Sustainable Design of High-Performance Microsized Microbial Fuel Cell with Carbon Nanotube Anode and Air Cathode

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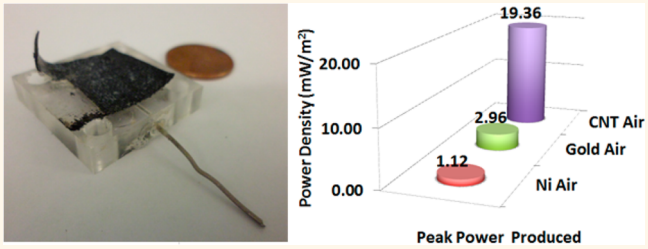
ABSTRACT Microbial fuel cells (MFCs) are a promising alternative energy source that both generates electricity and cleans water. Fueled by liquid wastes such as wastewater or industrial wastes, the microbial fuel cell converts waste into energy. Microsized MFCs are essentially miniature energy harvesters that can be used to power on-chip electronics, lab-on-a-chip devices, and/or sensors. As MFCs are a relatively new technology, microsized MFCs are also an important rapid testing platform for the comparison and introduction of new conditions or materials into macroscale MFCs, especially nanoscale materials that have high potential for enhanced power production. Here we report a 75 μL microsized MFC on silicon using CMOS-compatible processes and employ a novel nanomaterial with exceptional electrochemical properties, multiwalled carbon nanotubes (MWCNTs), as the on-chip anode. We used this device to compare the usage of the more commonly used but highly expensive anode material gold, as well as a more inexpensive substitute, nickel. This is the first anode material study done using the most sustainably designed microsized MFC to date, which utilizes ambient oxygen as the electron acceptor with an air cathode instead of the chemical ferricyanide and without a membrane. Ferricyanide is unsustainable, as the chemical must be continuously refilled, while using oxygen, naturally found in air, makes the device mobile and is a key step in commercializing this for portable technology such as lab-on-a-chip for point-of-care diagnostics. At 880 mA/m^2 and 19 mW/m^2 the MWCNT anode outperformed the others in both current and power densities with between 6 and 20 times better performance. All devices were run for over 15 days, indicating a stable and high-endurance energy harvester already capable of producing enough power for ultra-low-power electronics and able to consistently power them over time.



KEYWORDS: microbial fuel cell (MFC) · carbon nanotubes · silicon chip · electrolyte · nanotechnology

Microbial fuel cells (MFCs) are devices that utilize the naturally occurring decomposition pathways of electrogenic bacteria to both clean water and produce electricity.[1−3] Microsized MFCs are therefore essentially miniature energy harvesters requiring only the insertion of a liquid feed source containing organic materials for the bacteria to feed.[4,5] Feed sources range from environmental waste waters (domestic or industrial wastes) to medical liquids (glucose or urine), making the MFC a versatile power generator for a variety of applications.[6] As a new technology, a full range of microbial fuel cell conditions and materials must be rapidly tested to determine the optimal parameters for maximum power production and future commercialization. From that perspective, microsized MFCs offer a unique miniature platform for rapid testing of MFC components.[7,8] In addition, as miniature power harvesters, microsized MFCs can be integrated onto silicon, the dominant material in the micro- and nanoelectronics industry, particularly in lab-on-a-chip applications or other point-of-care diagnostics systems that can use the liquid itself for diagnostic or sensing purposes while also producing the energy needed to power the electronic components on the chip.[9,10]

At a macroscale, bioenergy has been growing rapidly as a major role in the renewable energy portfolio. Consisting in the use of ethanol, butanol, biodiesels, and bioelectricity, bioenergy encompasses a wide range

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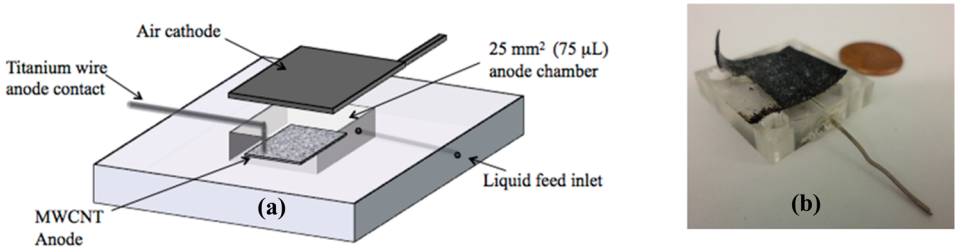

