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Living and Conducting: Coating Individual Bacteria with Polypyrrole

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Abstract: Coating individual bacteria with conjugated polymers to endow them with more functionalities is highly desirable. In this research, we developed an in-situ polymerization method to successfully coat polypyrrole on the surface of individual *Shewanella oneidensis* MR-1, *Escherichia coli* K-12, *Ochrobacterium anthropic* N058 or *Streptococcus thermophilus* LMD-9. These as-coated bacteria displayed enhanced conductivities without affecting viability, therefore suggesting the generality of our coating method. Because of their excellent conductivity, we employed polypyrrole-coated *Shewanella oneidensis* MR-1 as an anode in microbial fuel cells (MFCs) and found that not only direct contact-based extracellular electron transfer is dramatically enhanced, but the viability of bacterial cells in MFCs also improved. Our results indicate that coating individual bacteria with conjugated polymers could be a promising strategy to enhance their performance or enrich them with more functionalities.

The coating of functional materials onto the surfaces of individual living systems not only protects their bioinformation under harsh environments, but is also helpful to increase their stability and performance as well as to introduce more functionalities in bio-related devices, including sensing, bioreactors, and microfluidic devices.^[1] Moreover, such coating would provide scientists more fundamental information during the study of cell biology. Inspired by biological preservation

mechanism, several protective coatings including metal-organic frameworks (MOF), iron-tannate coordination complex, silica and silica-titania have been demonstrated to extend cellular viability to environmental stresses.^[2] In addition, recent studies have already demonstrated that the encapsulation of yeast cells with conducting coatings (e.g., graphene and polydopamine) not only prolongs the cell lifetime but also offers good electrical conductivity.^[3] Although such coatings have already exhibited many advantages and introduced additional functionalities to cells, the potential of these surface-modified cells have not been fully exploited in above mentioned researches. Thus, advancing the development of some important research fields like microbial fuel cells (MFCs) by slickly integrating basic functions of biological units with intrinsic properties of surface coatings is essential to inject new vitality into the field of cell-surface modification.

MFCs are typical bioelectrochemical systems (BESs) that harness the metabolism of exoelectrogenic bacteria to harvest electricity from organic substrates, and have attracted continuous attention. This is due to their huge potential for simultaneous sustainable energy production and wastewater treatment.^[4] Although huge improvements have been achieved in recent years, MFCs are still far from reaching the level of practical application due to their relatively low power density.^[5] Generally, the extracellular electron transfer (EET) between exoelectrogens and anodes is keenly considered as a key step to determine the power output of MFCs.^[6] In the past, extensive studies have been devoted to tailor the anode for improving the exoelectrogen-anode interactions and thus the EET efficiency.^[7] One strategy is to enhance the surface properties of anodes. For example, polyaniline (PANI) and positively-charged ionic liquids have been used as anode modifiers to enhance the contact between anode and bacterial cells due to the electrostatic attraction.^[4c, 8] A further way is to fabricate novel nanomaterials with sophisticated structures as anodes. As an example, a conductive nanosucker array has been demonstrated to promote the affinitive mechanical contact through the vacuum suction that result from the depletion of oxygen in the inner space of the nanosucker.^[9] In these mentioned researches, planktonic bacteria attach onto the anode in a naturally growth manner, which limit bacteria loading to some extent.^[10] In view of this, researches on the anodes of MFC have begun to flourish in fabricating electroactive hybrid biofilms, as they possess high bacterial cell density and enhanced EET efficiencies.^[11] However, it is inevitable that some of bacterial cells in electroactive hybrid biofilms cannot be directly associated with conductive materials. In this case, the electron propagation between these bacterial cells and anodes is only through adjacent nonconductive bacteria,^[12] resulting in a reduction in EET efficiency. Obviously, encapsulation of individual bacterial cells with conductive materials would allow the electron transport more efficiently from inner cell to the electrode. Therefore, employing conducting-nanomaterial-coated bacteria should be a promising strategy to resolve the aforementioned problem in such engineering MFCs.

