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Inkjet-printed porous polyaniline gel as an efficient anode for microbial fuel cells

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Abstract: Future application of microbial fuel cells (MFCs) requires a high-throughput and more convenient pathway to manufacture high-performance anodes. In this research, inkjet-printed PANI gel on carbon paper was first fabricated and was successfully employed as anodes in MFCs. Thanks to the inkjet-printing technology, such anodes can be easily produced in large quantities. Moreover, these anodes possessed good conductivity and a porous structure as well as the ability to electrostatically interact with bacteria cells, which contributed to a 6.1-fold increase in the output power than that of the unmodified carbon paper. Taken together, our study presented a novel strategy in preparing highly scalable, high-performance MFC anodes, in promoting the practical application of MFC technology.

As an integrated technology to address energy generation and environmental bioremediation simultaneously, microbial fuel cells (MFCs) have drawn much attention in recent years.¹⁻⁴ In MFCs, exoelectrogens are harnessed for highly effective energy conversion of organic wastes into electricity.⁵⁻¹⁰ The electron transportation from exoelectrogens to electrode usually relies on three distinct extracellular electron transfer (EET) mechanisms, including outer membrane redox-active proteins or conductive pili mediated direct electron transfer, and electron-shuttle molecules mediated indirect electron

transfer.¹¹⁻¹⁸ Although the potential of MFCs as a novel wastewater treatment technology, green energy sources or BOD (biological oxygen demand) biosensors has been demonstrated,¹⁹⁻²¹ the practical application of these potentials is heavily limited by their relatively low power density. Thus, exploring new alternative solutions in addressing the aforementioned problem is highly desirable.

MFC anodes that display a great impact on bacterial EET, bacterial adhesion and substrate oxidation, have been considered as a key factor to strongly affect the performance of MFCs.²²⁻²⁴ However, the traditional MFC anode materials such as carbon cloth and graphite rod suffer from poor bacterial loading and low EET efficiency.²⁵⁻²⁶ Therefore, developing more advanced nanostructured anodes through the modification of existing carbon materials to enhance the performance of MFCs is now the main focus.²⁷⁻³³ Among various nanostructured modifiers, polyaniline (PANI) has become an important coating layer of the active electrode owing to its good electrical conductivity, facile processability, excellent chemical stability and biocompatibility.³⁴⁻³⁵ For instance, an enhanced bacterial adhesion has been found after the modification of carbon felt with PANI, leading to a 35% increase of output power.³⁶ Vertically-aligned PANI nanowire array (PANI-NA) has been employed as a solid-state polymeric mediator to facilitate the EET of *Shewanella Loichica* PV-4, which exhibited a 25-fold growth in the EET current.³⁷ Moreover, Schroder et al. used PANI to preserve the platinum electrode from being poisoned to improve the microbial current of *Escherichia coli* K12 by one order of magnitude.³⁸ Unfortunately, all the above-mentioned studies have to use electrodeposition, dip-coating or paste methods to coat PANI onto the surface of electrodes. These technologies make them very difficult to manufacture the modified electrodes in a large scale and to realize the future industrialization of MFCs as a viable technology.

Inkjet printing (IJP) is a high-throughput technique that has already been demonstrated to accurately and rapidly place inks onto various substrates with any desired patterns, and has gained wide recognition in a variety of fields such as

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electronics, sensors and optics.³⁹⁻⁴³ Such an excellent method should find its position in fabricating electrodes of MFCs for practical applications. Herein, we first present the inkjet printing of porous PANI gel onto carbon papers (inkjet-printed PANI/CP) for anode application in MFCs. A representational bacterium, *Shewanella oneidensis* MR-1 (*S. oneidensis* MR-1), was selected to decompose organic substrates, while simultaneously producing electrons. The inkjet-printed PANI/CP electrode has been demonstrated to show a 6.1-fold growth in the power density over that of the unmodified carbon paper electrode due to its extended active surface area, good electrical conductivity as well as the electrostatically interaction for bacterial loading. Considering its high-throughput production, highly scalable size, facile fabrication process and good electricity generation capability, the inkjet-printed PANI/CP electrode should have the great potential to push MFCs into practical applications.

Fig. 1 a) Photograph of the inkjet-printed PANI on CP; SEM images of the inkjet-printed PANI/CP (b) and the unmodified carbon paper; d) FTIR spectrum of the inkjet-printed PANI/CP. The insets are the corresponding images in high magnification.

