Enhanced Performance of Microbial Fuel Cells by Using MnO₂/Halloysite Nanotubes to modify carbon cloth anodes

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ABSTRACT: The modification of anode materials is important to enhance the power generation of microbial fuel cells (MFCs). A novel and cost-effective modified anode that is fabricated by dispersing manganese dioxide (MnO_2) and Halloysite nanotubes (HNTs) on carbon cloth to improve the MFCs' power production was reported. The results show that the MnO_2 /HNT anodes acquire more bacteria and provide greater kinetic activity and power density compared to the unmodified anode. Among all modified anodes, 75 wt% MnO_2 /HNT exhibits the highest electrochemical performance. The maximum power density is 767.3 mWm^{-2} , which is 21.6% higher than the unmodified anode (631 mW/m^2). Besides, CE was improved 20.7, indicating that more chemical energy transformed to electricity. XRD and FTIR are used to characterize the structure and functional groups of the anode. CV scans and SEM images demonstrate that the measured power density is associated with the attachment of bacteria, the microorganism morphology differed between the modified and the original anode. These findings demonstrate that MnO_2 /HNT nanocomposites can alter the characteristics of carbon cloth anodes to effectively modify the anode for practical MFC applications.

KEYWORDS: Microbial fuel cell, Manganese oxide/Halloysite nanotube, Modified anodes, Carbon cloth, Power density.

1. Introduction

Electricity is the main energy style in modern human society, which facilitates the daily life to be easy. The electricity energy can be acquired from hydroelectricity

power [1], concentrated solar power [2], wind power [3], thermal power [4] and nuclear electricity [5]. Thermal power generated by combustion of fossil energy is operated with low converting efficiency and the serious environmental pollution occurs simultaneously. The huge potential security risk is always considered as the key factor to influence the widely applied in the world. And hydraulic, wind and solar clean energy are good choices to get electricity but limited by the climate and geography factors in large scale application. Biomass is one of the important renewable carbon sources and has been recognized as the promising energy supplier in the future. There is the high theoretical utilization efficiency in the case of converting biomass into electricity directly.

Microbial fuel cells (MFCs) are a promising biotechnology that harvests electrical energy from the oxidation of organic matter through the catalytic reaction of electrogenic microorganisms [6 - 7]. In such devices, electrons and protons are produced in the anode chamber by the microbial metabolism of the substrate. Electrons are then transferred through an external circuit to the cathode and combine with electron acceptors and protons that diffuse through the solution, generating electrical current and reduced products.

The anode was considered to limit the power production in MFCs because its structure can affect microorganism attachment, substrate oxidation, and electron transfer [8]. Traditional carbon-based materials such as graphite plate, carbon brush, carbon cloth, and carbon paper were widely used as anode materials in MFCs due to their chemical stability and conductivity. However, these carbon materials still have

space to improve the conductivity and biocompatibility, and thus, modification of these materials is necessary for higher power production [9]. Anode modification by chemical methods such as soaking [10], heat treatment [11], and treatment with ammonia [12] to add a nitrogenous group and to enhance the hydrophilicity has been successful in promoting the current density of MFCs. The treatment of anode materials by electrochemical oxidation [13] can also increase the power output. Synthesized conductive polymers and carbon nanotube coatings such as polyaniline/carbon nanotubes are ideal anode materials due to the high electrochemical surface area, electrocatalytic ability, and favorable biocompatibility, which has a positive impact on power generation [14].

Owing to their low cost, being non-toxic and environmentally benign, high chemical stability, and catalytic activity, the incorporation of transition metals and metal oxides into carbon materials has proven to be an effective way to accelerate the electron transfer and to promote power generation of MFCs [15]. MnO_2 was considered to be one of the most effective materials for MFC electrodes [16-17]. However, the properties and activity of MnO_2 can be highly affected and reduced upon agglomeration to a bulk material, resulting in unsatisfactory electrochemical performance. Hence, MnO_2 incorporated into composite materials that enhanced the dispersion of MnO_2 and increased the electrochemical surface area is an effective method to improve the performance of MnO_2 . The use of nanotubular materials as supports for MnO_2 has received increased interest by researchers recently. These nanotubes are excellent support models to obtain an active center by forming

