Vertically Grown Multiwalled Carbon Nanotube Anode and Nickel Silicide Integrated High Performance Microsized (1.25 μL) Microbial Fuel Cell

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Supporting Information

ABSTRACT: Microbial fuel cells (MFCs) are an environmentally friendly method for water purification and self-sustained electricity generation using microorganisms. Microsized MFCs can also be a useful power source for lab-on-a-chip and similar integrated devices. We fabricated a 1.25 μL microsized MFC containing an anode of vertically aligned, forest type multiwalled carbon nanotubes (MWCNTs) with a nickel silicide (NiSi) contact area that produced 197 mA/m² of current density and 392 mW/m³ of power density. The MWCNTs increased the anode surface-to-volume ratio, which improved the ability of the microorganisms to couple and transfer electrons to the anode. The use of nickel silicide also helped to boost the output current by providing a low resistance contact area to more efficiently shuttle electrons from the anode out of the device.

KEYWORDS: Microbial fuel cell, carbon nanotube, nickel silicide, surface-to-volume ratio, power density

Microbial fuel cells (MFCs) are an innovative method for generating power that can also be used for treating wastewaters.1–3 Milli- to microliter scale MFCs provide a unique on-chip power source that could be used at a remote location or in lab-on-a-chip applications making external power sources or refined chemicals unnecessary.4 Microsized MFCs can also be used for rapid screening of electrode materials and electrochemically active microbes.5,6 Microsized MFCs offer high surface area-to-volume ratios, short electrode distances, and fast response times. Many nanomaterials are electrically conductive and biocompatible with microorganisms. Microfabrication techniques can therefore not only be used for precise and inexpensive production of these devices but also allow for direct incorporation of advanced nanomaterials, like carbon nanotubes, into the reactor.

The most versatile and frequently used anode materials are carbon-based. Different carbon forms have been used to increase surface areas and promote microbial adhesion to the surface, including graphite,6 carbon cloth,7,8 carbon paper,9 carbon foam,10 and reticulated vitrified carbon.11 Higher power production in MFCs is possible with increased surface area-to-volume ratios and novel anode designs.10,12 For example, graphite fiber brushes have been used to increase surface-to-volume ratios but their use in microsized cells is difficult due to their bulky architecture.12 Because of the unique electrical and structural properties of carbon nanotubes (CNTs), recent studies have included CNTs13–15 and CNT textiles16 in MFC anodes. Several other studies also use DC and AC electrochemical characterization of CNT-based electrodes, through cyclic voltammetry and electrochemical impedance spectroscopy (EIS), that show enhanced electrochemical properties compared with conventional materials.17–21

In order to enhance current generation in an MFC, we developed an anode containing a vertically aligned forest of...
pure multiwalled carbon nanotubes (MWCNT) in a 1.25 μL reactor (Figure 1). The vertically aligned MWCNTs were grown with controlled and uniform shapes and sizes using vapor–liquid–solid (VLS) self-assembly processes and microfabrication techniques. The specific materials and methods used for assembly of the entire MFC are described in the Supporting Information. The MWCNTs had a high surface area-to-volume ratio (66,000 cm⁻¹ before functionalization) that was expected to be helpful for bacterial colonization, and a high electrical conductivity (resistance of 2.1 mΩ m for a single nanotube) to enhance transfer of electrons to the anode surface. Other possible biological advantages of the MWCNT surface included increased biocompatibility, chemical stability, catalytic activity, and resistance to decomposition.16,22,23 Surface properties such

Figure 1. 3D Schematic and real images of the fabricated 1.25 μL microbial fuel cell. (a) Schematic (3D) of various components of the fabricated vertically stacked microbial fuel cell; (b) the digital image of the assembled microbial fuel cell in plexiglass clamp showed sidewise it occupying 5 cm on each side; and (c) transmission electron microscopic (TEM) image of nickel silicide region on top of silicon.

Figure 2. Scanning electron microscopic (SEM) images of CNT forest after growth and functionalization: (a) top view and (b) cross section at one edge of anode trench.

Figure 3. SEM images of bacterial growth after operation: (a) cross section view, (b) top view, and (c) zoomed top view show excellent compatibility with MWCNT and further colonization for enhanced performance. Images are taken after operation showing the sustainable nature of CNTs in context of mechanical and longevity perspective.
as hydrophilicity, hydrophobicity, and functional groups can affect cell adhesion, growth, and metabolism. A functionalization process was performed on the CNTs in which they were cleaned in an acid treatment (nitric and sulfuric acids) to remove residual metal catalysts and other impurities. The acid treatment also has been found to improve cell adhesion by thickening the MWCNTs in an oxidation process that generates carboxylic groups in the walls and tips of the MWCNTs, and forms 3D structures using capillary tensile forces, which make the MWCNTs collapse onto each other.  

