Graphene-Based Flexible Micrometer-Sized Microbial Fuel Cell

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Microbial fuel cells harvest electrical energy produced by bacteria during the natural decomposition of organic matter. We report a micrometer-sized microbial fuel cell that is able to generate nanowatt-scale power from microliters of liquids. The sustainable design is comprised of a graphene anode, an air cathode, and a polymer-based substrate platform for flexibility. The graphene layer was grown on a nickel thin film by using chemical vapor deposition at atmospheric pressure. Our demonstration provides a low-cost option to generate useful power for lab-on-chip applications and could be promising to rapidly screen and scale up microbial fuel cells for water purification without consuming excessive power (unlike other water treatment technologies).

Introduction

Generally, a microbial fuel cell (MFC) is a lab-based technology to treat and to purify water. It provides a unique opportunity contrary to all the known energy-intensive technologies for water purification as the MFC simultaneously produces electricity while also cleaning the waste water. Bacteria within the MFC naturally decompose the organic wastes in water while also producing electrons that are carried across a load to generate electricity.[1, 2] The bacteria can decompose organic matter from a wide variety of substrates that are generally abundant and nontoxic, ranging from wastewater and industrial wastes to urine and blood, which makes the process of refueling simple and inexpensive.[3, 4] At a smaller scale, micrometer-sized microbial fuel cells are essentially self-powered generators that use microliters of liquids containing organic matter, such as wastewater, to produce nanowatts of power. Miniaturized MFCs have vast potential for application in portable power devices, sensors, or with integration into labs on chips.[5, 6] Lab-on-a-chip devices integrate a variety of laboratory functions onto a micrometer-sized chip, which makes them very appealing as they can rapidly perform needed tests with substantially lower volumes of liquid.[7] Existing lab-on-a-chip designs rely on microfluidics and advanced semiconductor techniques to make products that can detect anything from cancer[8] to chemicals[9, 10] or anything in between. Advances in MFC technology are required to make a robust and practical device that can be used for lab-on-a-chip applications on a mass scale.

Typical MFCs are composed of a two-chamber set up with the anode and cathode chambers separated by a proton exchange membrane. The anode and cathode chambers are conductive with the additional requirement of the anode to be biocompatible as the bacteria will be injected into the anode chamber and form a biofilm on the anode. After an organic substrate is introduced, the bacteria oxidize the substrate and produce protons and electrons. The protons are passed through the proton exchange membrane to the cathode and the electrons are shuttled through an external circuit from the anode to the cathode to drive an external load and reduce the electron acceptor at the cathode.[1, 4] As part of a more sustainably designed MFC, we made changes to the typical two-chamber system to make a one-chamber MFC that is more adapted to lab-on-a-chip applications. As many medical lab-on-a-chip devices are point-of-care diagnostics used to diagnose infectious diseases and test for certain drugs, often in the developing world where large-scale laboratories are not available, these applications require a more robust architecture to be viable in the field, by focusing more on ease of use and durable, inexpensive designs.[11, 12] As a recent technology, micrometer-sized MFCs require extensive testing under a variety of conditions and designs to make them suitable for a commercial product. Inserting specialized materials can improve the power performance of a MFC dramatically and micrometer-sized MFCs are ideal venues to test new anode and cathode materials such as nanoengineered anodes[13–16] or improved reactions at the cathode.[17] With a more robust architecture in mind, we have developed an inexpensive easy-to-use 25 μL MFC that incorporates two important sustainable design features. A process improvement is achieved by depositing a graphene thin film anode on nickel by using atmospheric chemical vapor deposition (APCVD); the improved performance produces ≈1 nW power directly from wastewater (Figure 1).

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Results and Discussion

Most importantly for a sustainable design, we first integrated an air cathode into the architecture. An air cathode utilizes ambient oxygen directly from the air as the cathode electron acceptor. The cathode is a specially prepared air cathode composed of carbon cloth with a thin layer of platinum catalyst and Nafion binder on the anode side; layers of polytetrafluoroethylene (PTFE) and carbon powder were used on the air side for waterproofing. Previously, micrometer-sized MFCs used chemical electrolytes, most often ferricyanide, that provided higher power but required continuous refills with the chemicals to function. In utilizing an air cathode, we eliminate the need for these toxic chemicals and do not need to refill the cathode electrolyte, as now oxygen is taken directly from the air, therefore, enabling the device to be completely mobile and functional outside of the laboratory. The air cathode also reduces the structure from two chambers to one chamber and eliminates the need for a membrane. Not only does this lower the cost of the entire system as the most commonly used membranes (Nafion 117) cost more than US$1500 m$^{-2}$, a one-chamber system without a membrane has actually been shown to increase power density. As the first micrometer-sized MFC utilizing an air cathode without a membrane, we are better able to test the scale-up conditions of microbial-fuel-cell technology and more rapidly reach the technology’s potential in mass-scale water-treatment facilities.

Secondly, in our sustainable design, we included a low-cost structural architecture made of rubber that is thin and flexible, which allows the device to be easily handled and inexpensively made. As part of the structure, we utilized syringe tips for ease of insertion of the liquid; in this way, any fuel for the device is able to be stored in syringes and used for immediate fueling.

