One-step electrochemically synthesized graphene oxide coated on polypyrrole nanowires as anode for microbial fuel cell

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Abstract

A novel polypyrrole nanowires coated by graphene oxide (PPy-NWs/GO) has been successfully synthesized by one-step electrochemical method, whose structure was different from previously reported PPy/GO composites. The microbial fuel cell equipped with PPy-NWs/GO as anode was fabricated and compared with PPy-NWs ones. The SEM images show that the synthesized PPy-NWs/GO materials possess more surface areas than PPy-NWs. The electrochemical analysis indicated that PPy-NWs/GO anode had lower charge transfer resistance, which may be attributed to synergistic effect of them. The MFC equipped with PPy-NWs/GO anode have higher circle voltages and the power density is about 22.3 mW/m², which is great higher than that of PPy-NWs about 15.9 mW/m². These improvements of the MFCs may be due to more bacteria on the larger biofilms based on GO nanosheets, indicating that the PPy-NWs/GO is more effective anode for improving electricity generation.

Keywords Microbial fuel cell · Polypyrrole nanowires · Graphene oxide · Anode · *Shewanella oneidensis* MR-1

Introduction

Human development are increasingly troubled by global energy shortage and environmental pollution. Microbial fuel cell (MFC) can exactly resolve the above-mentioned problems as they have been evidenced not only to produce electricity, but also to simultaneously treat wasted water (Zhou et al. 2011; Rahimnejad et al. 2015; Xie et al. 2015). They have, therefore, attracted considerable attention in recent years, and a lot of improvements have been made in the technologies of MFC (Kumar et al. 2013; Wei et al. 2011). However, bottlenecks for the application of this methodology are still existing, such as low efficiency, weak output

of power and so on. Principally, the performance of MFC depends on many factors, such as degradation of substrate, the rate of electron transfer from bacteria to anode, the proton mass transfer in the liquid, the conductivity of electrode and external operating conditions. Three of them refer to the properties of electrode, especially for anode. Different anode materials and nanostructure would vary significantly in physical and chemical performances (e.g., surface area, conductivity and chemical stability) (Mustakeem 2015). Thus, they also vary a lot in microbial attachment, electron transfer, resistance and the rate of electrode surface reaction. Obviously, it is of great significance to select suitable materials and to synthesize effective nanostructure for the progressive performance of MFC.

Due to excellent performances in conductivity, biocompatibility and chemical stability, polypyrrole (PPy) is always regarded as ideal anode material for MFC and has been deeply studied to replace traditional anode (Feng et al. 2010; Yuan and Kim 2008). Meanwhile, various nanostructures of PPy have been successfully fabricated to improve the performance for applications, including nanotubes, nanoparticles, cauliflower and nanowires (Hermsdorf et al. 2005; Guo et al. 2011; Mahmoudian et al. 2012). Polypyrrole nanowires (PPy-NWs), one-dimensional (1D) nanostructures, are well ordered pyrrole monomers chain structure which not only provide a conducting

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backbone carrying charge, but also boost the exposed surface and space benefitting for bacterial attachment in MFC (Chen et al. 2013). Besides, graphene, as another kind of ideal electrode materials, has been widely concerned in applications due to large specific surface area and extraordinary high electronic conductivity (Allen et al. 2010; Chen et al. 2012). But it may be greatly limited in electrochemical application due to its insolubility and irreversible agglomeration. Due to the process of fabrication usually using strong acid and oxidizing agents, graphene oxide (GO) is commonly attached many oxygen-containing groups on its basal planes and edges (Dreyer et al. 2010; Sun et al. 2008). The abundant oxygen-containing groups can effectively improve the hydrophilicity of graphene. Thus, GO exhibit well hydrophilic behavior in electrolyte, which provide fertile opportunities for preparing GO-based hybrid nanostructure using electrochemical methods (Zhu et al. 2012; Pumera 2013).

