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CARBON NANOTUBES AND CARBONIZED POLYANILINE NANOSTRUCTURES AS 3D MODIFIED ANODE FOR MICROBIAL FUEL CELLS

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Abstract. This paper presents an approach of improving power generation of microbial fuel cells (MFCs) by using three dimensional (3D) anodes modified with commercial carbon nanotubes (CNTs) and nitrogen-containing carbon nanostructures derived from polyaniline (PANI) precursors. The materials used for anode modification were characterized using X-ray photoelectron spectroscopy (XPS), Raman Spectroscopy and Scanning Electron Microscopy (SEM). The power output, chemical oxygen demand (COD) and biological oxygen demand (BOD) of two-chamber MFCs with 3D modified anodes were compared. Results showed that the maximum power density of 3D anodes modified with nitrogen-containing carbon nanostructures could reach 17.8 mW/cm^2 compared with MFC anode modified with commercial CNTs. The inflow and outflow wastewater analysis show that both MFCs units lead to an improvement of wastewater quality with a better performance for the MFCs using 3D anode modified with nitrogen-containing carbon nanostructures.

Key words: microbial fuel cells, nitrogen-containing carbon nanostructures, carbon nanotubes, polarization curves, wastewater treatment.

1. INTRODUCTION

Microbial fuel cell (MFC) is a promising alternative technology for wastewater treatment and self-sustained electricity generation via microbial metabolism. Relatively low power density and high installation costs associated with fabrication and operation processes are the main limitations for large-scale application of MFCs. One of the main factors affecting the overall performance of MFC is the anode materials, which is influencing the bacterial attachment, electron transfer and substrate oxidation.

Previous researches have successful applied the anode modification with nanomaterials as an important strategy for the improvement of MFC performance [1]. Among different modification strategies, anode modification with carbon nanotube (CNTs) and CNTs based composite positively influence the MFC performance. High surface area to volume ratio and electrical conductivity are the main properties of CNTs-based materials, which in the anode side improves the electrocatalytic activity of bacteria by enhancing cell adhesion, mass transfer of nutrients and facilitate biofilm formation [2].

Recent developments of electrode materials explored the advantages of 3D macroporous based-anode which can provide large surface area for reaction, minimizing the anode energy loss in the MFC system and increasing the MFC power density output [1, 3, 4]. 3D macroporous structure can provide an open 3D space available for internal bacterial colonization and efficient transport of substrates, minimizing the anode energy loss in the MFC system [5, 6]. A number of 3D bioanodes such as CNTs–textile [3], CNTs-sponge [4], chitosan/vacuum-stripped graphene scaffold, [7] polyaniline (PANI)/graphene-coated nickel foam, [8] graphene-sponge [9] and 3D graphene-coated nickel foam [10], reduced graphene oxide and carbon nanotube (rGO-CNT) sponges [11] have been reported as a promising alternative for improving the power generation of MFC devices.

On the other hand, nitrogen-containing carbon materials have drawn much attention due to their excellent electrocatalytic activities as well as low cost, good durability, and environmental friendliness. MFCs anode based on nitrogen-containing carbon materials could improve the charge transfer efficiency, bacterial biofilm loading and as a consequence the power generation of MFC [12–15]. Thus, the preparation of conducting-polymer nanostructures has been systematically investigated in recent years [16, 17] especially due to their conversion in nitrogen-containing carbon nanostructures, preserving the morphology of the polymer precursors [18, 19].

The purpose of the present study is the investigation of the MFCs performance of modified commercial sponge with commercial CNTs and nitrogen-containing carbon nanostructures derived from polyaniline as 3D based-anode in terms of bioenergy production and wastewater treatment.

2. EXPERIMENTAL DETAILS

2.1. Materials

Commercial carbon nanotube (CNT) with diameters between 20 and 40 nm and purity > 97% were purchased from Shenzhen Nanotech Co. Ltd. All other chemicals, aniline, ethanol, acetic acid and ammonium peroxydisulfate were purchased from Sigma Aldrich.