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Since polypyrrole (PPy) has been widely demonstrated as a biocompatible and excellent electrical conducting medium,^[13] modification of bacterial cells with PPy is hopeful to improve the electrical conductivity of bacterial cells without decreasing their viability. Therefore, in this research, we will employ this system to prove the possibility of coating *in-situ* formed PPy onto the surface of individual bacteria. Typically, *Shewanella oneidensis* MR-1 was chosen as an exoelectrogen model because the formation of PPy on the surface of bacterial cells can enhance the affiliative mechanical contact with c-type cytochromes, which locate on the out membrane of bacterial cell and play an important function to transfer electrons from *S. oneidensis* MR-1 to anodes.^[14] Our results clearly indicated that the direct contact-based EET process and bioelectricity generation are superior to that of unmodified exoelectrogen. Furthermore, with the same procedure, PPy can also be coated on the surface of three other individual bacteria, including *Escherichia coli* K-12, *Ochrobacterium anthropic* N058 and *Streptococcus thermophilus* LMD-9. In all cases, PPy can improve the conductivity of bacterial cells while maintaining cell viability.

The PPy-coated *S. oneidensis* MR-1 were fabricated by *in-situ* polymerization of pyrrole on the surface of individual bacterial cells. Since the outer membranes of bacterial cells carried negative charges, Fe^{3+} cations could be bound to the surface of bacteria cells due to the electrostatic interaction. The ferric-ion functionalized bacterial cells then served as the oxidative initiator. After removing unbound residual ferric ions in the solution, pyrrole monomers could only be polymerized on the surface of *S. oneidensis* MR-1. To probe the effect of PPy coating on the viability of bacterial cell, we performed the confocal scanning laser microscopy (CLSM) analysis of bacterial cells before and after formation of the PPy coating. For this experiment, a LIVE/DEAD BacLight bacterial viability kit^[15] that consists of green fluorescing SYTO 9 and red fluorescence propidium iodide (PI) was employed to discriminate between metabolically active/inactive *S. oneidensis* MR-1 cells. The CLSM image of PPy-coated *S. oneidensis* MR-1 displayed strong green fluorescence and slight red fluorescence (Figure 1a), indicating that the percentage of active cells were extremely high. Such results were also approximate to that of unmodified *S. oneidensis* MR-1 (Figure 1b), which confirmed that the viability of *S. oneidensis* MR-1 cells was essentially unchanged by the application of PPy coating. We then investigated the morphology of PPy-coated *S. oneidensis* MR-1 by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Unlike the smooth surface of native *S. oneidensis* MR-1 (Fig. 1d), the PPy-coated *S. oneidensis* MR-1 possessed a rough surface (Figure 1c). The high magnification revealed that PPy covered on the surface of bacterial cells to form a shell-like structure (Figure 1c, inset). The TEM images of bacterial cells before and after coating PPy (Figure 1e, f) further confirmed the existence of PPy shells on the cell surfaces.