nanoparticles inside the tubes [16]. However, compared to carbon nanotubes and boron nitride nanotubes, halloysite nanotubes (HNTs) are natural, economical, and abundant. HNT $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}]$ ($n=0$ or 2), a naturally available aluminosilicate clay mineral, is composed of multiple alumina/silica layers with a gibbsite-like array of aluminol groups ($\text{Al}-\text{OH}$) on the internal surface and siloxane groups ($\text{Si}-\text{O}-\text{Si}$) on the external surface [18]. This chemical difference in the structure resulted in a negatively charged external surface and a positively charged lumen. This allowed a broad variety of biologically active substances to be loaded to the surfaces. Due to the hollow nanoscale tubular structure, large surface area, high porosity, and tunable surface chemistry, the dispersion of metal, metal oxide, and metal sulfide nanoparticles onto the HNT surface is a promising method to improve the catalysis and stability of the nanoparticles [19,20]. Moreover, the adequate hydroxyl groups on the HNT surface allowed the nanoparticles to be directly grown on the HNT surface [21]. To the best of our knowledge, there have been no previous reports on the study of MnO_2/HNT as an anode modifier for MFCs. Based on former studies, we can speculate that the MnO_2 can disperse on the HNT surface uniformly by adsorption, which will enhance electron transfer and the adhesion of bacteria and improve the performance of the whole MFC.

In this study, MnO_2/HNT nanocomposites with varying contents (25, 50, and 75 wt%, in this article, wt% means weight percent) were coated onto carbon cloth and utilized as the MFC anode material. The electrochemical performance of the modified anode was evaluated through comparison with bare carbon cloth. X-Ray powder

diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), water contact angle measurements, scanning electron microscopy (SEM) and cyclic voltammetry (CV) were applied to characterize their structural and electrical properties.

2. Materials and methods

2.1 MnO₂/HNT nanocomposite preparation

The HNT (Zhengzhou Golden Sunshine Ceramics Co., Ltd.) that supported the MnO₂ nanocomposites was prepared using a reduction–oxidation method according to a modified procedure reported by Devaraj et al [22] and Boonfueng et al [23]. MnO₂/HNT composites with different weight percentages of MnO₂ were obtained by varying the HNT concentration. First, 1.58 g of KMnSO₄ was added to 30 ml of a HNT solution of varying concentrations (83.2, 27.7, 9.2 mg/ml) before being stirred continuously at room temperature for 0.5 h, and this mixture was called solution A. Second, 0.97 g of MnSO₄ · H₂O was dissolved in 10 ml of distilled water in a beaker, and then the MnSO₄ solution was subsequently added to solution A drop-wise. The resulting mixture was stirred continuously at room temperature for 4 h. After the reaction was finished, the resulting brown–black precipitates were washed with distilled water for several times to remove excess ions, and finally dried at 80 °C in air. The MnO₂ nanoplatelets were prepared following the same synthetic route of the MnO₂/HNT nanocomposites in the absence of HNT. The reaction involved in the synthesis of the crystallographic form of MnO₂ is listed below:

2.2 Electrode preparation

Five types (MnO_2 , MnO_2 (25 wt%)/HNT, MnO_2 (50 wt%)/HNT, MnO_2 (75 wt%)/HNT, and HNT) of anodes (50cm^2) were prepared according to the following procedures. Briefly, 0.2 g of the as-prepared powders was mixed with 4 ml of distilled water to prepare a paste. The mixture was then coated onto the surface of the carbon cloth to produce a uniform film. The bare carbon cloth was used as the control anode. Air cathodes which were prepared as previously described [24] were made of carbon cloth (E-TEK, USA) with 0.1 g of a 40% Pt/C catalyst (Pt on Vulcan XC-72, BASF, USA) on the side exposed to the solution. In this article, the dosage of the Pt catalyst was 2 mg/cm^2 .

2.3 MFC construction, inoculation and operation

Six air-cathode single-chamber, cylindrical-shaped reactors with an anode chamber 115 mm in length and 3 cm in diameter (effective liquid volume of 100 ml and the effective surface area of the anode of 28.26 cm^2) were constructed as previously described [25], as figure 1 showed. The anode electrode was connected by a wire via an external resistor ($1000\ \Omega$, except where noted otherwise) to the cathode.