Figure 1. (a) Schematic of the 75 μL microsized microbial fuel cell with MWCNT on silicon chip anode and air cathode. Gold and nickel on silicon chip anodes were also tested and compared in the same setup. (b) Photograph of MWCNT on silicon chip microbial fuel cell in plastic encasing with titanium wire contact visible as well as the black air cathode compared to a U.S. penny.

of energy sources and related technologies. Microbial fuel cells are an innovative technology in the bioelectricity sector. Bacteria inside an MFC serve as catalysts that convert chemical energy in organic materials into electricity. MFCs are uniquely able to convert organic matter in waste waters and industrial wastes, which is currently not being used, into bioelectricity.[11] Integrating nanotechnology into energy or biology sectors has vast potential for highly enhanced capabilities as we better understand and mimic these systems.[12] We have taken the typical MFC system (described below) and miniaturized it as well as integrated nanomaterials to increase the electricity generated.

Microbial fuel cells typically have an anode and a cathode separated by a proton exchange membrane in a two-chamber setup. Both electrodes must be conductive, and the anode must also be biocompatible, as bacteria introduced into the system will form a biofilm on the anode. Bacteria used can be naturally found in wastewater or grown as a pure culture but have unique electrongenic qualities in their ability to decompose organic materials and release electrons extracellularly. When an organic liquid feed is inserted, the bacteria oxidize the substrate and produce protons and electrons. The protons pass through the proton exchange membrane to the cathode, and electrons are transferred through an external circuit from the anode to the cathode, driving an external load and reducing the electron acceptor at the cathode.[1,11] In designing a more sustainable system, we removed the membrane, making it a one-chamber device, and changed the cathode/chemical electron acceptor combination with an air cathode and ambient oxygen electron acceptor, making the entire device mobile. Additionally, the addition of a membrane comes with extra expense ($1500/m^2 for Nafion membrane) and loss in sustainability of the device, as membranes can degrade quickly. By building this mobile, sustainable device on a silicon chip we are enabling the simple integration of nanoelectronics[12,13] or on-chip functions powered by the microbial fuel cell.

Silicon process technology is the most matured and frequently used technology in fabrication. The most advanced circuits and functions are integrated into a silicon chip system to run almost all of our modern day electronics. Therefore, the fabrication of a microbial fuel cell onto a silicon chip allows it to be integrated as an on-chip power source into existing systems-on-chip (SoC). The unique liquid feed source allows the MFC to essentially be a power generator recharged with the addition of organic-containing liquids such as domestic[14] and industrial food processing waste waters[15] or urine.[16] Optimizing this technology on a silicon chip is essential in the development of the MFC as an on-chip energy source.

Therefore, we have focused on making an MFC on silicon so that it could be easily integrated onto a device on the silicon chip. Using CMOS-compatible processes, we have integrated multiwalled carbon nanotubes (MWCNTs) on silicon as an anode (Figure 1). As carbon is the most typically used large-scale anode material, we sought to utilize carbon in a nanostructured form that can be easily assimilated into the other on-chip design processes. We compared the MWCNT anode with the conventional expensive microsized anode, gold, and an inexpensive anode, nickel.

In making the material selection for the anode, we chose carbon, as many large-scale MFCs utilize carbon as an anode due to its high biocompatibility. Electrogenic bacteria require extracellular electron transfer (EET) mechanisms to transfer electrons from their cells into an anode. The fabrication of electrode materials can affect the performance of MFCs by enhancing the surface area and improving the EET between the bacteria and the anode. Large-scale MFCs have used a variety of carbon materials chosen to increase surface areas and subsequent microbial attachment, with the most typical being carbon cloth,[17,18] graphite,[19] and graphite fiber brushes.[20] Nanoengineered carbon materials have also been utilized generally in a hybrid form such as graphene or carbon nanotubes integrated into carbon cloth,[21−23] stainless steel,[24] or polymer composites.[25] These hybrids are not CMOS compatible and cannot be integrated on-chip for microscale applications. Here, we chose to test pure MWCNTs as anode, as they have excellent electrochemical capabilities, can be fabricated directly on chip, and can be functionalized to improve cell adhesion.