2.2. Material Synthesis

Polyaniline nanostructures (PANI) were synthesized using a template-free self assembly-methods reported by Huang et al. [20]. The reaction medium is a mixed solution of 0.4 M acetic acid and 0.4 M ethanol. A volume of 1.82 mL of aniline monomer and 5.71 g ammonium peroxydisulfate were dissolved in 100 mL of mixed solution. Both solutions of aniline and oxidant were cooled at 0-5 °C for 30 min and then poured rapidly into a beaker, stirred vigorously for 30 s. The mixture was left still to react for 10 h at 0°C. The product was filtered and washed with deionized water and finally dried in air for 24 h to obtain the PANI. The corresponding carbon nanostructure is obtained by a thermal treatment at 900 ^{0}C under nitrogen atmosphere. The carbonized samples are denoted as PANI-900.

2.3. Material Characterization

X-ray photoelectron spectroscopy (XPS) and micro Raman Spectroscopy were used to characterize the samples used for anode modification. XPS was done using a Kratos Axis Nova instrument, using monochromatic Al Ka X-rays (1486.69 eV). Raman spectra were collected on a Renishaw InVia Raman microscope with Argon laser excitation at 514.3 nm and 2 μm diameter spots with neutral filters limiting laser power. In order to exclude the temperature effects a very small laser power of about 0.3 mW was applied. The morphology of nitrogen containing carbon nanostructure (PANI-900) was investigated by Scanning Electron Microscopy (Carl Zeiss, Germany).

2.4. Microbial fuel cell setup, operation and characterization

A typical double-chamber MFC separated by a proton exchange membrane (PEM) (Nafion 117, Dupont, USA) were used for the evaluation of MFC performance. The volume of both chambers was 250 mL. The anode consisted of commercial sponge modified with CNTs (MFC1) and PANI-900 (MFC2). In both cells the carbon cloth cathodes modified with 40% Pt/C were used. 1kohm resistor completed the external circuit. The anode chambers were inoculated with municipal wastewater (Bucharest-Magurele, Romania) and maintained under anaerobic conditions, while the catholyte consisted of phosphate buffer (pH 7, 0.05M) which was purged with bubbling air during the operation. Wastewater sample was kept in a refrigerator at 4 ^{o}C, when not in use. The MFCs were operated under the fed-batch mode condition and the anolyte was replaced after the voltage drop below 50 mV. Pico Data Logger ADC-24 was used to record the cell voltages over the time for on each cell.

The performance of the MFCs was evaluated by measuring current, current density, potential and power density along with Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) removal efficiency. The polarization and power density curves were obtained by varying the external resistor from 0.5 MΩ to 10Ω. Current density (I) was calculated as $I = V$ (cell) voltage)/R (external resistance), and power density (P) was calculated as $P = I \times V$. Both I and P were normalized to the effective projected area of the anode surface as outlined by Logan et al. [21]. COD and BOD of both, the MFCs influent and effluent, were used to evaluate the efficiency of wastewater treatment through the MFC system and measured by the standard methods for water and wastewater [22].

3. RESULTS AND DISCUSSIONS

The SEM images of carbonized polyaniline nanostructures with different magnification show a tubules-like morphology as presented in Fig. 1.