All of the MFCs were inoculated with a mixture of bacterial cultures collected from the wastewater treatment plant in Nanjing. The analyte was prepared by dissolving 1 g of glucose, 0.3063 g of NH_4Cl , 0.125 g of KCl , 11.875 g of $\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$, 2.548 g of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 0.1875 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 1.0 L of deionized water with the addition of 10 ml of the trace nutrient [26]. All of the tests were conducted in batch-fed mode at a constant temperature at $33\ ^\circ\text{C}$. The output voltage of most MFCs was at a low degree when operated after 38 h, so the anode

substrate was replaced when reactors were operating for over 38 h to remove planktonic and dead cells.

Fig. 1

In this study, the performance of MFCs fixed with anodes modified differently was investigated using the same cathodes and system preferences. First, the crystal structure and functional groups of the anode modifiers was explored through XRD and FTIR. Second, the basic parameters used to describe the operation process of the MFCs were analyzed, which included output voltage, power density, COD removal, and coulombic efficiency. Third, water contact angle measurements were carried out to describe the hydrophobic/hydrophilic properties of the anode surface and to explore the impact of the hydrophilic group on the MFC performance. Fourth, CV indicated the oxidation-reduction ability of the different anodes. Finally, the biofilm on the anodes was studied using SEM to determine how the properties of the modified and unmodified anodes differed. All of the above parameters are evidence of the feasibility of improving the performance of anode by material modification.

2.5 Analysis and calculations

The crystal structures of the anode modifiers were examined by XRD using an ARL X'TRA X-ray diffractometer at room temperature, operated at 2.2 kW with a Cu radiation source. FTIR was used to characterize the functional groups. The procedure used was as follows: 1 mg of sample was ground with 100 mg of KBr before being pressed into a thin disc, the sample was then analyzed on a Nicolet iS5 FTIR spectrophotometer under N₂ with a KBr background. Water contact angle

measurements were used to investigate the wettability of the anodes using a dropmeter A-100. Distilled water droplets were used as the contacting liquid with the anode surface.

CV was used to characterize the electrochemical properties of the electrode by using a potentiostat (model LK3200, Gamry Instruments, LanLiKe. Co. Ltd., China) with a conventional three-electrode configuration: the anode acted as the working electrode, the reference electrode consisted of a Ag/AgCl electrode (218 Leici. Co. Ltd., China), and a platinum foil (2×2 cm) served as the counter electrode. CV was performed at scan rate of 10 mV/s and from -0.8 to 0.2 V in a 50 mM PBS electrolyte.

The morphological characteristics of the modified and unmodified anode were obtained using a scanning electron microscope (SEM) after inoculation. The pretreatment of the inoculated sample was carried out as follows: A 0.5 cm^2 sample (cut from the anode) was stabilized in a 3.0% glutaraldehyde solution for 1.5 h in a 4 °C refrigerator. The sample was rinsed with phosphate buffer three times and then dehydrated by successively immersing in a series of graded ethanol and isoamyl acetate twice. The sample was then dried at the CO_2 -critical point for 8 h and sputter-coated with a thin layer of gold. The sample was then observed using an environmental scanning electron microscope (Autoflex speed, Brooker) at an acceleration voltage of 30.0 kV.

The voltage across a 1000Ω external resistor was recorded per min with a data acquisition system (Hpu100-F, HePu. Co. Ltd., China). Polarization curves were obtained using the single-cycle method by applying a serious of external circuit

resistances to the MFC circuit (from 2000 to 40 ohms) during a fed-batch operation at its maximum potential [27]. The current density (A/m^2) was calculated as $I = U / (R_{ex} S)$, and the power density (mW/m^2) was calculated according to $P = 1000U^2 / (R_e S)$, where U (V) is the voltage, S (m^2) is the projected surface area of the anode electrode, and R_e (Ω) is the external resistance.