High electrical conductivities (resistance of 2.1 mΩ-m for a single nanotube) allowed electrons to be

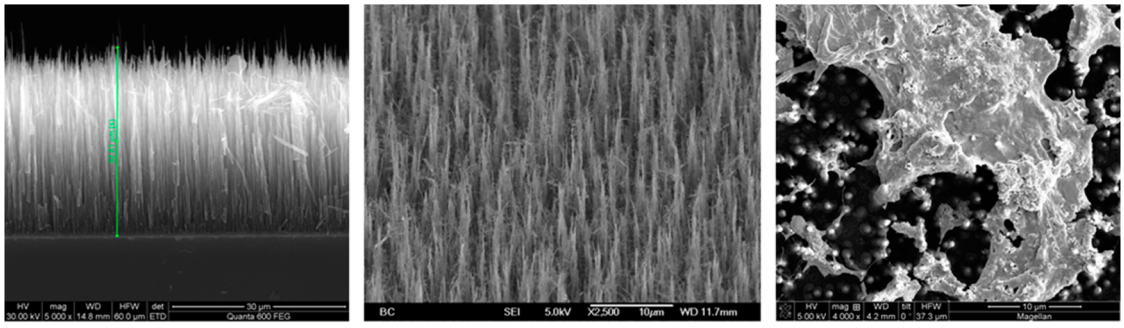

Figure 2. (a) SEM images taken of a MWCNT anode with CNT heights of 30−40 mm and diameter ranging from 200 to 400 nm with a side view. (b) Top-down view of the MWCNT forest; (c) Electrogenic bacteria formed a conductive biofilm on the functionalized and biocompatible MWCNTs and transferred electrons to the anode.

transferred more quickly from the bacteria to the anode surface. The most important feature of MWCNTs, though, is high surface area-to-volume ratios (66 000 cm^{-1} before functionalization), which provide larger areas for bacterial colonization. Other features that aid in biocompatibility include increased chemical stability, catalytic activity, and resistance to decomposition.[26−28] In order to improve cell adhesion, a functionalization process was performed on the CNTs in which they were rinsed in nitric and sulfuric acids to remove residual metal catalysts and other impurities. The acid treatment also has been found to improve cell adhesion by generating carboxylic groups in the walls and tips using an oxidation process as well as encouraging the MWCNTs to collapse on each other to form 3D structures using capillary tensile forces.[29,30] After functionalization, the average height of the MWCNTs was 35 mm and their diameter ranged from 200 to 400 nm (Figure 2). We previously demonstrated a CMOS-compatible MWCNT anode in a 1.25 μL microsized microbial fuel cell, achieving high current densities but in an unsustainable two-chamber ferricyanide system.[30] In order to build a more sustainable microsized MFC, we focused on redesigning the cathode and electron acceptor into a one-chamber membraneless system.

