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A micro-sized bio-solar cell for self-sustaining power generation

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Self-sustainable energy sources are essential for a wide array of wireless applications deployed in remote field locations. Due to their self-assembling and self-repairing properties, "biological solar (bio-solar) cells" are recently gaining attention for those applications. The bio-solar cell can continuously generate electricity from microbial photosynthetic and respiratory activities under day-night cycles. Despite the vast potential and promise of bio-solar cells, they, however, have not yet successfully translated into commercial applications, as they possess persistent performance limitations and scale-up bottlenecks. Here, we report an entirely self-sustainable and scalable microliter-sized bio-solar cell with significant power enhancement by maximizing solar energy capture, bacterial attachment, and air bubble volume in well-controlled micro-chambers. The bio-solar cell has a ~300-µL single chamber defined by laser-machined poly(methyl methacrylate) (PMMA) substrates and it uses an air-cathode to allow freely available oxygen to act as an electron acceptor. We generated a maximum power density of 0.9 mW/m^2 through photosynthetic reactions of cyanobacteria, *Synechocystis sp.* PCC 6803, which is the highest power density among all micro-sized bio-solar cells.

Introduction

Nowadays, society has an insatiable appetite for energy, especially in the form of petroleum, which the world is almost completely dependent upon. Since petroleum-based fuels have a limited supply and are the major contributor of atmospheric CO_2 emissions, finding sufficient supplies of clean and renewable energy, which can complement or replace the current fossil fuel, has become a popular area of interest for many researchers and entrepreneurs. Many see solar energy and biomass as promising alternative technologies (clean and green, with self-sustaining potential) that could alleviate energy crises and environmental pollution. First, solar energy is gaining traction and attention as an extremely abundant and a carbon-free, renewable energy source.[1] Techniques for harnessing solar energy, however, are still limited primarily to semiconductor-based photovoltaic devices that, while proven to work, are suboptimal because of high price/low energy efficiency (10~15%) and because they are subject to interruption or significantly reduced energy production at night and on cloudy days.[2]

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Biomass is another of the most plentiful and well-utilized sources of renewable energy, which can be used for biofuels, power production, and products that can be made from fossil fuels.[3] However, the loss of ecosystems and increase in food prices has weakened such bioenergy approaches.[4] In order to exploit the advantages of both solar and biomass approaches, a technology is required which makes use of the high-energy efficiency from an innovative system while keeping the merits of a low-cost biological approach. Several photosynthetic microorganism-based options have shown great potential to produce large amounts of renewable energy without ecological or economical disruptions. One of the options is to utilize cyanobacteria as a main electricity-generating source since their photosynthesis capabilities can convert up to 30% of the sun's energy into biomass-stored chemical energy at the rate of ~450 TW.[5] Compared to the 1% conversion rates seen in conventional bioenergy crops, cyanobacteria indeed have the potential to pioneer the next green and renewable energy era with their high efficiency and low cost–enough to replace a substantial fraction of today's fossil fuel economy.

In the last decade, new approaches to convert sunlight into bioelectricity through cyanobacteria evolved with biological solar (bio-solar) cells.[6] Bio-solar cells are microbial fuel cells that utilize electrochemically active and photosynthetic microorganisms such as cyanobacteria or algae to create electricity.[6,7] Photosynthesis plays a central role in a bio-solar cell's operation as it drives the first step in the conversion of

light into electrochemical energy and is thus responsible for the production of the feedstock required for all other subsequent synthesis.