Since the poor solubility and high viscosity of PANI solution would cause the nozzle clogging, the inkjet-printed PANI/CP was obtained by sequentially depositing two precursor inks onto the carbon paper. Briefly, we first printed ink A that contained the oxidative initiator onto the carbon paper. Subsequently, a second ink containing the aniline monomer and the phytic acid gelator was printed onto the same region where ink A was deposited. During the polymerization process, the phytic acid with six phosphate groups in molecular structure simultaneously protonated the nitrogen groups on different PANI chains and crosslinked the PANI chains to form a hydrogel network.⁴⁴ After dialysis with ultrapure water, the inkjet-printed PANI/CP was dried by a freeze-drying method to prevent the network from collapse. It is worthy to note that the formation of PANI network was completed in approximately 3 min. Such fast fabrication process makes the PANI/CP more suitable for scalable industrial manufacture.

The photograph of inkjet-printed PANI/CP after drying was shown in Fig. 1a and a well-arranged PANI gel dot array could be clearly seen to be deposited onto the surface of carbon

paper. The diameter of these as-printed dots was about 1 mm. The morphology of these printed regions was further investigated by scanning electron microscope (SEM). As shown in Fig. 1b, the printed PANI presented a porous, mesh-like network with continuous pores ranging from several nanometers to micrometers. This unique porous network would provide a large surface area for collecting electrons from the exoelectrogens. Unlike the porous structure of the printed PANI/CP, the unmodified carbon paper only displayed a few carbon fibers (Fig. 1c), which further confirmed that the PANI gel had been successfully deposited onto the surface of carbon paper. To better understand the chemical structure of phytic acid-doped PANI, the FTIR spectrum of the inkjet-printed PANI/CP was measured (Fig. 1d). The peak located at 798 cm⁻¹ could be assigned to N-H out-of-plane bending absorption. The peaks at 1570 cm⁻¹ and 1140 cm⁻¹ attributed to the stretching and bending vibration of the quinoid ring, while the peaks at 1480 cm⁻¹ and 1300 cm⁻¹ corresponded to the benzenoid ring.⁴⁵⁻⁴⁶ Notably, the relatively same intensities at the absorption bands of 1570 cm⁻¹ and 1480 cm⁻¹ suggested that the as-printed PANI on carbon paper was in the form of emeraldine salt, which had superior conductivity.⁴⁷

Fig. 2 The Nyquist curves of carbon paper and inkjet-printed PANI/CP in 2 mM [Fe(CN)₆]^{3-/4-} and 0.1 M KCl solution. Inset: higher-magnification view.

As reported previously, PANI could efficiently enhance the EET efficiency between electrodes and bacterial cells due to its good electro-conductivity.^{37, 48-49} To further confirm this, the electrochemical behaviors of carbon paper and inkjet-printed PANI/CP were investigated by the electrochemical impedance spectroscopy (EIS). The Nyquist plots for these two tested electrodes were shown in Fig. 2, and both displayed a semicircle in the high-frequency region and a straight line in low-frequency region. According to the estimate of the semicircle diameter, the charge-transfer resistance (R_{ct}) for the inkjet-printed PANI/CP was about 27 Ω , and 200 Ω for the carbon paper. The smaller R_{ct} indicates faster electron transfer rate, leading to a higher efficient EET between inkjet-printed PANI/CP and microbial. Interestingly, the R_{ct} of the as-printed PANI/CP was also obviously lower than that of our previously reported HCl-doped PANI/CP (~90 Ω),⁵⁰ which could be

ascribed to the better superposition of the molecular orbital of the organic anions in phytic acid with the π atomic orbitals of the carbon in the polymeric chain. Such an improvement in conductivity could further increase the EET efficiency. Moreover, the porous structure of the as-printed PANI network on carbon paper can enlarge the active surface area to collect electrons from riboflavin molecules self-excreted by bacteria.

In addition to the highly efficient EET, the bacteria-hosting capability of anodes is another key requirement for high-performance MFCs.⁵¹ To evaluate this, the morphology of anodes after 100h incubation with *S. oneidensis* MR-1 was investigated through SEM analysis. As shown in Fig. 3a, the entire surface of the inkjet-printed PANI/CP was fully covered by a confluent bacteria biofilm, while for the surface of carbon paper, the bacteria cells could only be found in certain regions. Moreover, the active biomass attached on the inkjet-printed PANI/CP was calculated to be $1346.5 \pm 11.3 \mu\text{g}\cdot\text{cm}^{-2}$ using a phospholipids analysis,⁵² while that of carbon paper was only $298 \pm 7.6 \mu\text{g}\cdot\text{cm}^{-2}$. Those results clearly suggested that the inkjet-printed PANI/CP possessed a largely increased bacteria-hosting capability. Since the backbones of PANI have positive charges in neutral solutions, while the outer membrane of bacteria carried negative charges, the electrostatic attraction has great contribution to the excellent bacteria-hosting ability of the inkjet-printed PANI/CP. Additionally, the intimate contact through the electrostatic attraction between the redox-active proteins in outer membrane of *S. oneidensis* MR-1 and the inkjet-printed PANI/CP can further enhance the stability of microbial biofilm and increase the direct EET efficiency.