Some efforts have been made to explore composite nanostructure of PPy and GO for application in anode of MFC or supercapacitor electrodes. Li et al. have exploited an in situ chemical polymerization method to synthesize GO/PPy-NWs composites material for supercapacitor electrodes (Mindroui et al. 2013). The surface morphologies of the composites showed that the PPy-NWs were uniformly dispersed on the surface of GO nanosheets, which increased the surface area of the material and the charge transfer rate. Lv et al. (2013) have fabricated PPy/GO composites on graphite felt for electrode of MFC by electropolymerization of pyrrole while GO as the anionic dopant. A distinctive morphology of the resulting PPy/GO composites is the incorporation of GO in the PPy films during electropolymerization. Then, these PPy/GO composites were specifically and homogeneously grown on fiber surface of graphite felt, resembling a wrinkled paper structure with many pores.

In this report, one novel PPy-NWs/GO hybrids was explored using one-step electrochemical approach. The obtained PPy-NWs/GO hybrids exhibited the most distinguishing morphology feature was GO coated on the top of PPy nanowires, which is different from both above-mentioned composites in nanostructure. The nanostructure and electrochemical behaviors of PPy-NWs/GO hybrids were characterized and compared to PPy-NWs. The MFCs equipped with both materials as anode were assembled and further studied in its behaviors of cell voltages and power densities.

Experimental

Materials

All the reagents were of analytical grade and were used without further purification. GO were purchased from Sinopharm Chemical Reagent Co., Ltd.

Anodes modified by PPy-NWs and PPy-NWs/GO

The starting bare substrate was a piece of nickel (Ni) plate with a dimension of 40 mm × 20 mm, which was rinsed thoroughly with alcohol, acetone and deionized water in turn and finally dried at 60 °C in vacuum dryers before using. The process of synthesis was performed in a three-electrode electrochemical cell including a working electrode (Ni plate), a counter electrode [platinum (Pt) plate] and a reference electrode (saturated calomel electrode). 0.2 M $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 0.01 M $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ and 0.15 M monomer pyrrole were ultrasonically dissolved in 100 mL distilled water as the electrolyte for preparing PPy-NWs (Chen et al. 2013). A potentiostatic method (CHI604D, Shanghai CH Instrument Company, China) was used for controlling the current applied on work electrode. Upon a constant potential of 0.8 V, the PPy-NWs were electropolymerization on the surface of Ni plate. The obtained nanowires was then rinsed by deionized water and dried in vacuum dryer at 25 °C. Similarly, the anodes of PPy-NWs/GO were prepared in the same way besides adding 2.5 mL GO solution (0.25 mg/mL) in electrolyte.

Characterization of PPy-NWs and PPy-NWs/GO anodes

The surface morphology of anodes modified by PPy-NWs/GO and PPy-NWs hybrids were observed by field-emission imaging scanning electron microscope (SEM, Quanta 200, FEI Ltd, USA). The cyclic voltammetry (CV) analysis was performed to investigate electron transfer mechanism using CHI604D electrochemical workstation. In a conventional three-electrode electrochemical cell, the prepared anodes were performed as the working electrode, whereas Pt plate and Ag/AgCl were used as the counter and reference electrodes, respectively. A potential range of −0.6 to 0.8 V with the scanning rates from 20 to 200 mV/s was applied on the working and counter electrode in 100 mL electrolyte containing 50 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$. Prior to measure, N_2 was purged into solution for 20 min to drive away O_2 . In the solution of riboflavin, electrochemical impedance spectroscopy (EIS) measurements were conducted over a frequency range from 0.1 Hz to 100 kHz with a perturbation signal of 5 mV.

The construction, operation and characterization of MFC

The single-chamber MFCs were assembled according to schematic illustration, which is shown in Fig. S1 of Supplementary Information (SI), mainly consisting of three parts including anode, anode chamber and air cathode.