During photosynthesis, cyanobacteria convert H_2O and CO_2 into carbohydrates with the energy harvested from light, while concurrently generating electrons near the bacterial membrane. In addition, they metabolize carbohydrates during respiration and produce ATP for their internal biological functions, and re-generate H_2O, CO_2 and electrons.[8] The generated electrons are released through extracellular electron-transfer pathways and transferred from anode to cathode through the external electrical circuit, creating a potential difference between electrodes (Fig. 1).[9] Finally, the released protons diffuse from the anodic chamber to the cathode, where they re-combine with electrons and O_2 to re-form H_2O simultaneously. Through the aforementioned processes, the bio-solar cells can continuously generate electricity from solar energy without additional organic matter by increasing the electrochemical potential inside the cell to split and recreate water, producing oxygen, protons, and electrons.[6] Requiring only sunlight, water, and carbon dioxide to operate, bio-solar cells offer advantages over potentially competing sustainable power sources such as microbial fuel cells or photovoltaic cells because the photosynthetic microorganisms used in bio-solar cells (i) do not require an organic fuel, obviating the need for an active-feeding system, and (ii) are capable of producing power both day and at night. This system resembles Earth's natural ecosystem, where living organisms work in conjunction with the nonliving components of their environment to offer self-sustainable and self-maintainable features as a system. To date, successive efforts have focused on demonstrating the photosynthetic electrogenic activities of various cyanobacteria or algae.[6-8, 10,11] However, despite the vast potential and promise of bio-solar cells, they have not yet successfully translated into commercial applications, as they possess persistent performance limitations and scale-up bottlenecks.

One of the major issues with conventional bio-solar cells is that the anode material and the device architecture were inappropriate for adequate solar energy capture, bacterial attachment, and light penetration into the first layer of any biofilm growing on the surface (Fig 2a). This is mainly because the bio-solar cell had a conventional dual-chamber device configuration with a face-to-face arrangement of electrodes, leading to the usage of transparent anode materials such as thin gold anode or indium tin oxide (ITO).[10,11] These anode materials showed low electron transfer efficiency due to poor interaction between the bacteria and anode,[12] resulting in a decrease in power/current generation. Another concern was the need to continuously introduce an oxidant, such as potassium ferricyanide, as an electron acceptor (catholyte).[11,13] Although this chemical has the advantages of a fast cathodic reaction and low overpotential, these liquid-state electron acceptors may be impractical and unsustainable for applied use due to its need to be continuously replenished. Finally, although the concept of the bio-solar cells have been validated by the successful demonstration of macro-sized devices, small-scale bio-solar

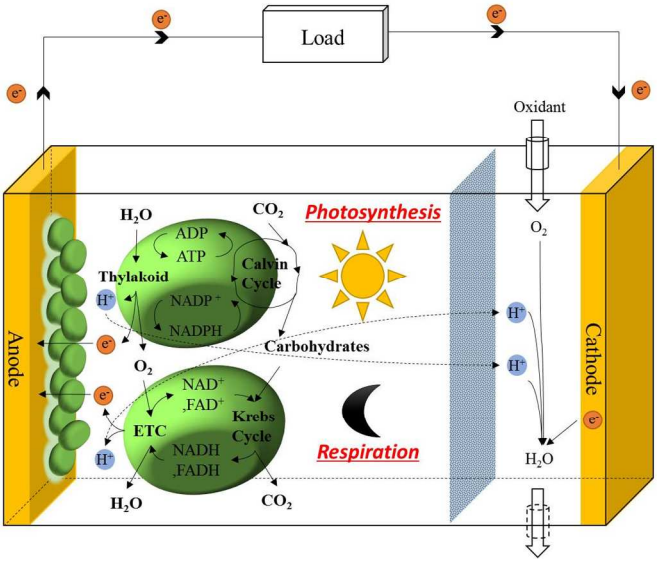

Figure 1. Principle of operation in a bio-solar cell. Schematic representation of the photosynthetic and respiratory electron transport pathways of cyanobacteria.