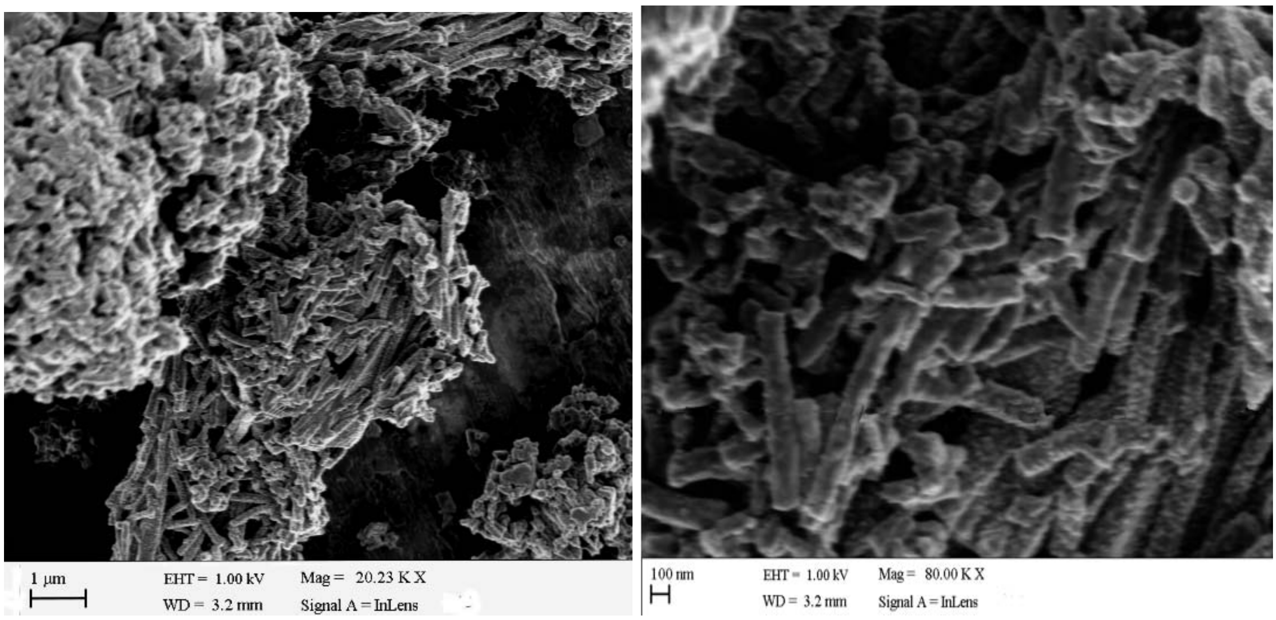

Fig. 1 – SEM images of PANI-900 with different magnifications.

The chemical composition from XPS data of commercial carbon nanotubes, PANI and PANI-900 are presented in Table 1. The chemical composition from XPS data of commercial CNTs shows the presence of C1s (284.08 eV) and O1s (532.08 eV). Compared with chemical composition of CNT, in the case of PANI and PANI-900 additional contribution of nitrogen is observed for both samples, with a subsequent reduction of oxygen content for PANI-900 due to the thermal treatment.

Table 1

Chemical composition of CNT, PANI and PANI-900 samples

Sample	**C1s**		**O1s**		**N1s**		**S2p**	
	BE (eV)	**(at%)**	**BE (eV)**	**(at%)**	**BE (eV)**	**(at%)**	**BE (eV)**	**(at%)**
CNT	284.1	98.3	532.1	1.66	–	–	–	–
PANI	284.5	77.5	530.5	11.5	398.5	8.1	168.5	2.79
PANI-900	284.5	88.1	532.5	4.8	400.5	7.1	–	–

The Raman spectra, comparing commercial CNTs and PANI-900 are shown in Fig. 2. The Raman spectra of the investigated samples display the characteristic features of carbonaceous materials with two maxima corresponding to the Raman active D and G-bands [23].

The D-band is due to the breathing vibrations of sp^2 sites in the aromatic rings and it is commonly associated with structural defects and reduction in symmetry due to the incorporation of hetero-atoms inside the graphitic lattice and the G-band is the primary Raman active mode caused by the E2g vibration mode of graphitic network [23, 24]. The ratio of integrated intensities of the two bands ($R = I_D/I_G$) is considered as a key parameter often used to characterize the degree of structural defects present in carbon based materials [24]. From the Raman spectra, the I_D/I_G ratio of CNTs and PANI-900 was 1.40 and 3.39 respectively, indicating a significant disorder in the structure of PANI-900, which can be due to the presence of nitrogen and oxygen atoms in the carbon structure. The *R* value of PANI-900 is similar with the results reported in the literature in the case of carbonized polyaniline [24, 26].