After functionalization, the average height of the CNTs was 35 μm and their diameter ranged from 200 to 400 nm (Figure 2).

An MFC electrode requires a contact area to measure the voltage generated. In macro scale MFC designs, a titanium or stainless steel wire is often pressed to the electrode to provide contact with the surface. Here, we integrated a low resistance nickel silicide contact area onto the silicon surface so that the electrode contact point did not directly touch the anode. This method provided good electrical contact and avoided the need to make contact with the anode inside the solution chamber. The use of nickel silicide also enabled the entire fabrication process to be more state-of-the-art complementary metal oxide semiconductor (CMOS) compatible, allowing for rapid manufacturing and deployment as an on-chip power source.

The device was constructed using a highly doped silicon wafer in a specially designed microfabrication process (details and a summarized flowchart in the Fabrication section of the Supporting Information; Figure S1). Since the process to fabricate the microsized MFC did not use any unconventional or expensive materials (the MWCNTs were synthesized using nickel catalysts instead of conventionally used gold, for example), the use of CMOS compatible fabrication processes substantially decreased cost and fabrication times.

The MWCNT anode was tested for current and power generation using a mixed culture inoculum and a ferricyanide catholyte solution (see the Supporting Information for experimental and operational setup). MFCs were initially inoculated with wastewater then switched to an acetate nutrient medium after at least three stable cycles had occurred, indicating growth of a functioning biofilm on the anode (Figure 3). The anode chamber was operated in fed-batch mode, with fresh medium added when the current decreased to <0.5 μA. The ferricyanide catholyte was continuously pumped through the cathodic chamber. Current started to increase immediately after initial acetate introduction but showed stabilized cycles after the second acetate feed, approximately 15 h later (Figure 4). The current reached initial stable peaks of 2 μA within 5 h after anolyte addition. Following acclimation, repeatable cycles of current generation were obtained that lasted between 10 and 13 h. After only 1.7 days following the initial addition of the acetate medium, the maximum repeatable current was reached of 3 μA.

The total energy loss in the system can be understood in terms of the different internal resistances as seen in the equation

\[ V_{\text{Device}} = OCV - IR_{\text{int}} = OCV - I(R_a + R_m + R_c + R_e) \]

where the internal resistance \( R_{\text{int}} \) consists of the sum of the anode \( R_a \), membrane \( R_m \), cathode \( R_c \), and electrolyte \( R_e \) resistances. Minimizing these resistances provides higher power densities from the cell. The total internal resistance was estimated to be \( R_{\text{int}} = 25 \text{ kΩ} \), based on the slope of the linear section of the polarization curve (Figure 5). This value is the same as that obtained based on the peak in the power density curve. To compare the performance with a widely used MFC anode, carbon cloth, we also set up 28 mL cube- MFCs (14 mL anode chamber) in which we tested the same size anode when stable cycles began.

![Figure 4](image-url) Current generation vs time plot showing a steady rise in current and short start-up time. Arrow marks show the acetate inoculation moment. Data shown 15 h after initial acetate introduction when stable cycles began.

![Figure 5](image-url) Polarization plot of the 1.25 μL MFC.
exchange membrane (PEM) area was 5 mm × 5 mm. Based on these values, $R_e = 6.4 \, \Omega$. Multiplying this resistance by the maximum current achieved (4.43 $\mu$A) results in an estimated energy loss of only 28 $\mu$V for the electrolyte solution. Reported area resistances for the Nafion 117 membrane are in the range of 0.09 to 0.35 $\Omega$ cm.$^{1-25}$ Assuming the highest value for Nafion, the membrane resistance in the phosphate buffer solution is estimated to be $R_m = 1.4 \, \Omega$ or a loss of 6.20 $\mu$V for the membrane. Therefore, the combined losses due to the membrane and solution would be only 34.2 $\mu$V. This is negligible compared to the total energy loss at 134 mV (OCV 243–109 mV at the maximum power). Thus, the anodic and cathodic resistances were responsible for almost the entire 25 k$\Omega$ of internal resistance. Reducing the electrode resistances is therefore a goal for improvement of future designs. Part of an improved resistance design includes improving the contact area resistances. The resistance between the MWCNT anode and the NiSi contact area was more than 15 times lower than the resistance to the silicon only contact area. Therefore, the integrated nickel silicide contact areas in our devices enabled higher maximum drive current output (197 mA/cm$^2$ from 1.25 $\mu$L device) than that possible with regular silicon-only contact areas.