The PPy-NWs/GO and PPy-NWs grown on Ni substrates (40×20 mm) using as anode were rinsed by deionized water and alcohol, respectively, and then were dried in vacuum drier at 60°C for 30 min. After removing redundant PPy-NWs/GO and PPy-NWs on substrates, the available area of anode was circle with a diameter of 6 mm. A rectangular polydimethylsiloxane (PDMS) plate ($30 \times 20 \times 2$ mm) was prepared with mold. Then, the plate was excavated out a cylinder with the same diameter of 6 mm as the space of chamber. The Nafion membrane with the Pt/C electrode was used as proton exchange membrane (PEM), which was put on top of PDMS and also used as air cathode. These three parts were assembled together by silica gel to form a simple single-chamber MFC, whose volume was about $56\ \mu\text{L}$. The *Shewanella oneidensis* MR-1 (Gorby et al. 2009) was used as producing electricity microbe for MFC. The *Shewanella oneidensis* MR-1 were inoculated into the single-chamber MFC with mineral medium containing: 2.5 g/L NaHCO_3 , 0.1 g/L KCl, 1.5 g/L NH_4Cl , 0.6 g/L $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 1 mL vitamins, 1 mL trace minerals and 10 mM lactate.

Results and discussion

Surface morphology of PPy-NWs/GO and PPy-NWs

The surface morphology of PPy-NWs/GO and PPy-NWs were measured by SEM technique. Figure 1a, b shows the SEM images of PPy-NWs anode. It can be observed that the obtained PPy exhibited wire shape and smooth surface, agreeing well with our previous results (Chen et al. 2013). The width and length of nanowires are about $0.2\ \mu\text{m}$ and more than $1\ \mu\text{m}$, respectively. Although these nanowires are intertwined together, we still obviously distinguish each nanowire as there are no forks and cross observed from all nanowires, indicating each nanowire randomly individual growth and no influence on each other. Figure 1c, d shows the SEM images of PPy-NWs/GO anode. The behaviors of PPy-NWs in PPy-NWs/GO hybriide are similar to the ones of PPy-NWs anodes. A distinct difference for PPy-NWs/GO hybriide was the attachment of GO on top of the PPy-NWs and part coverage of PPy-NWs net. The growth of

Fig. 1 SEM images of PPy-NWs (a, b) and PPy-NWs/GO (c, d), respectively

PPy-NWs under GO was restrained because its stop more pyrrole monomer polymerizing continuously. Moreover, there were no PPy-NWs observed on the top of GO, indicating that PPy were also not able to continue growing on GO. The observed nanostructure of PPy-NWs/GO or position of each other roughly indicated the process of growth. Upon a constant potential applied on electrode, PPy bulge firstly attached and synthesized on substrate of Ni plate due to pyrrole monomer with smaller size comparing to GO. On basis of bulge, PPy will continue polymerizing into nanowires with different length and width. These nanowires increased roughness of surface benefitting the attachment of GO on top of PPy-NWs. The attachment of GO might be caused by the strong π - π stacking interaction between the monolayer of GO and the electronic structures of conjugated backbones of PPy (Mindroiu et al. 2013).

Electrochemical analysis

Cyclic voltammetry (CV) was used to characterize electrochemical behaviors of the as-prepared materials. Figure 2 shows the CV curves of PPy-NWs and PPy-NWs/GO anodes, which were measured in solution of $K_3[Fe(CN)_6]$ with a potential range of -0.6 to 0.8 V at the scan rate of 60 mV/s. It is noted that the quasi-reversible redox behavior of ferricyanide ions was found for the PPy-NWs or PPy-NWs/GO anode, whereas the Ni plate does not show obvious redox peaks in the CV plot. Moreover, the peak current of ferricyanide ions relative to the PPy-NWs or PPy-NWs/GO anode was much higher than that of the Ni plate. According to the Cottrell equation, with the same projected surface area, the active surface area of PPy-NWs/GO anode is larger than PPy-NWs one, which

Fig. 2 CVs curves of different materials in 50 m M/L $K_3[Fe(CN)_6]$ with the potential of -0.6 to 0.8 V at scan rate of 50 mV/s

is obviously beneficial to the adhesion of more microbe. Besides, the peak current of PPy-NWs/GO anode is higher than PPy-NWs one, which may be of great significance for the improvement of performance.