The material selection for the cathode, like that of the anode, requires a highly conductive material and is most typically carbon. In this case, we are using a specially designed carbon cloth air cathode, which will be further described below. The use of an electron acceptor at the cathode is required to capture the electrons and protons produced by the anode. In microsized MFCs, chemical electron acceptors are almost exclusively used, with ferricyanide being most frequent.[4,5] The use of ferricyanide as electron acceptor is generally found to increase power 1.5 to 1.8 times that of oxygen.[1] The reason that ferricyanide has been used is that it has a low overpotential when using a plain carbon cathode, making the cathode working potential close to its open circuit potential.[31] The use of ferricyanide or other chemical electron acceptors, though, is not recommended for four main reasons. First, since they cannot be reoxidized by oxygen efficiently, chemical electron acceptors must be replaced continuously. Second, ferricyanide can diffuse through the membrane into the anode chamber, which affects the long-term performance of the device.[31] Third, they do not produce pragmatic results that could be used for scaling up systems for a large-scale practical application, such as integrated into a wastewater treatment plant, which would not be using ferricyanide.[32] Lastly, the use of ferricyanide increases the cost of a system by requiring a membrane to separate the chambers as well as continuous resupply of the chemical into the system. Therefore, the use of oxygen as electron acceptor is preferred, as it can be taken from the ambient air, making it inexpensive and abundant. Additionally, as shown by the following chemical formulas, the use of oxygen as an electron acceptor in MFCs is kinetically and thermodynamically favorable, compared to the commonly used acceptors:[31]

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

with a theoretical cathode potential of 1.229 V

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$$

with a theoretical cathode potential of 0.361 V

Air cathodes are frequently used in larger scale MFC setups where a carbon cloth cathode is painted with platinum as a catalyst on the water-facing side and a hydrophobic carbon/polytetrafluoroethylene (PTFE) layer on the air-facing side.[33] In this paper, we are presenting, for the first time, an air cathode μMFC with a nanoengineered anode as well as a more in-depth material study of the comparative performance of gold and nickel anodes in the same architecture. This is also the first time an air cathode is being integrated directly onto a silicon-based MFC chip. The only other two reported studies using an air cathode in a microsized MFC used a highly pressurized membrane on a carbon cloth cathode as well as a gold anode on glass.[8,34]

It is to be noted that usage of gold makes the system more expensive, and for large-scale manufacturing silicon foundries do not allow access of gold to the silicon-based devices because of its high diffusivity, which shortens integrated circuits unintentionally. In the first anode material study using an air cathode in a microsized microbial fuel cell, not only did we show the durability of the air cathode system under a variety of anodic conditions and the enhanced performance of the nanoengineered MWCNT anode in this system, but by running the devices for more than 15 days, we showed a stable and reliable power supply in the longest ever run air cathode microsized MFC.

RESULTS AND DISCUSSION

All of the devices were started up using wastewater from the primary clarifier of a local wastewater treatment plant. After bacterial inoculation, a wastewater substitute, 1 g/L acetate, was introduced and fed to each device in a batch mode at the end of each current cycle, approximately every 10−15 h for over 15 days. As seen from the current production graph in Figure 3, the initial current produced after the introduction of acetate was about 20 times greater for the MWCNT device (880 mA/m^2) than for gold (29 mA/m^2) or nickel (37 mA/m^2), which indicates that bacteria were able to more rapidly grow and transfer electrons on the MWCNT anode than the others. Due to the increased surface area and exceptional conductivity of multiwalled carbon nanotubes, their incorporation into an anode can improve electron transfer between the bacteria and the electrode.[35] There have been several studies using dc and ac electrochemical characterization of CNT-based electrodes, through cyclic voltammetry and electrochemical impedance spectroscopy (EIS), that show enhanced electrochemical properties of CNTs compared with conventional materials.[26−29] Interestingly, recent studies have also come out highlighting the positive effects MWCNT exposure has on cell growth. The study showed highly enhanced growth of plant cells that were exposed to MWCNTs, which could also play a role in the enhanced performance of our MWCNT device and would provide interesting microbiological and genetic modification areas for future study.[36]

A further analysis of the duration of the current production graph (Figure 3) indicates that while all three devices continued to produce current even after more than 15 days, only the MWCNT device drastically decreased current production after the first three cycles. The current produced in the MWCNT device decreased with each cycle from a maximum current density of 880 mA/m^2 to stable reproducible cycles of about 130 mA/m^2 after 10 days. The gold device reached similar stable values (115 mA/m^2) but from a start-up time of more than 3 days with minimal current production and never exhibiting current