Coulombic efficiency (C_E) is the ratio between the electrons recovered as current relative to the total number of available electrons from the substrate consumption. The evaluated CE was calculated using the following Equation:

$$C_E = \frac{8 \int_0^t I dt}{F V_L \Delta COD}$$

where 8 is a constant based on the molecular weight of oxygen (32 g/mol) and the number of moles of electrons transferred per mole of O_2 consumed of 4, $I = U / R_e$, t is the time of a cycle (s), F is Faraday's constant (96485 C/ (mol $\times e^-$), V_L is the volume of the reactor (L), and ΔCOD is the change in the chemical oxygen demand. The COD of the solution at the beginning and end of each batch was measured using a standard method [28].

3 Results and discussion

3.1 Structure analysis of the MnO_2 /HNT nanocomposites

XRD was first employed to confirm the successful fabrication of the MnO_2 /HNT composite. The crystalline structures of the pristine HNT, MnO_2 , and the MnO_2 /HNT nanocomposites are shown in Fig. 2. For the pristine MnO_2 sample, three well-defined peaks are observed at approximately $2\theta = 12.28^\circ$, 36.8° and 65.7° , attributable to

δ -MnO₂ (JCPDS no. 18-0802) [22]. The external surface of the HNT (Al₂(OH)₄Si₂O₅ n H₂O) consisted of siloxane (Si–O–Si) groups, while the internal surface was composed of a gibbsite-like array of aluminol (Al–OH) groups. The characteristic peaks of native halloysite appeared at approximately $2\theta = 12.1, 20.1, 35.0^\circ$ (JCPDS no. 29-1487), which corresponds to halloysite-(7 Å) [29]. The characteristic peaks of quartz (SiO₂, $2\theta = 26.6^\circ$) and alumite (KAl₃(SO₄)₂(OH)₆, $2\theta = 29.8^\circ$, JCPDS no. 71-1776) can also be observed [30]. From Fig. 1, a characteristic peak at approximately $2\theta = 29.8^\circ$ is also observed in the MnO₂/HNT composites, indicating that the MnO₂ was loaded onto the surface of the HNTs. Additionally, it is noted that with an increasing MnO₂ content, the peak at a $2\theta = 29.8^\circ$ gradually decreases. These observations indicate that the MnO₂/HNT composites were successfully synthesized.

Fig. 2

The FTIR spectra of HNT, MnO₂, and 75 wt% MnO₂/HNT are shown in Fig. 3. The peak at 1635 cm⁻¹ is attributed to the O–Mn–O stretching vibration, indicating the presence of the MnO₂ crystal cell. Characteristic groups of HNTs were also observed in the FTIR spectra. The peaks at 1035 and 1180 cm⁻¹ can be assigned to the bending absorption of the Si–O group, and the stretching absorption bands of the Al–OH group was observed at 920 cm⁻¹. In addition to the peak at 3622 cm⁻¹, the 3696 cm⁻¹ peak was attributed to the stretching vibration of the hydroxyl groups present on the surface of the HNTs, which may have a positive effect on the absorption of microorganisms. Additionally, characteristic groups of the HNTs and MnO₂ can be observed in the 75

wt% MnO_2/HNT nanocomposite, further indicating the successful synthesis of the MnO_2/HNT composites.

Fig.3

3.2 Morphology analysis

A commercial clay HNT was selected as an example of parent support for preparing the crystalline heterogeneous inorganic/metallic nanocrystal-halloysite composite nanotubes. SEM was performed to observe the morphology and microstructure of MnO_2/HNT composites. The SEM images were presented in Fig. 4. It can be seen that the prepared MnO_2 (Fig. 4a, 4b) without HNT exhibits agglomerating and anomalous particles. The natural halloysite nanotube predominately composed of a lot of cylindrical nanotubes and a small amount of agglomerates. Meanwhile the MnO_2/HNT composite was fluffy which improve the dispersibility of MnO_2 reduced its' agglomeration, and the MnO_2 grew on the surface of the HNT. This may due to the different charged outer/inner surface of halloysite nanotube. This resulted mostly in a positively charged Al_2O_3 inner with a negatively charged SiO_2 outer surface. Thus, the negatively charged SiO_2 outer surface of the HNT could adsorb the positively charged growing crystalline MnO_2 species, which could induce the MnO_2 nanocrystals to grow onto the halloysite in situ [31]. Hence, the MnO_2/HNT composite improves the connectivity of MnO_2 particles and thus the conductivity.