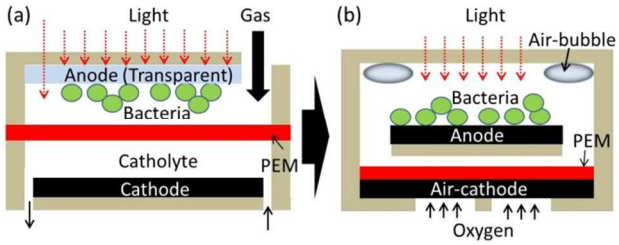

Figure 2. (a) Conventional two-chambered bio-solar cell with face-to-face electrode configuration and open-air system and (b) an innovative single-chambered device proposed in this work with face-up configuration and air-bubble trap

cells have higher energy density than larger units.[14,15] Bio-solar cell miniaturization inherently produces favorable conditions for increasing power density by reducing internal resistance and improving mass transport.[16] Further, small-scale bio-solar cells are more easily scaled as the bio-solar cells can be arranged and connected as multiple units in a stack configuration to collectively produce higher energy output.[14,15,17] Only a very small number of research groups have made efforts to scale down standard macro-sized bio-solar cells toward the micro regime.[18,19] Even more recent milliliter-sized bio-solar cells with enhanced power output seem to be overlooked as a potential platform for self-sustaining, practical use, because their anode chambers are exposed to the air making them vulnerable to other bacteria or contaminants (Fig 2a).[20-22]

In this work, we developed a miniature microfluidic-based single-chambered (air-cathode) device that is different from the conventional dual-chambered bio-solar cells with a face-to-face electrode arrangement (Fig 2b & Fig 3). Both the anode and cathode were configured upright (face-up) to ensure that (i) the capture of solar energy can be maximized and (ii) the carbon-based materials can be utilized as an anode material instead of

an inefficient, transparent ITO or thin gold for bacterial attachment/electron coupling. Generated protons travel toward the air-cathode through perforations on the anode instead of through aqueous cathode systems so that oxygen is used as an electron acceptor. Moreover, (iii) the device was designed to have a closed system to air to avoid vulnerability to contamination. Instead, a microfluidic space was provided for the air-bubble trap in the device so that the bacteria store the produced carbon dioxide/oxygen through their photosynthesis and respiration. This air-bubble is expected to facilitate gas exchange to the bacterial biofilm and allow long-term sustainable operation. Moreover, the bubble trap will be helpful to enhance the device performance because the bubble will be negatively related to the power generation as the trapped bubbles normally occupy significant chamber volume and likely hamper bacterial growth and their subsequent electron transfer.[23] Based on this innovative device structure, we significantly increased the power density of the micro-sized bio-solar cell and potentially established a general design platform for a scalable and sustainable bio-solar cell array. Further scientific and technological directions in this field are also discussed.

Experimental procedure

Device fabrication and operation

The photographs and schematics of the fully-assembled micro-sized bio-solar cell are illustrated in Fig. 3. Enclosed by the two supporting layers, the newly designed bio-solar cell consisted of five different functioning layers, among which the proton exchange membrane (PEM) was placed in between an anode layer and an air-cathode layer while outlet and inlet layers were at different surface levels to provide a space for air bubbles. This configuration is to secure and maintain air bubbles outside the microfluidic channel by using their buoyancy in a liquid (Fig 3a).[24,25] While the bubble trap will be able to store the produced carbon dioxide/oxygen/nitrogen through their metabolism, the generatd bubbles are expected to float not disturbing the microfluidic flow in the channel.[23] A thin rubber layer (~100 μm) was sandwiched between each layer to prevent leakage after applying uniformly distributed pressure using bolts and nuts in the fully-assembled device. Polymethly methacrylate (PMMA) substrates, the main layer material, were precisely laser-machined to define the 300 μL chamber. The carbon was deposited on the pre-defined area of the anode layer through screen/stencil printing. A hole was created at the anode layer, at its periphery, for relaying protons produced from the bacteria toward the cathode through the PEM (Fig 4). Unlike other conventional two-chambered devices, the bio-solar cell utilized the air-cathode to allow freely available oxygen to act as an electron acceptor by the installation of the catalyst side of the air-cathode face toward the chamber while the opposite side was exposed to air.[26] The assembled device was sterilized with 70% ethanol and ultraviolet light for 24 hours.

