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Control of geometrical properties of carbon nanotube electrodes towards high-performance microbial fuel cells

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HIGHLIGHTS

- Providing systematic studies on the effect of CNT properties on MFC power generation.
- CNTs grown on stainless steel mesh (SSM) provide 3D surface for microbial biofilm.
- Longer and loosely-packed CNTs provide more sites for microbes to transfer charge.
- CNTs with minimum amorphous carbon improve electron transfer from microbes.
- CNT anode (3360 mW m^{-2}) produces 7.4 times higher power compared to carbon cloth.

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ABSTRACT

In microbial fuel cells (MFCs), physical and electrochemical interactions between microbes and electrode surfaces are critical to performance. Nanomaterial-based electrodes have shown promising performances, however their unique characteristics have not been fully utilized. The developed electrodes here consist of multi-wall carbon nanotubes (MWCNTs) directly grown in the radial direction from the wires of stainless steel (SS) meshes, providing extremely large three-dimensional surfaces while ensuring minimal ohmic loss between CNTs and SS meshes, fully utilizing the advantages of CNTs. Systematic studies on how different lengths, packing densities, and surface conditions of CNTs affect MFC power output revealed that long and loosely packed CNTs without any amorphous carbon show the highest power production performance. The power density of this anode is 7.4-fold higher compared to bare carbon cloth, which is the highest reported improvement for MFCs with nanomaterial-decorated electrodes. The results of this study offer great potential for advancing the development of microbial electrochemical systems by providing a highly efficient nanomaterial-based electrode that delivers large surface area, high electrochemical activity, and minimum ohmic loss, as well as provide design principles for next-generation nanomaterial-based electrodes that can be broadly applicable for highly efficient microbial electrochemical cells.

1. Introduction

Microbial fuel cells (MFCs) are sustainable “green” technologies that generate electricity by converting the biochemical energy of microbial metabolism into electrical energy [1,2]. However the

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current power performance of MFCs is not sufficiently high to make the technology commercially viable. Maximizing contact and minimizing electron loss between electrochemically active bacteria (EAB) and anodes of MFCs provide routes to improve MFC power performances and lowering the cost of MFCs [3]. A key event occurring at anode-microbe interfaces is electron generation by metabolically and electrochemically active microorganisms [4,5] followed by the transfer of generated electrons to anode surfaces through a combination of direct contact, microbial pili (or nanowires), and/or soluble mediators [6,7]. Regardless of the electron transfer routes, large electrode surface areas promote interactions between microbes (and their corresponding electron shuttle systems) while minimizing the internal electrical resistance.

Carbon cloth is a common electrode material for MFCs because of its relatively low cost and biocompatibility [8]. Three-dimensional (3D) carbon electrodes, in the form of electrospun carbon fiber electrodes [9] or carbon brush [10] electrodes are also used in MFCs, as their 3D structures can provide large surface areas for microbial attachment. However, these conventional electrodes have limited surface areas when compared to nanomaterial-based electrodes. Nanomaterials offer exceptionally large surface-to-volume ratios as well as unique electrochemical properties such as strong charge interactions with organic matter. Recently, various nanomaterials such as metal nanoparticles [11], carbon nanotubes (CNTs) [12–17], and CNT composites [18,19] have been used as additives to MFC anodes. For example, multi-wall (MW) CNTs were attached to carbon cloth, papers, or textiles by using simple dipping methods in CNT solutions to increase the electrical conductivity and surface area of electrodes, resulting in 20–150% enhancement in power density [12,15,17]. The observed improvements in power generation with these electrodes were thought to arise as a consequence of better interactions between EABs and electrodes mainly due to improved electrical conductivity and increased surface areas. Nevertheless, the influence of the physical and geometrical properties of these nanomaterials on power output has not been systematically studied. This analysis is of high importance as nanomaterials can have wide varieties of different physical and geometrical properties depending on their synthesis conditions, including those of CNT-based electrodes.

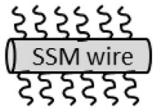
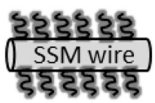
Notwithstanding large surface-to-volume ratios of CNTs, the aforementioned relatively low power improvement is likely to come from non-optimal use of nanomaterials. For instance, the dipping method makes CNTs lie on the surface of carbon cloth rather than stand erect on this substrate [17]. This configuration significantly impairs the full utilization of large surface-to-volume ratio of CNTs. In cases where CNTs are embedded in polymer composites, CNT surfaces are not fully exposed for charge interactions. These electrode designs also require electrically insulating (or poorly conducting) matrices (e.g., polymer binders) and/or surfactants for CNT dispersions. Thus, electrical contacts between CNTs themselves as well as between CNTs and host electrodes are often poor due to the presence of the intervening insulating organic matter. Here, we attempt to investigate how different lengths, packing densities, and surface conditions of CNTs used as anodes affect MFC power output, as well as propose a CNT-decorated anode configuration that maximizes electron transfer. We expect that this systematic study will result in design principles for developing next-generation nanomaterial electrodes.

2. Experimental

2.1. Synthesis of CNT electrodes

MWCNTs were grown on stainless steel (SS) meshes by using a water-assisted chemical vapor deposition (CVD) method. SS 304 and 316 meshes with 400 x 400 mesh size (opening width ~38 μm) and ~25 μm wire diameter (McMaster-Carr) were used as base electrodes. In order to control the physical properties of CNTs, different catalyst layers were prepared to have five different physical attributes of CNTs (Table 1). For samples S-LD, M-LD, and L-

Table 1
A list of CNT-SS mesh electrodes developed to understand how different attributes of CNTs affect MFC power performances.

Sample[a]		CNT length [μm][b]	Packing density	Surface condition
S-LD		~8	Low (loosely packed)	–
M-LD		~13	Low (loosely packed)	–
L-LD		~19	Low (loosely packed)	–
L-HD		~19	High (aligned)	–
M-LD-AC		~10	Low (loosely packed)	Amorphous carbon layer on CNT surface

[a] Sample name nomenclature: (length; S = short, M = medium, L = long) – (density; LD = low density (loosely packed), HD = high density and aligned) – (surface condition; none = pure CNT, AC = CNTs covered with amorphous carbon).
[b] CNT lengths were estimated by measuring the straight distance from the surface of mesh wires to the tip of CNTs. Actual lengths of the CNTs are likely to be longer than the numbers shown in this table due to the wavy morphology of CNTs.