Fig.4

3.3 Electric performance of the MFCs with different modified anodes

3.3.1 Electricity generation

The efficiency of a single MFC equipped with HNTs, MnO_2 , 25 wt% MnO_2/HNT , 50 wt% MnO_2/HNT , and 75 wt% MnO_2/HNT were evaluated by comparison to the MFC with the unmodified anode under the same conditions. In this system, each batch was repeated a minimum of three times to ensure repeatability and accuracy. As observed from Fig. 5, a steady voltage is generated in the 3rd hour after closing the circuit, and the substrate exhausted after 38 h. The results obtained indicate that the anodes generate electricity in the order of 75 wt% MnO_2/HNT > 50 wt% MnO_2/HNT > 25 wt% MnO_2/HNT > MnO_2 > HNT > unmodified. A relatively minor difference among the observed voltages of the different electrodes tested was observed after operating for 190 h, which implies the long-term stability of the developed anodes. Table 1 summarizes the results obtained for the MFCs using modified anodes in comparison to the unmodified anode. The 75 wt% MnO_2/HNT anode presents the highest electrochemical performance with an output voltage of 663 mV. The coating of the HNT anodes compared to the bare carbon cloth resulted in an increase in the output voltage of 605 and 589 mV, respectively. In the MnO_2/HNT nanocomposites, the maximum voltage output was substantially increased as the percentage of MnO_2 was increased from 25 to 50%. These results were consistent with the cyclic voltammetry measurements (see Fig. 8).

In real life, there are a few of portable or small size electrical devices driven with low voltage direct current, such as cell phone, laptop, micro-sensor etc, which offer the promising way for the application of electricity generated by MFCs. Ieropoulos

et.al [32] reported that telephone batteries can be directly charged by a stack of MFCs feeding on urine. Recently, a self-sufficient system, powered by a wearable energy generator based on MFC is reported to acquire the electricity from the utilization of wastewater [33]. The higher the output voltage of MFCs is, the smaller the relevant size of device will be, which benefits for the portability of device. It is significant that the power output of MFCs is raised to improve the actual applicability by anode modification in this study.

Fig. 5

Table 1

3.3.2 Removal of organic compounds and coulombic efficiency of the MFCs

CE is one of the key parameters used to evaluate the capacity of MFCs for converting the chemical energy of the organic matter into electric energy. The potential chemical energy is released by biodegradation on anode in form of electrons transferring from in vivo to physical anode. The excellent performances on organic compounds biodegradation are obtained and shown in table 1 in terms of COD removal efficiency higher than 90%. Electron transfer will be the limited step to influence the electricity generation because of the inner property of physical anode. The modification on anode is recognized as the technological way to improve the ability of electron capture and transfer producing from organic compounds biodegradation.

After 4 weeks of operation, the CE of the bare carbon cloth, HNTs, MnO₂, 25 wt% MnO₂/HNT, 50 wt% MnO₂/HNT, and 75 wt% MnO₂/HNT modifier-based MFCs was estimated to be 6.34, 6.58, 6.72, 7.03, 7.27, and 7.65%, respectively. These

results are consistent with the electricity generated. Obviously, the CE of MFC modified by 75 wt% MnO₂/HNT was 20.7% higher than of the controlled MFC. Generally, the CE is relatively low in our experiments and it is likely that oxygen penetrated through the cathode and diffused into the anode chamber, which would make the anodic operation partially aerobic and consequently, many substrates degraded through fermentation and without generating electricity. Furthermore, electron transfer is generally hampered by various losses that reduce the output voltage of MFCs [34]. The electron transformation needs to overcome various barriers including biocatalyst (bacteria) to anode and activation losses.

The CE is still exhibited to be low although the advanced modification on carbon cloth has been processed. However, in view of the great performance on COD removal, the MFCs model can be adopted in large scale wastewater treatment plant, which will generate a larger power output. The numerical relationship between energy and COD in organic matter can be presented by following equation:

$$P = \frac{\text{COD} * V * 14.7}{3600 * 24} * \text{COD}_{\text{removal}} * \text{Energy Recovery} \quad [35]$$

There, the 14.7 was the energy content values (KJ/g COD) [36], V (L) was the volume of wastewater. The unit of COD and power was g/L, Kw respectively. Here, for example, the capacity of wastewater plant is set as 10000t/day with influent COD 3000mg/L. Basing on COD removal (93.1%) energy conversion rate(7.65%) as 75 wt% MnO₂/HNT, the total power output can be estimated by the equation above to be 363.5kw. The generated electricity can be adjusted to be applied for the regular illuminating lights or low power electric system in wastewater plant.