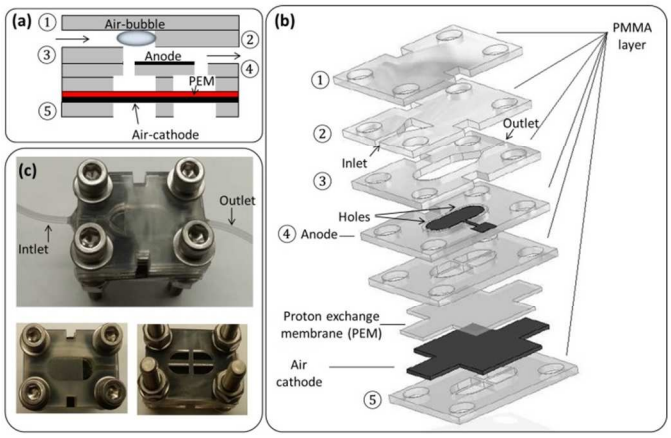

Figure 3. (a) Schematic of the micro-sized bio-solar cell (side view), (b) schematic of the individual layers in the device. There are holes at the periphery of the anode layer. (c) A photo-image of the fully assembled MEMS bio-solar cell, its top-view, and its bottom-view. The cell has a ~300-μL single chamber defined by PMMA and rubber layers.

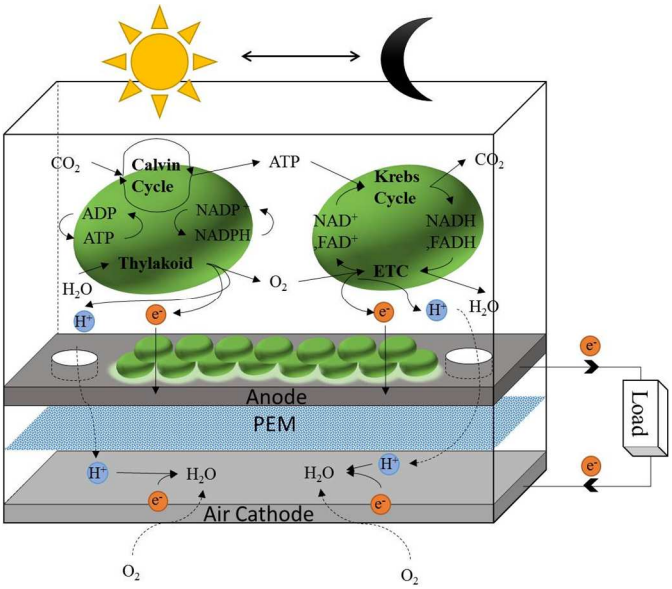

Figure 4. Principles of operation of our new bio-solar cell. The anode structure is designed to face the sun while producing protons that travel toward the cathode through holes at the periphery of the anode.

Inoculum

Cultures of *Synechocystis sp.* PCC 6803 were cultivated at 30 °C, using BG-11 medium, which contained 1.5 g $NaNO_3$, 40 mg K_2HPO_4, 75 mg $MgSO_4$, 36 mg $CaCl_2$, 1 mg of EDTA, and 6 mg of citric acid and of ferric ammonium citrate per 1 L of distilled water. The continuous aeration and illumination were provided by fluorescent lamps for 3 weeks. Growth was monitored by measurement of the optical density at 600 nm (OD_{600}) and the culture we used reached an OD_{600} of 2.4. The single anode chamber was filled with the cyanobacteria-suspended anolyte at an injection rate of 1 μL/min until fully occupied. Once completely filled, we stopped supplying the

anolyte and clogged the tubes with clamps to prevent additional flow and operate the device self-sustainably.

Measurement setup

The measurement for the potential difference between electrodes was carried out by a data acquisition system (NI, USB-6212). The voltages were measured every 1 minute and recorded via a customized LabVIEW interface. An external resistor was connected between the anode and cathode to induce the flow of current, which was calculated via Ohm's law. Output power was calculated by multiplying the potential to the current with power densities being normalized to the anode area.

