent years, polydopamine (PDA), an environmental-friendly material, has attracted explosive attention as an easily modification material with superhydrophilicity (water contact angle less than 5°) [13], and has been successfully applied to diverse surfaces (including nanoparticles [14,15], polymers [16], bioactive macromolecules [17,18] and even functional living cells [19]). The PDA has excellent adhesive force to various substances, efficiently selective to bacteria and more conducive for biofilm formation [20] due to its rich functional groups (amino group, catechol or quinone functions, carboxylic acid group, planar indole units, and indolic/catecholic π -systems) [21]. It is a major pigment of naturally occurring melanin (eumelanin) with outstanding biocompatibility and good stability (swelling only slightly when being subjected to PBS for 30 days) [22], which has a potential advantage over those artificial polymers as a new modification material for the anode. However, so far as we know, there is no literature on the performance of PDA modified anode in MFCs.

Here PDA was proposed as an anode modifying material to improve MFC performance because PDA is superhydrophilic with abundant functional groups on its surface. Activated carbon (AC) was used as the host matrix, and PDA was added to the host with contents of 25 wt%, 50 wt% and 75 wt%. Current and power productions of these anodes were evaluated compared to an unmodified control. Physical characteristics (hydrophilicity and texture), electrochemical capacitance and bacterial community of PDA modified anodes were also discussed.

2. Experimental

2.1. Electrode preparation

Dopamine hydrochloride (98%, Sigma-Aldrich, Germany) was dissolved in deionized water, and then mixed with ammonia aqueous solution and ethanol for PDA formation [23]. A detailed manufacturing process was described in Supporting Information.

Anodes with PDA contents of 25%, 50% and 75% (wt.) and the unmodified control were prepared according to following procedures. The control was manufactured by mixing 6 g AC with 250 μL of 60% polytetrafluoroethylene (PTFE) and 45 mL ethanol. The mixture was stirred in 80 °C water bath to get a dough-like paste. It was then roll-pressed to a stainless steel mesh (4 cm × 4 cm, Type 304 N, 60 meshes, Detiannuo Commercial Trade Co. Ltd., Tianjin, China) according to our previous method [2]. PDA modified anodes were made following the same procedure except that PDA was individually added to AC powder for final contents of 25%, 50% and 75% (wt.), denoted as PDA25, PDA50 and PDA75, respectively (Fig. 1a).

Air-cathodes were made using rolling-press method as previously described [2,24]. The catalyst layer was made of AC and PTFE with a mass ratio of 6:1, and the diffusion layer was made of carbon black and PTFE with a mass ratio of 3:7. Catalyst layer was roll-press into the SSM, and then the diffusion layer was rolled to the opposite side to reach a final thickness of 1 mm [25].

2.2. MFC construction and operation

Different anodes and same air-cathodes were assembled to cylindrical chambers (4 cm in length and 3 cm in diameter, net volume 28 mL) as MFC reactors, and all MFCs were operated in batch mode under 25 ± 2 °C in an incubator. Two parallel reactors were operated for each sample as duplicate tests. The external resistance was 1000 Ω except as noted. Wastewater collected from the primary sedimentation tank in a municipal wastewater treatment plant was amended with the equal volume of 50 mM phosphate buffer solution (NH_4Cl 0.31 g L^{-1}, KCl 0.13 g L^{-1}, NaH_2PO_4 2.452 g L^{-1}, Na_2HPO_4 4.576 g L^{-1}) containing 12.5 mL L^{-1} trace minerals, 5 mL L^{-1} vitamins and 1 g L^{-1} acetate as the inoculums [26]. Wastewater was removed from the medium when the maximum voltage was higher than 500 mV. The medium was refreshed when the cell voltage was lower than 50 mV, forming a complete cycle.

2.3. Electrochemical and chemical analysis

Cell voltages were recorded every 30 min with a programmed data acquisition system (PISO-813, ICP DAS Co., Ltd., China). Polarization curve was measured by varying external resistance from 1000 to 50 Ω with a 30 min of time interval when repeatable voltages were obtained in all MFCs. Error bars (±SD, standard deviation) were calculated based on measurements in duplicate reactors. Both anode and cathode potentials were recorded using Ag/AgCl as the reference electrode (+197 mV, 3.5 M KCl, versus the standard hydrogen electrode).

Coulomb efficiency (CE) was calculated according to equation (1):

$$CE = \frac{8\int_0^{t_b} Idt}{FV\Delta COD} \times 100\% \quad (1)$$

where I is the current (A) over time (s), V is the volume (mL) of the MFC, F represents Faraday's constant (96,485 C mol^{-1}).

2.4. Characterization of anode material and biofilm

Scanning electron microscopy (SEM, Shimadzu SS-550, and Japan) was employed for observation of surface morphologies. Hydrophilicity of each anode was tested using a contact angle system (JC2000C, Powereach, Shanghai, China). 10 μL deionized water was dropped on each anode, and the morphology of the water droplet was recorded at the momentary contact for hydrophilic material. The balance of cohesive and adhesive forces between the solid surface and the liquid drop were calculated according to equation (2) [27]:

$$\gamma^{sv} = \gamma^{sl} + \gamma^{lv}\cos\theta \quad (2)$$

where γ^{sv}, γ^{sl} and γ^{lv} represent the solid-vapor, soild-liquid and liquid-vapor interfacial surface tension, respectively. θ is the momentary contact angle (0° - 180°).

The elemental composition and functional groups of the synthesized PDA were analyzed using an X-ray photoelectron spectroscopy (XPS; PHI 5700 ESCA System, Physical Electronics, USA)