Fig. 3 SEM images of inkjet-printed PANI/CP (a) and carbon paper (b) electrode after 100 h incubation with *S. oneidensis* MR-1 cell suspension.

Given the above-discussed advantages including large surface area, high electron transfer efficiency and excellent bacterial-hosting capability, the inkjet-printed PANI/CP is expected to be promising as anodes that would enhance the performance of MFCs. To verify this hypothesis, an anode-limiting MFC was firstly constructed. In this system, the Pt cathode with a much larger surface area than that of the anodes was used, thereby reducing the cathode polarization. The carbon paper was used as a control electrode for accurate manifestation of performance improvements. For an anodic reaction, the more negative the anode discharge potential, the better the electrocatalysis performance.⁵³ During the discharge, the inkjet-printed PANI/CP (-0.42 V) gave a much more negative potential than the carbon paper (-0.19 V),

demonstrating its better electrocatalytic performance (Fig. S1, ESI). The microbial electricity generation of the inkjet-printed PANI/CP in H-shaped two-chamber MFC was also evaluated. Fig. 4a presented the constant-load (1000Ω) current generation profiles of MFCs with these two different anodes. Clearly, the MFC with inkjet-printed PANI/CP produced a maximum current density of $396 \text{ mA}\cdot\text{m}^{-2}$, while the maximum current density of MFC with carbon paper was only $138 \text{ mA}\cdot\text{m}^{-2}$. Such significant increment in electricity generation strongly confirmed the superior functionality of inkjet-printed PANI/CP in MFCs.

Fig. 4 The performance of MFCs equipped with inkjet-printed PANI/CP and carbon paper. (a) The time courses of the current output curves of MFCs with a constant external resistance of 1000Ω . (b) Polarization curves and power density curves of MFCs.

To further assess the performance of MFCs, the polarization curves and power density curves were evaluated by varying the external load when the current output was in steady-state (Fig. 4b). The output voltage of MFC with inkjet-printed PANI/CP anodes decreased more slowly with the decrement of external load compared to that of MFC with carbon paper, indicating a much smaller internal resistance caused by the facilitated EET. With regards to maximum power output, the MFC based on inkjet-printed PANI/CP anodes had a value as high as $693 \pm 36 \text{ mW}\cdot\text{m}^{-2}$, which was 6.1 times higher than that of the MFC with carbon paper anodes ($98 \pm 5 \text{ mW}\cdot\text{m}^{-2}$). The inkjet-printed PANI/CP electrode also outperformed the carbon paper anode with phytic acid-doped PANI coating ($588 \pm 16 \text{ mW}\cdot\text{m}^{-2}$, Fig. S2, ESI). This result illustrated the advantage of the inkjet printing technology over directly paste method. To clarify the critical benefits of phytic acid doping,

we used hydrochloric acid-doped PANI as an electrode modifier for comparison. It was found that the carbon paper with hydrochloric acid-doped PANI coating possessed a much poor performance ($406 \pm 12 \text{ mW}\cdot\text{m}^{-2}$ Fig. S2, ESI). More impressively, as summarized in Table S1, the output power density of the presented MFC was obviously superior to those of previously reported MFCs using PANI and PANI-based composites as anode materials. These results further confirmed that the inkjet-printed PANI/CP is a favorable anode for MFCs.

In summary, an inkjet-printed PANI/CP electrode was successfully fabricated as an anode for microbial fuel cells. Apart from its high-throughput fabrication process, the inkjet-printed PANI/CP anode was demonstrated to effectively increase the performance of MFC. The impressive performance can be attributed to 1) the large surface area provided by the porous structure of PANI gel is helpful in connecting bacteria cells and to rapidly accept electrons from electron shuttles (riboflavin); 2) the enhanced conductivity of PANI resulted from the doping of organic acid was important in promoting electron transfer; and 3) the improved direct electron transfer process and the larger bacteria-hosting capability are due to the affinitive interaction between positively-charged PANI and negatively-charged bacteria cells. Clearly, our study not only provides a new opportunity to push the practical application of MFC technology, but also adds a new dimension to the application of inkjet-printing technology.

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