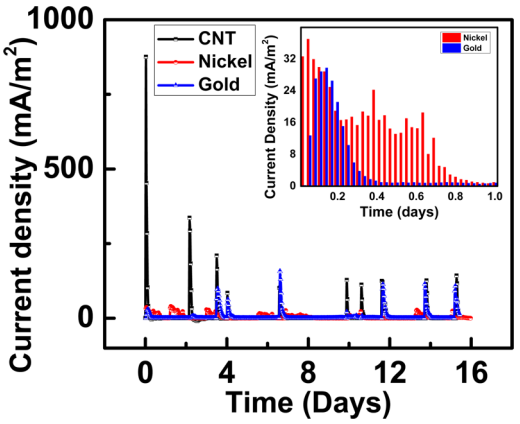

Figure 3. The 75 μL MFCs were run for over 15 days, longer than any other air cathode MFC. Although the MWCNT device had a high initial peak, it dropped over a few days due to (i) oxygen intrusion into the device; (ii) clogging of the anode with bacteria; and (iii) nonoptimal contact with the MWCNT anode. All devices, though, showed stable and reproducible power production by the end of the 15-day testing period. Stable power and current production, even at low quantities, is a desired feature for energy harvesting applications and indicates a promising device setup to either be set up in parallel or series to increase power to microdevices such as lab-on-a-chip where nano- to microwatt power is required. Inset figure shows the activity of the nickel and gold anode on day 1. In order to better see the data in the inset, each data point is represented as a line but still with only one fueling of the device occurring during this time at day 0. Each peak (appearing as a line) in the larger plot represents a refueling of the device, generally once a day. A polarization plot showing the activity with a carbon nanotube anode can be found in Supporting Figure 1.

densities above 200 mA/m^2 as MWCNTs. Nickel initially peaked at 39 mA/m^2 and stayed relatively steady at this value.

There are three main reasons we believe the MWCNT device slowly decreased in current produced over subsequent cycles before stabilizing: (i) oxygen intrusion into the device; (ii) clogging of the anode with bacteria; and (iii) nonoptimal contact with the MWCNT anode. First, many of the most efficient electrogenic bacteria (such as *Geobacter sulfurreducens*) are anaerobic. They are able to survive with minimal amounts of oxygen present and will then utilize this oxygen as an electron acceptor instead of the anode, decreasing the overall power produced in the system.[37] With too much oxygen, though, the bacteria will die. The usage of an air cathode system naturally introduces oxygen into the anode chamber through diffusion. The influx of oxygen from the air cathode could have killed the best electrogenic bacteria over time. The bacteria are first introduced to the device by inserting wastewater as previously mentioned in which the bacteria are naturally found and are adapted to the oxygen levels in the water. After a few hours during which a biofilm begins to grow, acetate is fed to the system and current measurements begin (the first peak in Figure 3). Given the high surface area of MWCNTs, the bacteria were better able to attach and grow a biofilm than

the flat surfaces of gold or nickel films. But with a short proton diffusion length between the anode and the cathode of 3 mm, oxygen at the cathode could diffuse through the chamber and to the anode quickly. The MWCNT biofilm that was grown in the initial inoculation produced high currents, but the outer layer of the biofilm began to consume the diffused oxygen, decreasing the amount of electrons reaching the electrode.[37] Over time, the second, and perhaps combined, reason for decreased current occurring is that the high surface area of the MWCNTs became clogged with bacteria including dead and other, nonelectrogenic, bacteria species that can survive with oxygen intrusion.[20,26]

The short proton diffusion length in microsized microbial fuel cells makes rapid oxygen intrusion an issue. There are possible options that can be implemented in order to decrease oxygen intrusion. We employed a fed batch feeding operation in which we fed the device with new acetate liquid after the completion of every cycle when current returned to 0 mA/m^2, but as seen from Figure 3 there were periods of time in which current production was insignificant for many hours before we fed the device again, providing ample time for high amounts of oxygen diffusion to the biofilm. By automating the feeding as a fed batch that occurs as soon as the cycle ends or as a continuously pumped feed, oxygen diffusion to the biofilm should be minimized. There are also chemical oxygen scavengers, such as L-cysteine, that can be added to the acetate feed in order to consume the oxygen within the liquid.[38] The addition of L-cysteine, though, once again makes the system unsustainable, as it must be continually refilled just as the usage of the ferricyanide electron acceptor did before the introduction of the air cathode. Nevin *et al.*[37] developed an innovative mechanism to fill their graphite anode with liquid feed and have the feed diffuse through the anode to the bacteria, providing a means for the inner bacteria in the biofilm to receive feed without relying on feed from the outer bacteria under high oxidative stress with the influx of oxygen. We are exploring future microsized designs that are able to be fed from below the silicon chip instead of from the top near the cathode.