Bacterial fixation and SEM imaging

The bio-solar cells were disassembled, rinsed, and adherent bacteria on each anode were immediately fixed in 2% glutaraldehyde solution overnight at 4°C. Samples were then dehydrated by serial 5 min transfers through 50, 70, 80, 90, 95, and 100% ethanol. Fixed samples were examined using a FESEM (Field Emission SEM) (Supra 55 VP, Zeiss).

Results and discussion

Light response and current/power generation

Fig. 5 shows a current profile generated from the micro-sized bio-solar cell under a 100 kΩ resistive load. The current shows a decreasing trend immediately after the supply of the anolyte stopped and the microfluidic tubings were clamped. Before long, the gradual increase in current was monitored under the operational condition of 2hr/2hr light/dark consecutive cycles, demonstrating the self-sustainable capability of the device. A positive light response of the cyanobacteria was also observed; approximately 30% higher current was generated during the 2 hrs of illumination than during the dark phases. Surprisingly, the immense increase in current generation was noticed after 40 hrs of operation without any modifications on operational conditions: no additional medium, 2hr/2hr light/dark cycle, and temperature at 30 ± 2 °C. The change in current output did not correlate to the minor fluctuations in temperature. The bio-solar cell loaded with BG-11 medium in the absence of the photosynthetic culture showed no light or temperature response. The only variable that may have contributed to the increase in current was the extensive green biofilm formation on the anode surface, which will be discussed in the next section in more detail. This rise of current production made the day/night current differences more distinctive, having a current magnitude of 30% greater during the daytime. This increase suggests that the photosynthetic electron transfer chain is the source of the electrons harvested on the anode surface. In contrast, previous studies observed a negative light response with more power generation during the dark phases.[6,12,27] The power decrease during the light phases in these studies was probably due to oxygen production which would have diverted electrons away from the anode.[6,12,27] In this study, it is likely

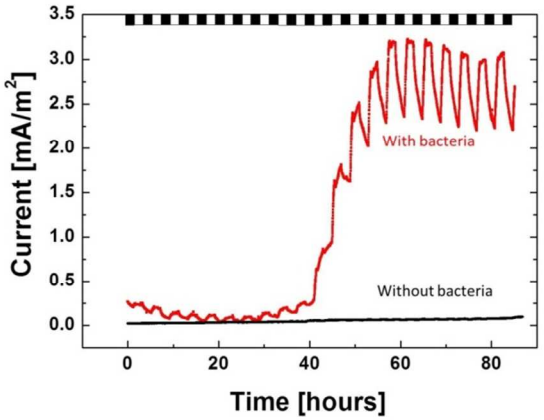

Figure 5. Positive light response of the bio-solar cell under 100 kΩ resistor. The device was examined under 2 hour light/dark intervals. The white bars indicate the illuminated period and the shadow indicates the dark period.

that during dark-light cycling, two hours were not long enough to generate a sufficient amount of oxygen to affect the electron pathways. The current reached a peak value of 3.2 mA/m^2 after 55 hours under illumination. During the dark periods, cellular respiration created energy from the carbohydrates, which is the waste product of photosynthesis, to keep the current generation above zero, in which the electrons are derived from the bacterial respiratory transfer chain. Based on these results, the bio-solar cell is shown to be light-powered without needing an organic substrate as an energy source to maintain self-sustainable power generation.

Fig. 6 shows polarization curves and power outputs of the bio-solar cell under light and dark conditions at 90 hours of operation. Both curves were drawn based on the maximum values recorded at a given external resistance (4.7M, 1M, 470k, 100k, 47k, 22k, & 10kΩ). The maximum power density obtained under four fluorescent lamps was 0.9 mW/m^2, the highest power density among all micro-sized bio-solar cells.[11,18,19] Nevertheless, the generated power density is still several orders of magnitude lower than that of even the smallest power microbial fuel cells.[28] The current limit in the performance of the bio-solar cell is primarily due to the high internal resistance, resulting in reduced power densities. Using the polarization curve in Fig. 6, we estimated their internal resistance which is equal to the external resistor values where the maximum power density is obtained.[29] The internal resistance of the bio-solar cell was about 470 kΩ both during day and night, which is several orders magnitude higher than that of other biofuel cells (several Ω).[12] The high internal resistance observed in our experiments might be due to the poor electron transfer from cyanobacteria to the anode surface and from the inefficient interactions between the biological material and anode. In order to increase current/power generation by decreasing the internal resistance, a comprehensive understanding of the metabolic pathways involved in extracellular electron transfer is necessary. More specifically, the physiology of those photosynthetic bacteria (and their biofilm) and their interaction with the electrodes must be studied at a new level of detail. Thus, micro-sized bio-solar