3.3.3 Power density–current density and voltage–current curves

Voltage–current and power density–current density properties of the MFC indicate the optimal current or voltage ranges at which the MFC should be operated to maximize the power generation. Prior to measuring the polarization, the MFC was stabilized at the maximum steady voltage for half an hour after opening the circuit. All experiments were operated at least for 3 times. The open circuit voltage (OCV) of the six MFCs exhibited no remarkable difference (~ 0.75 V), and the power density versus current density curves are presented in Figure 4A. The unmodified anode MFC delivered the least power density of 631.0 mW/m^2 , 4.1% less than the MFC with a HNT anode (658.6 mW/m^2). The concentration of MnO_2 significantly affects the power performance with the maximum power density improved on increasing the percentage of MnO_2 from 25 to 75%. The power density generated by MFC-25 wt% MnO_2/HNT , MFC-50 wt% MnO_2/HNT , MFC-75 wt% MnO_2/HNT was 717.3, 734.1 and 767.3 mW/m^2 , respectively. This shows that the power density produced by the MFCs with a MnO_2/HNT composite at all MnO_2 concentrations tested from 25 to 75% is higher than the MFC with an unmodified anode by 13.7, 16.3, and 21.6%, respectively. A power density of 658.6 mW/m^2 was obtained for the MnO_2 anode. It is clear that the MFC performance can be significantly improved using a modified anode, and the 75% MnO_2/HNT composite proved to be the most effective modifier tested.

The voltage–current curves of the different MFCs are shown in Fig. 6B. The slope of the voltage–current curve is the internal resistance (R_{in}) [37]. According to

the voltage–current curves, as the unmodified MFC exhibits the steepest slope, the corresponding internal resistance is highest. Two major parts that contribute to the R_{in} are the solution resistance and the anode mass diffusion resistance [38]. As the MFCs used in this research study possessed equivalent configurations (e.g., cathode material, substrate, electrode distance, and dimension), the differences in the R_{in} can be attributed to the various anodes used. For the anode, its performance was limited by i) the diffusion coefficient of the substrate to the bacteria that adhered onto the anode electrode; ii) the electron transfer rate of the cells to the anode through direct contact or through some mediator; and iii) the electron transfer among cells. However, the ‘mass transport limited’ current value is approximately 50 mA/cm^2 , and the reported current density of MFCs is $0.5\sim 1 \text{ mA/cm}^2$. This means that the electron transfer rate is the key obstacle [39].

From Table 1 and Fig. 6(B), the 75 wt% MnO_2/HNT anode shows the highest electrochemical performance and the lowest internal resistance. The lowest internal resistance may be due to the presence of MnO_2 , which generates a higher anode capacitance. The higher capacitance stabilizes the performance of the anode and affects the power output. This also supports that MnO_2 is electroactive and interacts with the bacteria. This allows MnO_2 to promote the extracellular electron transfer of the electrochemical reaction [40]. Fu [16] explored the synergistic mechanism of Mn ions as an electron transfer shuttle and the redox reaction between modified anodes and bacteria. Briefly, an electron of Mn (IV)/Mn (II) is formed in the anodic interface between the modified anode and bacteria biofilm to improve the kinetic activity due

to the microbial action of Mn-related bacteria. However, the δ -MnO₂ exhibits agglomerating and anomalous particles (see fig.4), which may reduce the effective specific surface area. The porous structure of HNT results in the uniform dispersion of MnO₂ particles throughout the HNT support, which provides a large specific surface area that promotes the performance of MFCs.