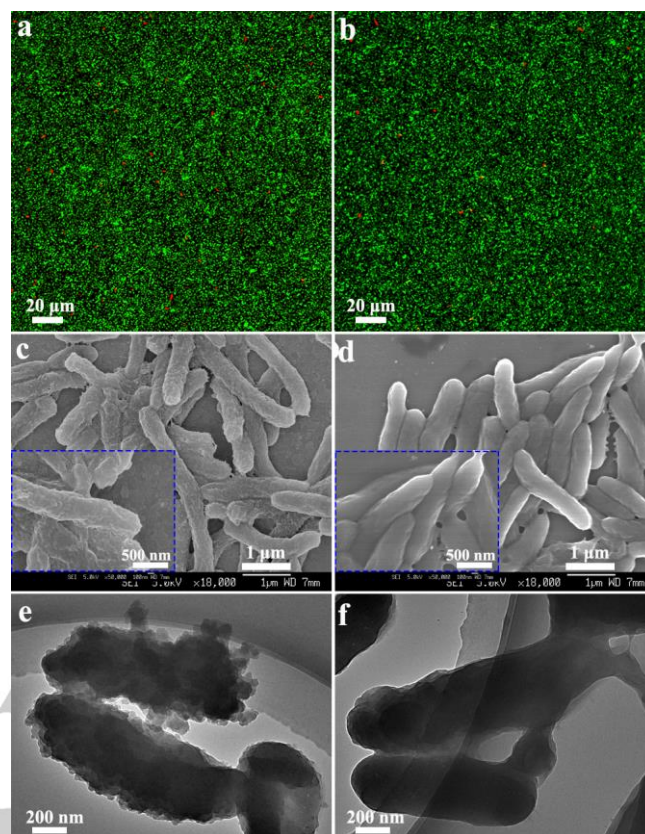


Figure 1. CLSM images of PPy-coated *S. oneidensis* MR-1 (a) and native *S. oneidensis* MR-1 (b) after staining with live/dead (bacLight) kit, the viability of PPy-coated *S. oneidensis* MR-1 was examined after the formation of PPy coating for 24 h. SEM (c, d) and TEM images (e, f) of PPy-coated *S. oneidensis* MR-1 (b, e) and native *S. oneidensis* MR-1 (d, f) after cell fixation, the insets in image c and d are the corresponding high-magnification SEM images.

To better understand the electronic structure of PPy layers formed onto the surfaces of individual cells, UV-Visible Spectroscopy analysis was carried out. As shown in Figure 2a, no obvious absorption peak (about 420 nm) was found for plain *S. oneidensis* MR-1, while this peak was clearly observed for PPy-coated *S. oneidensis* MR-1. Such absorption peak could be assigned to the characteristic $\pi - \pi^*$ or polaron absorption band of PPy,^[16] which was also found in the UV-Visible spectrum of PPy. Raman spectroscopy was also used to evaluate the molecular structure of PPy coatings (Figure 2b). In the Raman spectra of pure PPy, the characteristic peaks centred at about 1050 cm^{-1} and 1320 cm^{-1} were attributed to C–H in-plane deformation and ring stretching, and the peak at 1600 cm^{-1} was due to C=C backbone stretching.^[17] All of these characteristic peaks were found in the Raman spectrum of PPy-coated *S. oneidensis* MR-1, but not in the Raman spectrum of native *S. oneidensis* MR-1. Those results further demonstrate the successful fabrication of PPy on the surface of *S. oneidensis* MR-1. In order to evaluate the universality of this approach, we also tested if PPy could be coated onto the surfaces of *E. coli* K-12, *O. anthropic* N058 and *S. thermophilus* LMD-9. Based on our investigation, PPy coatings could be well-attached onto the

surface of all these individual microorganisms as well as *S. oneidensis* MR-1 (Supporting Information, Figure S1), and the viability of these microorganisms was unaffected after the modification of PPy (Supporting Information, Figure S2). Therefore, the proposed method possesses huge potential to fabricate PPy shells for a variety of biological units.

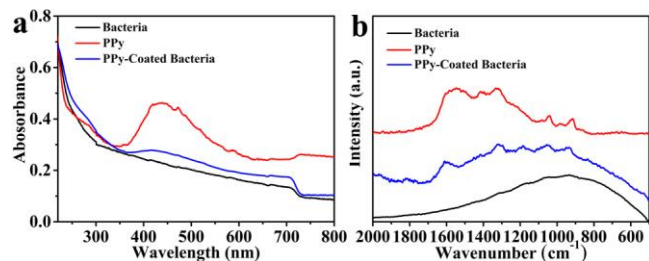


Figure 2. UV-Visible (a) and Raman (b) spectra of PPy-coated *S. oneidensis* MR-1, native *S. oneidensis* MR-1 and pure PPy.