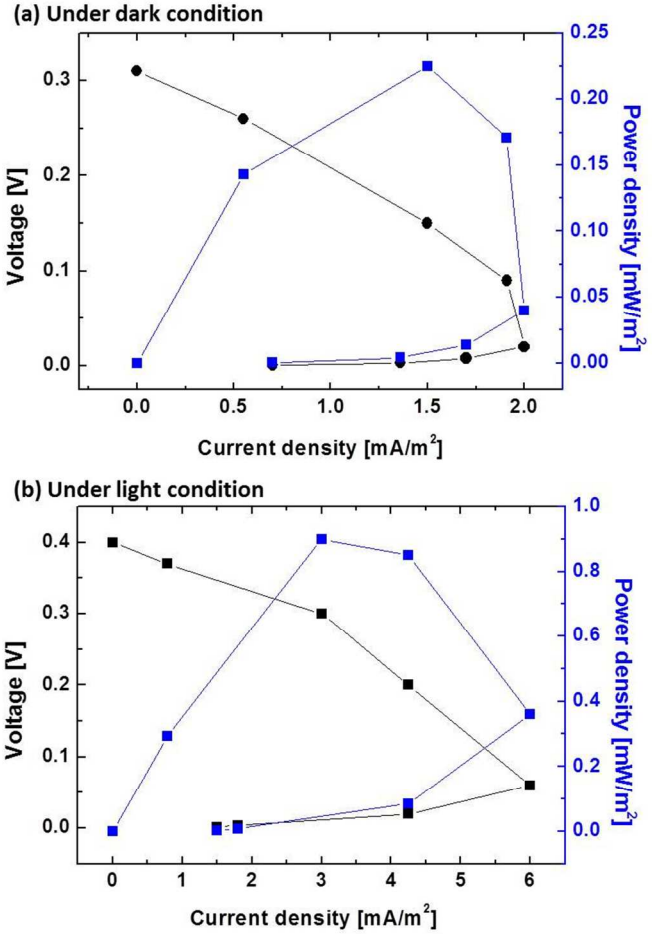

Figure 6. Polarization curve and output power measured as a function of current (a) under dark and (b) light conditions

cells can facilitate the studies of the microbial behavior in a smaller group of cells with excellent control over the microenvironment.

Biofilm formation

Fig. 7 shows photographic and SEM images of the carbon-based anode surfaces after bio-solar cell operation for 90 hours. The biofilm contained densely packed *Synechocystis sp.* PCC 6803 cells. Microorganisms in the device can be planktonic cells (cells in liquid suspension) and/or adherent cells (biofilms),[30] and it has been reported that both planktonic and biofilm cells contribute to electron transfer. Numerous reported bio-solar cells were demonstrated using planktonic cells by exploiting an exogenously-supplied redox mediator to facilitate electron transfer from the cell to the anode surface.[20,21,27] However, these devices were inefficient and inappropriate for self-sustainable use in that overall power production was very low and continuous injection of exogenous mediator was required. In contrast, biofilm cells utilize the endogenous exoelectrogenic properties of the bacterial biofilm to transfer the electrons, removing the need for exogenous mediators.[20] Davila's report correspondingly showed that 80% of the power density is driven from biofilm while the planktonic cells are only contributing to 20%.[31] Nam et al. also conducted another