CV analysis can be used to explore charge transfer kinetic of materials. Figure 3a, b shows the redox peak currents of PPy-NWs or PPy-NWs/GO anodes with the potential scan rates increasing from 20 to 200 mV/s, respectively. It can be easily found that both anodes showed redox peak currents, which indicate quasi-reversible charge transfer. In addition, the cyclic voltammetric behaviors of both anodes were also influenced by the potential scan rate. Laviron model is usually used to estimate the charge transfer rate of anode's surface reaction, k_s (Laviron 1979):

$$E_{pa} = E^{\circ'} + \frac{RT}{(1-\alpha)nF} \ln \frac{(1-\alpha)nF}{RTk_s} + \frac{RT}{(1-\alpha)nF} \ln \nu$$

$$E_{pc} = E^{\circ'} + \frac{RT}{\alpha nF} \ln \frac{RTk_s}{\alpha nF} - \frac{RT}{\alpha nF} \ln \nu.$$

Herein, α is the electron transfer coefficient; ν is the potential scan rate and $E^{\circ'}$ is the formal potential.

Semilogarithmic dependence of the cathodic peak potential, anodic peak potential and the scan rate of PPy-NWs and PPy-NWs/GO were shown in Fig. 3c, d. It can be obtained the plots on relationship of E_p vs $\ln \nu$ for both anodes. E_p can be calculated as the middle between the anode and cathodic peak potentials at a low potential scan rate (Luo et al. 2001). When the potential was at a high rate, the relationship of E_p vs $\ln \nu$ is nearly linear. The equations of the straight lines are obtained by fitting software and shown as follows:

The equations of PPy-NWs anode,

$$E_{pa} = 0.47455 + 0.05102 \ln \nu$$

$$E_{pc} = -0.09596 - 0.05061 \ln \nu.$$

The equations of PPy-NWs/GO anode,

$$E_{pa} = 0.60751 + 0.090541 \ln \nu$$

$$E_{pc} = -0.20545 - 0.08190 \ln \nu.$$

According to above equations, the values of k_s were calculated and shown in Table 1 of SI. The k_s of the anode and cathode were nearly equal due to the quasi-reversible redox reaction for both materials (Marsili et al. 2008), respectively, which agreed well with the results of CV curves. The k_s of PPy-NWs/GO anode is evidently greater than that of PPy-NWs one, which suggests that the nanostructures of PPy-NWs/GO can facilitate the electron transfer in the solution and electrode interfacial. The charge transfer rate of PPy-NWs/GO anode is 45% higher than PPy-NWs one in the efficiency of MFC, suggesting that the nanostructure of

Fig. 3 CVs of PPy-NWs and PPy-NWs/GO at different scan rates from 20 to 200 mV/s (**a**, **b**), respectively. Semilogarithmic dependence of the cathodic peak potential, anodic peak potential and the scan rate of PPy-NWs and PPy-NWs/GO (**c**, **d**), respectively

PPy-NWs/GO can further optimize electrochemical performance than only PPy-NWs.

The EIS technique has been widely used to evaluate resistances, mainly including ohmic resistance (R_{ohm}) and charge transfer resistance (R_{ct}). As on the Nyquist plots, the R_{ohm} is indicated by the high-frequency intercept with the x axis and the R_{ct} is indicated by the diameter of semicircle. The impedance spectra (Nyquist plots) of PPy-NWs/GO and PPy-NWs anodes are shown in Fig. 4. It can be observed that both Nyquist plots of anodes similarly exhibit a well-defined semicircle portion in high-frequency range, followed by a straight sloped liner in low-frequency region. The appearance of semicircle in each curve indicated that the impedance spectra followed the one-time constant model and the relevant equivalent circuit is shown in Fig. S2 (SI). According to the fitting data equivalent circle, the R_{ohm} value of PPy-NWs/GO anode is slightly larger than PPy-NWs one, which may be due to the poor electronic conductivity of GO. It can also be obviously seen that the diameter of semicircle measured from PPy-NWs/GO anode was far less than the PPy-NWs one, indicating that the PPy-NWs/GO anode have lower value of R_{ct} or better charge transfer efficiency. This higher charge transfer efficiency of PPy-NWs/GO hybrid

Fig. 4 Nyquist plots of PPy-NWs and PPy-NWs/GO in 0.1 g/L riboflavin solution from 0.1 Hz to 100 kHz with a perturbation signal of 5 mV

may be attributed to the synergistic effect between PPy-NWs and GO nanosheets (Lv et al. 2013). Although PPy-NWs/GO anode shows a little higher R_{ohm} value, it also has a remarkable lower charge transfer resistance. The interaction

of R_{ohm} value and charge transfer resistance exhibits a lower all-in resistance.