3.4 Wettability of the anode surface

Contact angle measurements are important to characterize the hydrophilicity or hydrophobicity of the material surface. Often, when the contact angle is more than 90 °, the material is considered to be a hydrophobic surface; otherwise, it is considered to be hydrophilic. In Fig. 7 (A), a photograph is shown of the water droplets on the unmodified anode surface in a static state. In Fig. 7 (B) and 7 (C), graphs exhibiting the relationship between the time and the dynamic angle are shown. The water droplet maintained a steady state on the unmodified anode surface, and the angle did not change with time (~136 °). When compared to the unmodified anode, the water droplet immersed the 75 wt% MnO₂/HNT anode surface quickly, and the angle decreased with time (from 62.6 to 0 °). These observations suggest that the modifier results in the formation of a hydrophilic surface as a consequence of the –OH hydrophilic functional group of the HNT (see Fig. 3).

Fig. 7

The HNT hydroxyl groups facilitate the adsorption of bacteria. Long-range forces (e.g., hydrophilic interactions of the anode material, electrostatic interactions between the bacteria and functional groups, van der Waals interactions) and

short-range forces (e.g., hydrogen bonding) influence the bacterial adhesion [41]. The hydroxyl groups make the surface more approachable for the planktonic bacterial species due to improved hydrophilic interactions. On the other hand, it may develop hydrogen bonds, resulting in bacterial adhesion to the anode electrode [42].

3.5 Kinetic characteristics of the different anodes

CV is a standard tool used in electrochemistry and has been extensively exploited to study and characterize the electron transfer interaction between microorganisms and the electroactivity of microbial biofilms and microbial fuel cell anodes [43-44]. In this study, CV was used to characterize the oxidation-reduction reaction of the anode biofilm. The cyclic voltammogram is composed of a reverse and forward scan to produce a positive and negative curve, which corresponds to the reduction and oxidation reaction.

The CV of the MnO_2/HNT -based modified carbon electrode in a 50 mM PBS solution was compared to the CV of the unmodified carbon cloth to evaluate the electrochemical performance of the anodes. As shown in Fig. 8, reduction peaks were observed at -0.31 and -0.51 V in the reverse scan, and an oxidation peak at -0.29 V was observed in the forward scan. The peak potential value remains unchanged in all MFCs with different modified anodes. This result indicates that the electrochemical activity is likely a consequence of bacteria [45]. The nature and role of the -0.51 V reduction peak has not been clarified, and one may speculate that it is associated with redox-active compounds of the cell itself or its surrounding extracellular matrix [44]. This means that the biological matter undergo more than one redox reaction at the

anode surface. From the CV curves, the MFC with a 75% MnO_2/HNT modified anode showed a maximum peak current output of 6.8 mA, while the MFC with a bare carbon cloth anode displayed a minimum peak current output of 2.0 mA. The MFC with the 75% MnO_2/HNT modified anode displayed the highest electrochemical activity over all anode biofilms explored, as seen by the relative peak intensity of the CV curves [46].

Fig. 8

3.6 Morphology of the anode biofilms

SEM was used to investigate the morphological characteristics of the bacteria on the biofilm. The differences in the bacterial morphology of the two anodes (unmodified anode and 75 wt% MnO_2/HNT anode) were observed by SEM at the end of the test. As figure 1 (B) showed, the modified anode was composited with 3 layers including carbon cloth, modifier layer and biofilm, hence, the characteristics of the modifier was very important to biofilm. Generally, the roughness of anode material affected the bacterial adhesion. From Fig. 9A, it is clear that bacteria were loaded onto the surface of the carbon fibers as well as coating the carbon cloth in intervals, while the carbon fibers which were bare and without any bacteria were smooth. The bacteria are responsible for the electron transfer and current generation in MFCs. On the surface of the unmodified anode, the biofilm was heavily inhabited by microbial communities of homogeneous coccoid cells ($\sim 0.56\text{-}1.48\text{ }\mu\text{m}$ diameter). However, the anode modified with 75 wt% MnO_2/HNT was rod-shaped (see the red circle in Fig. 9 (B), the bacteria were $1.48\text{-}\mu\text{m}$ long with a $0.6\text{-}\mu\text{m}$ diameter) and coccoid-shaped.