We further explored the use of a thin, flexible anode by using a graphene sheet grown on nickel. Other microbial fuel-cell studies have used graphene-oxide-enhanced anodes by inserting graphene oxide into carbon cloth or onto stainless steel. Compared to previous demonstrations with graphene oxide, we use graphene grown on nickel by chemical vapor deposition. This unique process enables the thin-film graphene-on-nickel anode to be used directly after growth without requiring any transfer; this eliminates possible rupture and polymer-based contamination. We produced multilayer graphene (confirmed with Raman Spectroscopy, Figure 2) on a nickel film (300 nm) deposited on silicon oxide (SiO$_2$) by using chemical vapor deposition. The anode (graphene layer/nickel/titanium) was subsequently peeled off of the silicon substrate by etching the silicon oxide to release the thin, flexible anode ($\approx$300 nm) in the MFC. We glued the graphene to the rubber anode chamber and left a space to contact the graphene. The anode area (available for bacterial growth) was 25 mm$^2$ and as the rubber anode chamber was 1 mm thick, the total volume of the device was 25 $\mu$L.

We compared the micrometer-sized MFC with a flexible architecture and graphene on nickel anode against a similar device with an enclosed plastic architecture and a graphene anode grown on Ni/Ti/SiO$_2$/Si stack. Due to the limitations of the plastic architecture, the graphene/Ni/Ti/SiO$_2$/Si cell...
had a larger volume of 75 µL with the same anode area (25 mm²) as for the graphene-on-nickel MFC. Both devices, though, had an air cathode to ensure design variations were not too large, because the cathode size and material can cause drastic changes in the device performance.[18]

First domestic waste water was inserted in the MFC (local waste water treatment facility, primary clarifier) to introduce the bacteria to the system and allow a biofilm to grow on the anode. Then a wastewater substitute with a defined concentration of organic material (acetate, 1 g L⁻¹) was fed to the device and the cycle of peak current density was recorded. After the current density dropped to 0.01 mA m⁻², we refueled the device with acetate. The graphene/Ni/Ti MFC consistently produced between 15–34 mA m⁻² current density (per anode area) (Figure 3). This is a two-fold increase in peak current produced compared to the graphene-on-SiO₂ MFC whose maximum current density was only 17 mA m⁻², and it is an increase of three- to seven-fold with all other current cycles of the graphene/Ni/Ti/SiO₂/Si device which were below 5 mA m⁻².

As improvements in research on ultralow power bioelectronics, such as lab on a chip, are constantly being made, power requirements are decreasing and sub-microwatt devices are becoming a reality.[23] The peak current of the graphene/Ni/Ti anode corresponds to power production of 0.7 nW, already almost enough to be a power source for ultralow power electronics.[24,25] Maximum power densities per anode area were further explored by systematically changing the resistance in a range from 1000000 Ω to 100 Ω and recording the corresponding voltage produced. For every change in resistance, we waited twenty minutes before taking measurements to ensure the device was stable at this resistance. Maximum power densities for the graphene/Ni/Ti MFC are seen in the power density curve in Figure 4, for which the power reached greater than 1 mW m⁻² with a correspond-
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resistance of this device owing to the better contact to the graphene as well as the closer distance from anode to the cathode. The internal resistance of the system, as estimated by the slope of the polarization curve, was high at approximately 19 kΩ for the graphene/Ni/Ti device and 37 kΩ for the graphene/Ni/Ti/SiO2/Si. Generally, micrometer-sized MFCs exhibit higher internal resistances than the large-sized versions,[5,6] but this indicates that the contact graphene was not ideal, particularly for the graphene/Ni/Ti/SiO2/Si MFC. Contact with the graphene was established in the graphene/Ni/Ti/SiO2/Si MFC by using a titanium wire (0.5 mm diameter) inserted into the device and bent to provide pressure on top of the graphene. As first assembled, the contact resistance was measured at less than 5 Ω, but variations of the liquid entering the device could have altered the pressure of the wire or its ability to effectively connect to the graphene. In the graphene/Ni/Ti MFC, a portion of the graphene was allotted to be used as the contact area to provide direct contact to the graphene anode. As the anode itself was thin, the contact area ripped after continual use which indicates that designs for long-term use of the device will require that further attention is paid to graphene contact engineering; however the direct external contact, in this case, was most beneficial. Contact engineering plays a key role in the ability to create an efficient fuel cell and further work in the area of graphene contact engineering is needed to truly optimize a system utilizing graphene.

We would also like to note that, in the handling of the device over time, there was no visual change in the layers of the air cathode. In previous large-scale air-cathode devices, the air cathodes were reused multiple times without diminishing results so we would expect similar outcomes in the micrometer-sized device. However, this is an area which needs careful consideration and future experiments. It is also to be noted that differences in how the device is fed (including the pressure at which the liquid is inserted and how much goes through the device or stays in the anode chamber) contribute to potential variations in the power produced. The small size of the micrometer-sized MFC magnifies some of these differences. Future experiments should include testing the flexible device by using continuous flow to see what the maximum continued current can be, as well as a more exact measurement of liquid entering the device from the syringe.

The other dimension that affects the internal resistance is the distance between the anode and cathode. Protons produced by the bacteria at the anode need to travel through the device to the cathode. A longer the distance for the protons to travel leads to a larger internal resistance in the device.[1] The set-up of the graphene/Ni/Ti device leaves a distance of 1 mm (the thickness of the rubber anode chamber) whereas the distance between the anode and cathode in the graphene/Ni/Ti/SiO2/Si device was approximately 3 mm (the thickness of the enclosed plastic).

Conclusion

In conclusion, we have designed a more-sustainable and flexible micrometer-sized microbial fuel cell and employed the two-dimensional material graphene, as deposited on a nickel anode, to achieve ≈ 1 nW of power by using wastewater and a wastewater substitute. Although only in the beginning research stages, there is a lot of potential for micrometer-sized microbial fuel cells in various applications. Such a design can be used as a testing array to understand the conditions for scaling up the technology or as directly integrated into a portable sensor or lab-on-a-chip device.

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