Performance of the PPy-NWs or PPy-NWs/GO anodes in MFC

Figure 5 shows the polarization and power output curves of MFC equipped with PPy-NWs anode and PPy-NWs/GO anode, respectively. The open circuit voltage is about 710 mV for the MFC with PPy-NWs/GO anode, which is higher than that for the MFC with PPy-NWs one (650 mV). Besides, the power density of the MFC with the PPy-NWs/GO anode is about 22.3 mW/m^2 , which is also higher than that of PPy-NWs about 15.9 mW/m^2 . The obviously better performance of the MFC equipped with PPy-NWs/GO is

Fig. 5 Polarization and power output densities of the MFC equipped with PPy-NWs and PPy-NWs/GO anode, respectively

attribute to the modification of GO nanosheets. According to the results of CV and EIS, the higher transfer efficiency of PPy-NWs/GO anode may lead to better power densities and open circuit voltages of MFC.

To further understand the role of PPy-NWs/GO, the morphologies of anodes equipped in MFC, which have been exhausted, were observed by SEM technique and the images are shown in Fig. 6a, b, respectively. The bacteria of *Shewanella oneidensis* MR-1 grew on the surface of anodes with a rod-shape, which were similar to that reported previously (Sanchez et al. 2015; Luckarift et al. 2012). Due to its own big size comparing to the dimension of PPy-NWs, most of bacteria were not able to enter and grow in gap of nanowires and generally began growing or attaching from the top part of nanowires. These bacteria accumulated and overlapped each other, which would form a layer of biofilm on top of PPy-NWs (Zhang et al. 2015). There were a few of biofilms with large area for PPy-NWs biofilms and more holes in films comparing to PPy-NWs/GO ones, which may be attributed to the lack of supporting point enough from nanowires. However, on basis of GO nanosheets, bacteria was able to construct biofilms with large area on PPy-NWs/GO anode. This can be evidenced by the image of Fig. 6b, in which the biofilms have large area and fewer or no holes. The larger area is well beneficial to the attachment of more bacteria. More amounts of bacteria on anode means higher ability of electricity generation, which maybe another reason to improve circuit voltages and power densities of MFC equipped with PPy-NWs/GO anode. These results are indicative of that GO nanosheets attached on PPy-NWs not only reduce the charge transfer resistance, but also enlarge area of biofilm for bacteria's attachment, both of which are very crucial factors for the improvement of MFC.

Fig. 6 SEM images of *Shewanella oneidensis* MR-1 attached on PPy-NWs (a) and PPy-NWs/GO (b) anodes in exhausted MFC

Conclusions

Here, we have successfully synthesized a novel PPy-NWs/GO anode for MFC by one-step electrochemical method. The images of SEM showed that the GO nanosheets coated on top of PPy-NWs for PPy-NWs/GO anode, which was of great difference from previous reports. CV curves showed both anodes possessing quasi-reversible redox and the active surface area of PPy-NWs/GO anode is larger than PPy-NWs one. Laviron model and EIS analysis have evidenced that PPy-NWs/GO anode had a much lower charge transfer resistance, which may be attributed to the synergistic effect between GO nanosheets and PPy nanowires. The MFC equipped with PPy-NWs/GO anode exhibited higher circle voltages and power densities than PPy-NWs. The morphologies of both anodes in exhausted MFC showed that PPy-NWs/GO anode had larger biofilms for the attachment of more bacteria, which was owing to the supplying basis from GO nanosheets. The performance of MFC with PPy-NWs/GO anode was enhanced in circle voltages and power densities due to the introduction of GO on PPy-NWs.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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