Besides, the nanostructure of amorphous MnO_2/HNT can be observed and this made the surface of anode to coarse, which make the bacteria much densely adhered than unmodified anode. The 75 wt% MnO_2/HNT anode exhibit effective bacterial attachment, and thus hydroxyl functional groups on the surface of the electrode appear to play a significant role in bacterial-cell adhesion. All of this indicates that the modifier can change the carbon cloth surface and the bacteria shape, which contributes to the performance of MFCs.

Fig. 9

4. Conclusions

In this study, MnO_2/HNT nanocomposites were initially fabricated and utilized as an alternative to modify the anode in MFCs. The MFCs with the 75 wt% MnO_2/HNT anode exhibited the better performance compared to the other anodes tested. The MnO_2/HNT nanocomposites delivered a higher electroactivity may be the homogeneous dispersion of MnO_2 over the surface of the HNT, which increased the bioaccessible surface area and facilitated the electron transfer. The synthetic materials greatly changed the electrode surface structure and introduced hydroxyl functional groups. The wettability of MnO_2/HNT was enhanced due to introduce hydrophilic groups. The hydrophilic interactions of the surface hydroxyl groups facilitated bacteria loading, which benefit the power density and voltage output. Furthermore, the SEM images showed that the biofilm attached onto the modified anode surface consisted of homogeneous coccoid and rod-shaped bacteria while the unmodified

anode consisted only of homogeneous coccoid bacteria. These observations indicate that the MnO₂/HNT nanocomposites affect the biofilm formed.

As the primary materials in this study, the cost of MnO₂ and HNT are lower owing to the wide distribution on the earth compared to precious metals [47] and carbon nanotubes [48]. Meanwhile, the power density of MFCs modified with 75 wt% MnO₂/HNT nanocomposites has been increased by 21.6% higher than the unmodified anode. It is a promising and economical technology to be applied actually to harvest electricity with high efficiency from wastewater with the development of science of modern materials.

Acknowledgments

The authors would like to thank the National Natural Science Foundation of China (No.21106072 and 51172107), the Research Fund for the Doctoral Program of Higher Education of China (No. 20113221110004), and the Key Projects in the National Science & Technology Pillar Program of China (No. 2012BAE01B03) for their support of this study.

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Table

Table 1 Summary of the different anodes and cell performance.

Anodes	Maximum Voltage (mV)	Power density (mWm ⁻²)	Coulombic efficiency (%)	COD removal (%)
Unmodified	589	631.0	6.34	92.7
HNT	605	658.6	6.58	92.1
MnO ₂	614	691.3	6.72	90.7
25 wt%	632	717.3	7.03	92.3
MnO ₂ /HNT				
50 wt%	640	734.1	7.27	92.7
MnO ₂ /HNT				
75 wt%	663	767.3	7.65	93.1
MnO ₂ /HNT				

Figures

1. Anode. 2. Cathode 3. Inlet. 4. Outlet. 5. Reference electrode. 6. Resistor.
7. Data collector. 8. Computer.

Fig. 1. (A) Schematic diagram of MFC and (B) Exaggerated side-view of a modifier anode

Fig. 2. X-ray diffraction patterns of (A) HNT, (E) MnO_2 and MnO_2/HNT nanocomposites with different MnO_2 contents: (B) 25 wt%, (C) 50 wt%, and (D) 75 wt%.

Fig. 3. FTIR spectra of the modified anodes.

Fig. 4. SEM images of the pure MnO_2 (A, B), natural halloysite nanotube (C) and 75 wt% MnO_2/HNT

Fig. 5. Voltage-time curves of the MFC with different anodes: (1) unmodified, (2) HNT, (3) MnO_2 , (4) 25 wt% MnO_2/HNT , (5) 50 wt% MnO_2/HNT , and (6) 75 wt% MnO_2/HNT after start up.

Fig. 6. (A) Power density–current density and (B) voltage–current curves for different anodes.

Fig. 7. Image of the contact angle measurement of unmodified anode (A) , the measured contact angle with time for a water droplet on the unmodified anode (B) and on the 75 wt% MnO_2/HNT modified anode (C).

Fig. 8. Cyclic voltammograms (10 mV/s) of bare and modified carbon cloth surfaces in a 50 mM PBS solution (CVs were obtained from the second cycle).

Fig. 9. SEM images of the unmodified anode (A) and the 75 wt% MnO_2/HNT -modified anode (B).