As reported previously, the formation of conductive nanomaterials on cells could endow electrical conducting pathways on cells surface. In this case, electrochemical impedance spectroscopy (EIS) analyses were performed to investigate the electronic property of PPy-coated *S. oneidensis* MR-1. Before the test, the acid-treated carbon cloth (CC) was soaked with concentrated PPy-coated *S. oneidensis* MR-1 solution and native *S. oneidensis* MR-1 solution, respectively, followed by lay-up overnight for the construction of electrodes. As shown in Figure 3a, the Nyquist plots for both PPy-coated *S. oneidensis* MR-1/CC electrode and *S. oneidensis* MR-1/CC electrode consisted of a semicircle and a straight line. Based on the estimate of the semicircle diameter, the charge transfer resistance (R_{ct}) of PPy-coated *S. oneidensis* MR-1/CC electrode was $\sim 45.6 \Omega$, which is 23 times smaller than that of *S. oneidensis* MR-1/CC electrode ($\sim 1106.9 \Omega$). Clearly, a smaller R_{ct} indicates a faster electron transfer rate.^[18] Therefore, the result suggested that the conductive PPy coatings facilitate EET from the exoelectrogen to the electrode. Moreover, after coating PPy on surfaces, the R_{ct} of *E. coli* K-12 (~ 1314.6 vs. $\sim 52.3 \Omega$), *O. anthropic* N058 (~ 2023.2 vs. $\sim 69.4 \Omega$) and *S. thermophilus* LMD-9 (~ 1009.1 vs. $\sim 28.9 \Omega$) also decreased dramatically (Supporting Information, Figure S3). This illustrates the potential of PPy coating to afford electrical conductivity on the surface of various biological units, which would advance the application of these biological units in the electronic-related field.

To probe the biocurrent generation of PPy-coated *S. oneidensis* MR-1, we constructed a classical double-chamber MFC using PPy-coated *S. oneidensis* MR-1/CC electrodes as anodes. A similar MFC with *S. oneidensis* MR-1/CC anode was also fabricated for comparison. Figure 3b displays the constant-load (1000Ω) biocurrent generation profiles of those two MFCs. The maximum current density of *S. oneidensis* MR-1/CC anode was $\sim 28.3 \mu\text{A cm}^{-2}$, while the PPy-coated *S. oneidensis* MR-1/CC anode produced a maximum current density of $\sim 163.9 \mu\text{A cm}^{-2}$. Such a 4.8-fold increment in electricity generation effectively reveals the superiority of PPy-coated *S. oneidensis* MR-1 in MFCs. Moreover, similar to *S. oneidensis* MR-1/CC

anode, the PPy-coated *S. oneidensis* MR-1/CC anode can continuously produce electric current for at least 240 h, suggesting that the PPy coatings didn't show any negative effect on the long-time activity of *S. oneidensis* MR-1. To further confirm this, the anodes after MFCs operation were stained with the LIVE/DEAD BacLight bacterial viability kit and then examined by CLSM. For PPy-coated *S. oneidensis* MR-1/CC anode, plenty of viable cells (green fluorescence) covered almost the entire area of the carbon cloth electrode, and slight red fluorescence resulted from dead cells was observed (Figure 3c), indicating high viability of PPy-coated *S. oneidensis* MR-1 in MFC. Interestingly, in contrast to that observed for PPy-coated *S. oneidensis* MR-1/CC anode, the CLSM image of *S. oneidensis* MR-1/CC anode mainly presented red fluorescence (Figure 3d), suggesting that the PPy coating improve the viability of *S. oneidensis* MR-1 in MFC. The PPy coatings facilitate the EET between bacteria and electrode (Figure 3a), leading to the improvement in release rate of produced electrons and decomposition rate of organic matters. In the same space of time, more energy can be produced for supporting the growth and function of bacterial cells, contributing to the increased viability.^[19] Another possible reason is that the high mechanical strength PPy coating offers an enhance protection of individual bacterial cells from unfavourable factors.^[3b, 13a]