Contact engineering is a very important aspect of microsized MFCs, as establishing a good contact to both the anode and cathode is essential in efficiently transferring electrons. Establishing effective contacts for nanomaterials is a challenge. In setting up the architecture of our device to as closely mimic larger scale devices as possible so that the results could be scaled up, we integrated titanium wire as direct anode contacts. The wire was pushed into the anode chamber through a hole halfway up the plastic holder, and the wire was bent to provide pressure on the anode chip, but this pressure was difficult to maintain. Before closing the devices, we tested resistance to be below

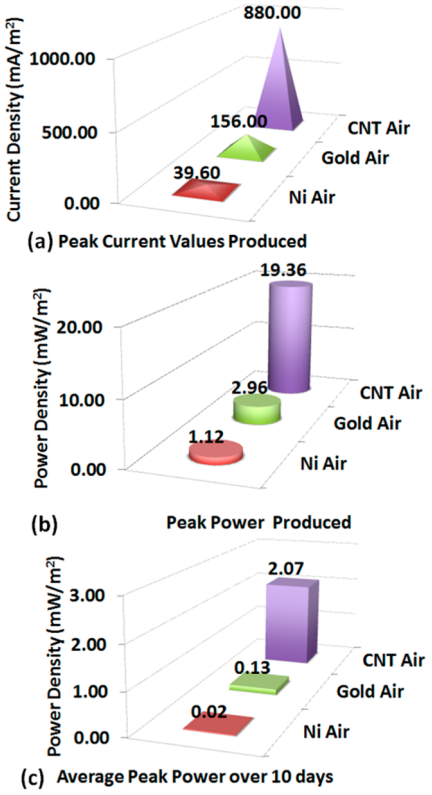

Figure 4. Maximum current densities produced by the devices (a) are about 800% higher for the MWCNT anode compared to the gold and more than 2200% higher compared to the nickel anode. Maximum power densities (b) indicate that the MWCNT anode produced more than 600% the power of the gold anode and 1900% the power of the nickel anode. Their peak power values over a 10-day period (c) show that all devices were able to have reproducible and stable power but not at the values of their peak power achieved, indicating a further need for optimization within the microsize MFC.

5 ohm, which shows that initially the pressure was maintained and the titanium was functioning as an adequate anode contact. With the introduction of liquid into the chamber, though, the titanium wire easily could have been moved within the device and the contact with the MWCNTs would have been compromised. We believe that it would serve us better to fabricate a contact on a different part of the silicon chip and shuttle electrons through the silicon instead of attempting to establish a direct contact to the MWCNTs. We have previously explored the use of nondirect contacts in our 1.25 μL MFC, where we fabricated a nickel silicide contact on top of the silicon and contacted this area.[30] We chose the current setup of cutting a 5 mm by 5 mm square of MWCNTs grown on a silicon substrate anode and placing it directly into the plastic anode chamber, as this was a design that could be most easily set up to scale-up the results in future experiments. Future designs should be made that can utilize the entire silicon chip so as to provide better sources of contact areas than direct contact to the anode.