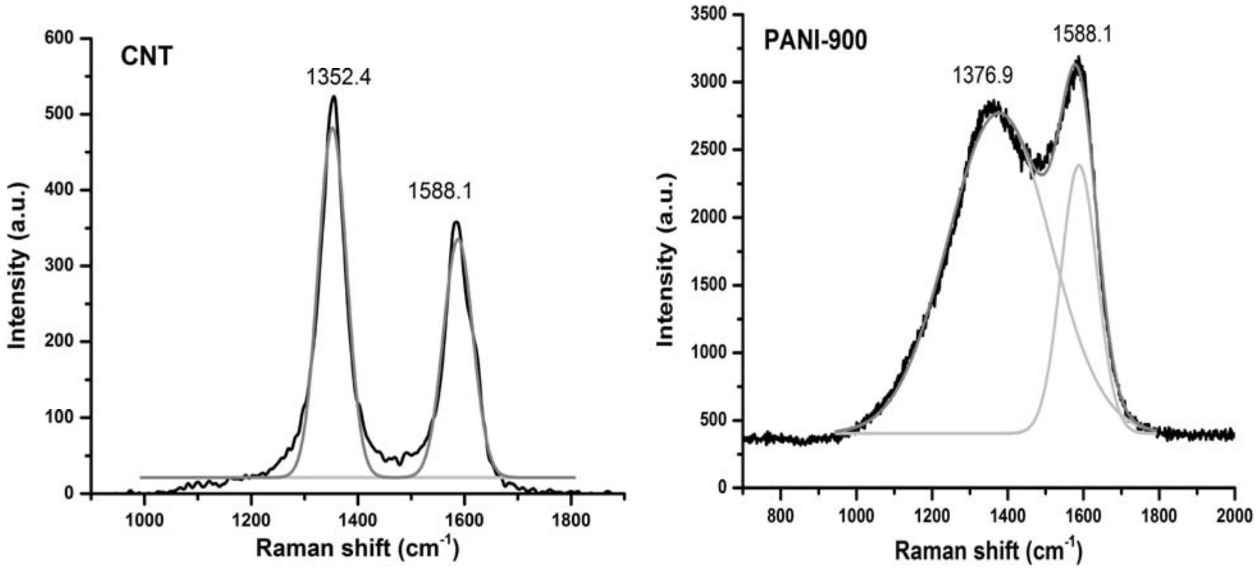

Fig. 2 – Raman spectroscopy of CNT and PANI-900.

The characteristics of the wastewaters for both MFC units compared with influent wastewater are shown in Fig. 3. In terms of COD inflow and outflow values, it can be clearly seen that ~69 % reduction of COD is achieved for MFC1 and ~76% for MFC2. From the inflow and outflow of BOD measurements decreasing concentrations of approximately ~79 % for MFC1 and ~87% for MFC2 were observed.

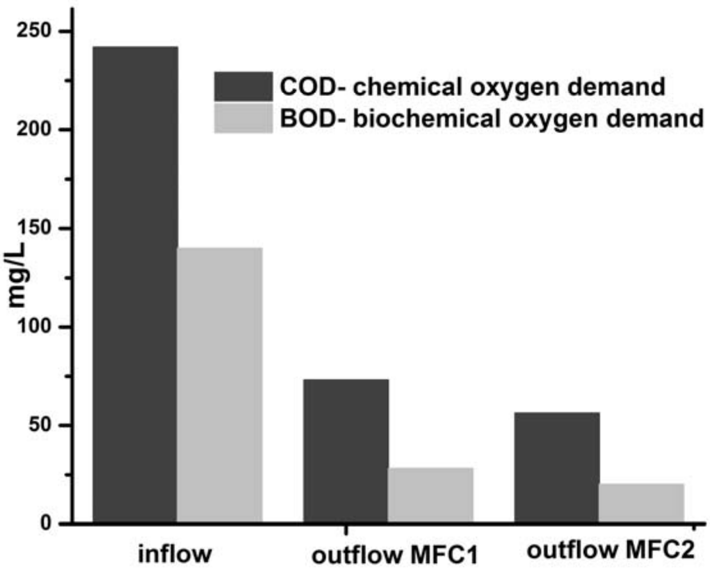

Fig. 3 – COD and BOD for influent and effluent for both MCFs units.