The current and power densities produced in this device are compared with those obtained in previous microscale MFCs (Table 1). The achieved current density at maximum power of 3947 A/m$^3$ was more than 3 times higher than the current density of the cell most similar to ours in size and architecture, Qian et al.’s 1.5 $\mu$L MFC.$^{30}$ The current density per area for our device was the highest yet attained by microsized MFCs.$^{3,30–32}$

Current and power generation are affected by a variety of factors, including oxygen intrusion, inoculum, external resistance used to condition the MFC, and other factors.$^{1,4,32}$ Oxygen intrusion likely played a major role in decreasing the maximum power density and increasing the anode resistance. Oxygen penetration into the anode chamber can produce an abiotic reaction at the anode that can decrease the voltage. Choi et al.$^{32}$ found that the open circuit voltage increased by 50% when adding l-cysteine (an oxygen scavenger) to the anode chamber. Thus, the use of an oxygen scavenger may be helpful in decreasing the anode resistance and improving current densities. Although we achieved the highest current density by area (by a factor of 2) compared to other microsized MFCs, our cell might further be improved through improvements in the bacterial community in the anode chamber. The 1.25 $\mu$L reactor is the smallest MFC tested so far with a mixed bacterial culture, with the next smallest at 2500 $\mu$L.$^{35}$ Watson et al.$^{34}$ found that mixed cultures achieved higher power densities than pure Shewanella, but Nevin et al.$^{38}$ found that Geobacter sulfurreducens performed better than mixed culture. Thus, it might be possible to increase power using a pure culture of G. sulfurreducens. Reactor acclimation at other external resistances might also increase power densities. The MFC was tested using a 100 $\Omega$ resistor, which resulted in higher power densities than most of the previous microsized MFC tests$^{30,31}$ where resistances of 15–40 k$\Omega$ were used. The use of a resistance more closely matched to the internal resistance, such as 20 k$\Omega$ for example, would increase power although the current density would be lower.

The power produced by the 1.25 $\mu$L MFC is sufficient for low power applications. The MFC produced a maximum net power of nearly 500 nW, with a current and voltage of 4.43 mA and 109 mV (Figure 5). If we consider a 50% efficient power supply in an on-chip module, then this is sufficient to run a 29.6 pW Phoenix processor,$^{36}$ integrated nanobiosensor,$^{37,38}$ or other ultra low power devices. In the past, biofuel cells using glucose$^{39}$ or human plasma and S. cerevisiae$^{40}$ for power generation have been demonstrated. However, they could be sustained for less than an hour. Other microsized demonstrations$^{30,32}$ were only tested for a few days to prove that they worked. Our device was operated in fed batch mode for 25 days, proving that the materials and design can endure long-term use.

These results demonstrate that it is possible to microfabricate a microsized MFC on a silicon substrate with forest type vertically aligned 3 million multiwalled carbon nanotubes (MWCNTs) and nickel silicide (NiSi) contact base that can produce a high current. Use of MWCNTs provided a very large surface-to-volume ratio, allowing for effective microbial interactions with the anode surface. The successful generation of power using the microsized MFC shows that the anode material has a good biocompatibility, and the design allows for state-of-the-art CMOS processes compatible with on-chip power generation.

### Table 1. Summary of the Characteristics and Performances of Demonstrated Micro-Sized MFCs

<table>
<thead>
<tr>
<th>$V$ (µL)</th>
<th>material (cm$^3$)</th>
<th>inoculum/fuel</th>
<th>$P_{\text{max}}$ (mW/m$^2$)</th>
<th>$P_{\text{max}}$ (W/m$^2$)</th>
<th>$I_{\text{max}}@P_{\text{max}}$ (mA/m$^2$)</th>
<th>$I_{\text{max}}@P_{\text{max}}$ (A/m$^2$)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>MWCNT (0.25)</td>
<td>mixed bacterial culture/acetate</td>
<td>carbon cloth</td>
<td>[Fe(CN)$_6$]$^3^{\text{-}}$</td>
<td>19.6</td>
<td>392</td>
<td>197</td>
</tr>
<tr>
<td>1.5</td>
<td>gold (0.15)</td>
<td>Shewanella putrefaciens/lactate</td>
<td>carbon cloth</td>
<td>[Fe(CN)$_6$]$^3^{\text{-}}$</td>
<td>1.5</td>
<td>15.3</td>
<td>130</td>
</tr>
<tr>
<td>4.5</td>
<td>gold (2.25)</td>
<td>Geobacteraceae-enriched/acetate+l-cysteine</td>
<td>gold</td>
<td>[Fe(CN)$_6$]$^3^{\text{-}}$</td>
<td>47</td>
<td>2300</td>
<td>116</td>
</tr>
<tr>
<td>15</td>
<td>gold (2.16)</td>
<td>Saccharomyces-cerevisiae/glucose</td>
<td>gold</td>
<td>[Fe(CN)$_6$]$^3^{\text{-}}$</td>
<td>4</td>
<td>32.1</td>
<td>167</td>
</tr>
</tbody>
</table>

### ASSOCIATED CONTENT

#### Supporting Information

Fabrication, experiments, and methods and polarization plot comparing MWCNT anode and carbon cloth anode. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES