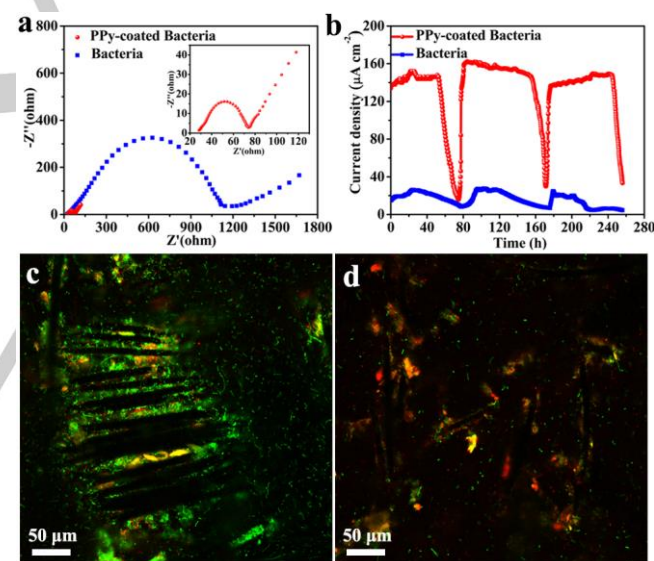


Figure 3. (a) The Nyquist curves of PPy-coated *S. oneidensis* MR-1/CC electrode and native *S. oneidensis* MR-1/CC electrode (frequency range: 10^5 – 10^2 Hz), inset is the enlarged view of the curve. (b) Time courses of the current generation in MFCs using different anodes with an external resistor of $1 \text{ k}\Omega$. CLSM images of PPy-coated *S. oneidensis* MR-1/CC anode (c) and native *S. oneidensis* MR-1/CC anode (d) after MFC operation.

By varying the external load, the polarization curves and power density curves were recorded for further evaluation of the MFCs performance. The PPy-coated *S. oneidensis* MR-1/CC anode produced a maximum power density as high as $147.9 \mu\text{W cm}^{-2}$ (Figure 4a), which was 14.1 times higher than that of *S. oneidensis* MR-1/CC anode ($9.8 \mu\text{W cm}^{-2}$). As shown in Table S1 (Supporting Information), this value is clearly higher than

those of previously reported MFCs using PPy and PPy-based nanocomposites as anodes.^[6c, 9, 20] More impressively, the maximum power density of the presented MFC is almost twice as high as those of MFCs based on sophisticated three-dimensional electroactive hydride biofilm anodes.^[11, 21] These results fully prove that the modification of individual exoelectrogenic bacteria is a powerful strategy for improving the performance of MFCs. To help understand the enhanced MFC's performance by PPy-coated *S. oneidensis* MR-1/CC anode, the direct contact-based EET was examined by cyclic voltammetry (CV) analysis. The CV plots of PPy-coated *S. oneidensis* MR-1/CC anode displayed a pair of obvious redox peaks at about -0.37 and -0.15 V (vs. SCE),^[22] which was associated with the c-type cytochromes on the outer membrane (OM) of bacterial cells. But no CV peaks were detected for *S. oneidensis* MR-1/CC anode (Figure 4b). These results indicate that PPy-coated *S. oneidensis* MR-1/CC anode was able to accept electrons via direct contact-based EET, which was hindered on the *S. oneidensis* MR-1/CC anode. As the c-type cytochromes are located at the outer membrane, the in-situ formation of conductive PPy on the surfaces enhances the affiliative mechanical contact between c-type cytochromes and PPy and consequently the direct contact-based EET. More importantly, multiplexed conductive pathways were formed in PPy-coated *S. oneidensis* MR-1/CC anode. In this case, even the electrons produced by the bacterial cells far away from the electrode can efficiently inject into electrode through the conductive PPy. On the contrary, without PPy coating, the propagation of above mentioned electrons only go along the adjacent nonconductive bacteria cells,^[23] leading to a poor EET efficiency (Figure 4c). Therefore, employing PPy as conductive coating for *S. oneidensis* MR-1 was beneficial to enhancing the direct contact-based EET, therefore improving the performance of MFC.