The polarization curves show the dependence of the cell voltage and power density versus current density, and are presented for both cells in Fig. 4. The maximum obtained open circuit potential was 776.3 mV for MFC1 (CNT) and 892.6 mV for MFC2 (PANI-900). In both cases, the power density increases with the increase of current density, reaches a maximum value, and then decreases with further increase in current density, which is a typical relationship of output power density against the current density.

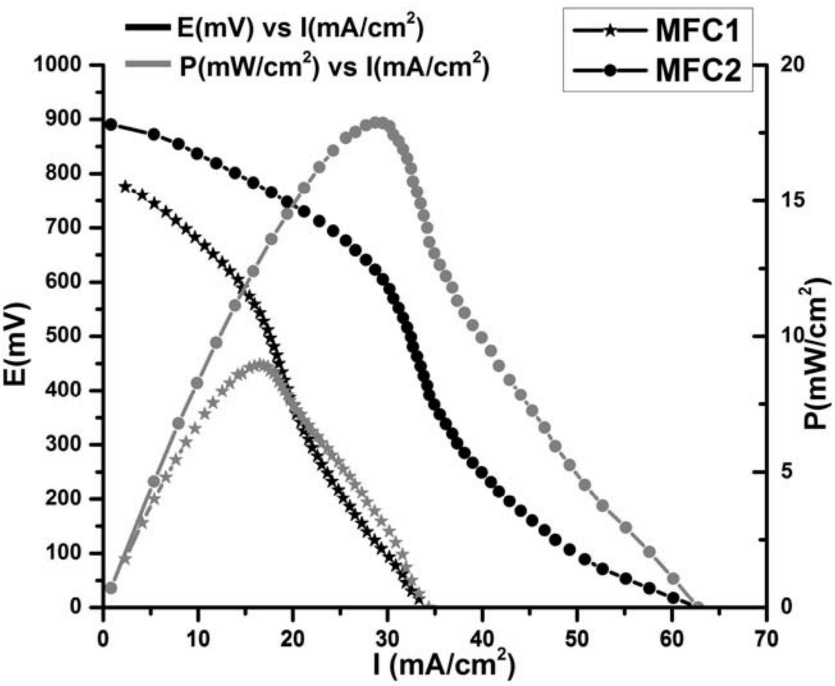

Fig. 4 – Power output and polarization curves of MCF1 and MCF2.

The polarization curves showed a maximum power density of 8.9 mW/cm^2, obtained for MFC1 and 17.8 mW/cm^2 for MFC2. Therefore, it can be concluded that the modification of 3D commercial sponge with PANI-900 gives a higher power density which is ~ 2 times higher than in the case of anode modification with commercial CNTs. According to XPS and Raman spectroscopy, the better performance of anode modified with PANI-900 can be attributed to the presence of nitrogen in the carbon nanostructure and to the structural defects and reduction in symmetry due to the presence of nitrogen inside the graphitic lattice.

4. CONCLUSIONS

The results of the polarization curves show that the MFCs with 3D-based anode modified with PANI-900 showed 2 times higher power production than 3D-based anode modified with commercial CNTs. The inflow and outflow wastewater analysis show that both MFCs units lead to an improvement of wastewater quality with over 60% COD removal efficiency and over 70% BOD removal efficiency. The better performance for the MFCs using 3D anode modified with PANI-900 is assigned with introduction of the nitrogen functionality on the surface as compared with commercial CNTs. As a conclusion, the modification of commercial sponge with nitrogen-containing carbon nanostructures is a promising strategy for development of low-cost and high performance anode that can be used in larger scale applications.

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