The maximum current densities produced by the devices are seen in Figure 4(a), with the MWCNT anode (880 mA/m^2) producing about 800% more current than the gold anode (156 mA/m^2) and more than 2200% more current than the nickel device (39 mA/m^2). We also compared maximum power productions (Figure 4(b)), with the MWCNT anode (19.36 mW/m^2) producing more than 600% the power of the gold anode (2.96 mW/m^2) and 1900% the power of the nickel anode (1.12 mW/m^2). At nearly 500 nW, the MWCNT device is within the power range required to power ultra-low-power devices such as Nanosens, which developed a 1 nW power hydrogen sensor,[39] eXtreme Low Power PIC microcontrollers with XLP Technology,[40] a nanowatt smart temperature sensor for dynamic thermal management,[41] and a low-voltage processor for sensing applications with picowatt standby mode.[42]

In our efforts to make a more sustainably designed microsized MFC, we tested the devices for over 15 days. Almost all other microsized MFCs show initial data over no longer than 2−3 days,[4,5,7,8,10,30,34] which does not give an indication of the endurance or durability of the design or materials used. The longest run microsized MFC was our 1.25 μL MWCNT uMFC using ferricyanide, which produced stable batch fed current over more than 45 days.[43] Over the 15 days we ran these devices, the MWCNT device had the most cycles, with 10 over the 15-day period, while both gold and nickel had 8. The average peak power height for the MWCNT device (shown for 10 days) was over 2 mW/m^2 with gold (0.13 mW/m^2) and nickel (0.02 mW/m^2) at only a fraction of the power (Figure 4(c)). Compared to Figure 4(b), although all devices showed stable and reproducible power production over the entire testing period, it was not at the same value as peak power produced, indicating the need for further optimization of the microsized MFC. Stable power and current production, even at lower quantities as seen here, is a desired feature for energy harvesting applications and indicates a promising device setup to be set up in either parallel or series to increase power to microdevices such as lab-on-a-chip where nano- to microwatt power is required.

CONCLUSIONS

The successful integration of the carbon nanomaterial multiwalled carbon nanotubes into the anode of a completely mobile microsized MFC using an air cathode was achieved. By comparing the same air cathode set up with the most commonly used but expensive gold anode as well as an inexpensive metal nickel anode we were able to confirm that air cathodes in microsized MFCs are feasible even without a membrane and that the devices are durable and long-lasting. The MWCNT anode outperformed the others in current and power production most importantly due to its increased surface area. This mobile environmentally friendly microsized MFC already generates enough energy to begin to power ultra-low-power electronics and with optimization holds potential to play a much larger role in microscale energy harvesting in the future.

METHODS

MWCNT Growth. Before beginning CNT growth, a 5 mm by 5 mm catalyst layer was deposited onto a 4 in. Si wafer. The Cr/Ni (200/65 nm) catalyst layer was sputtered and patterned using a lift-off process to only be within the 5 mm by 5 mm anode area. The CNTs were then grown in a plasma-enhanced chemical vapor deposition (PECVD) system at temperatures between 650 and 700 °C with acetylene and ammonia as carbon source gases. CNTs were grown to heights of 30 to 40 μm and functionalized in nitric and sulfuric acids for 2 h.

MFC Setup and Electrochemical Measurement. The 75 μL MFC device used in this experiment utilized a plastic anode chamber holder with a 5 mm by 5 mm hole drilled through the center of the plastic (thickness of 3 mm) to serve as the anode chamber. The anode was a 5 mm by 5 mm silicon chip anode with chromium and nickel deposited on top and multiwalled carbon nanotubes grown on the nickel catalyst (as described above). Two 0.5 mm holes were drilled on two of the thinner sides of the plastic, one for feeding and one for anode contact. Titanium wire was pushed through one of the 0.5 mm holes and bent to provide pressure and contact the silicon chip anode at the bottom of the chamber. Each contact was initially measured to have only 5 ohm resistance to the anode before inoculation. We had 50 nm of gold deposited on top using an evaporator, and the nickel had 300 nm of nickel using sputtering. A specially fabricated air cathode was glued to the top with a small tail protruding to be used as cathode contact. The cathode had a platinum catalyst on the water-facing side and a hydrophobic carbon/PTFE layer on the air-facing side, as described in Cheng *et al.*[33] All devices were inoculated with bacteria from wastewater from the primary clarifier of the local wastewater treatment plant and fed with 1 g/L acetate solution. Voltage measurements were taken using a continuous multimeter (Keithley).

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Polarization plot of carbon nanotube anode based MFC. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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