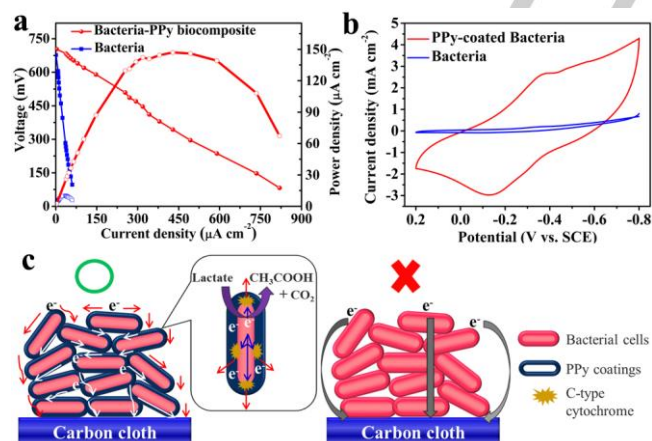


Figure 4. (a) Polarization and power-density curves of MFCs with different electrodes. (b) CVs of different anodes after MFC operation in fresh mineral medium at a scan rate: 10 mV s⁻¹. (c) Schematic depicting the direct contact-based EET mechanism of PPy-coated *S. oneidensis* MR-1/CC anode (left) and native *S. oneidensis* MR-1/CC anode (right).

In summary, we have described a general method to encapsulate individual bacteria including *S. oneidensis* MR-1 cells *E. coli* K-12, *O. anthropic* N058 and *S. thermophilus* LMD-9

with *in-situ* generated conductive polypyrrole (PPy). The PPy-coated bacterial cells afford an enhanced electrical conductivity without affect their viability. Because the polypyrrole coatings can both enhance the direct contact-based extracellular electron transfer through outer membrane c-type cytochromes and improve the long-time stability of bacterial cells, we employed PPy-coated *S. oneidensis* MR-1 films as anodes in MFCs. Our results indicated that the PPy-coated bacteria electrode exhibited a 14.1-fold increase in power output comparing to native *S. oneidensis* MR-1. We believe that the present study not only adds a new dimension to explore high-performance anodes for MFCs, but also provide a good start for the application of cell-surface modification in microbial electrochemical systems.

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Keywords: cell-surface modification • polypyrrole • electrical conductivity • microbial fuel cell • in-situ polymerization

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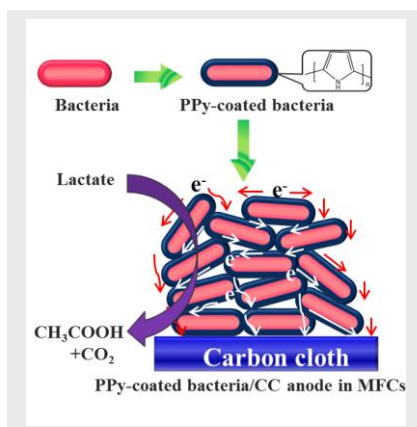
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Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Surface modification of bacterial cells: Polypyrrole can be formed on the surface of bacterial cells as a conductive coating to endow bacteria with enhanced electrical conductivity without affecting their viability. The PPy coating greatly promotes the direct contact-based electron transfer between *S. oneidensis* MR-1 and electrode, leading to a dramatically improvement in the bioelectricity generation of microbial fuel cells.



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Living and Conducting: Coating Individual Bacteria with Polypyrrole