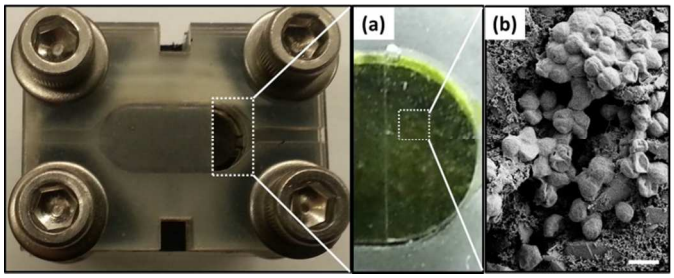

Figure 7. Anodic biofilm observed with (a) the naked eye and (b) SEM. Scale bar is 2 μm.

experiment where different electrical performances were characterized by the roles of suspended and attached bacteria in single-chamber cell.[32] As was expected, their result indicated that the higher current densities were associated with the increased density of the adherent cells on the anode. Therefore, cultivation of photosynthetic bacterial biofilms directly onto anode surfaces appears critical for high performance bio-solar cells. Biofilm may become denser over time but at a different rate depending on gas availability. The primary gases necessary for *Synechocystis sp.* PCC 6803 maturation are carbon dioxide (CO_2) and nitrogen.[33] Carbon dioxide plays a central role in that oxygenic photosynthesis must undertake carbon fixation to produce electrons. In order for cyanobacteria to fulfil oxygenic photosynthesis and carbon fixation, the Calvin Cycle (the light-independent reactions of photosynthesis) must be catalyzed by Ribulose-1, 5-bisphosphate carboxylase/oxygenase (RuBisCO), which is an enzyme sensitive to O_2. To prevent the pairing with oxygen, a unique organelle, carboxysome, encapsulates this enzyme, prohibiting the diffusion of oxygen and maintaining low carbon fixation rates during autotrophic growth.[34] Thus, even under a low CO_2 environment, *Synechocystis sp.* PCC 6803 has the capability to thrive. Moreover, *Synechocystis sp.* PCC 6803 can grow either photoautotrophically via the Calvin Cycle or photoheterotrophically on glucose via the glycolysis pathway.[35] Whichever method the cyanobacteria chose to obtain the carbon from, if the environment lacks the storage space for gas, it is practically impossible for them to grow in water due to the poor solubility of carbon dioxide in liquid. Besides the uptake of carbon dioxide, nitrogen is also the significant contributing factor of biofilm maturation. Cyanobacteria are well known for surviving highly adverse conditions, such as arid deserts, polar regions, and hot springs. Recently, their capability to survive under severely nitrogen-limited conditions has been analyzed by Krasikov et al.[36] Most cyanobacteria require nitrogen for their photosynthetic reaction I and II. When external nitrogen availability remains low, cyanobacteria manages to prolong their growth by using the internally stored nitrogen. But, upon the exposure to a completely depleted nitrogen atmosphere, cyanobacteria are found to demonstrate extreme loss of photosynthetic activity and may subsequently enter a form of dormancy.[37] Thus, the presence of nitrogen is critical for bacterial growth, biofilm maturation, and ultimately, power generation. In this work, our device configuration provided a space for the upward-floated

bubbles to presumably contain those necessary gases and thick bacterial biofilms were observed with increased power generation. However, further studies are needed for analysis of gas components and concentrations in the air bubble trap.

Another critical factor to form densely-packed biofilms is the anode. The anode materials play a profound role in influencing the power generation by determining: (i) the actual accessible area for bacteria to attach; (ii) the extracellular electron transfer efficiencies; and (iii) chemical species diffusion rates.[38] Therefore, many of the studies to date have concentrated on improving anode performance by searching for effective anode materials and/or modifications to the anode surface.[39,40] However, the conventional dual-chamber micro-sized bio-solar cells with a face-to-face arrangement of electrodes allowed for a very limited number of anode material candidates. The anode materials must not only be transparent to allow the sunlight to reach the bacterial cells but also be easy to manufacture in standard microfabrication processes. Accessible anode materials have been limited to thin gold and ITO.[12,21] However, poor interactions between the bacteria and those anode materials have been reported.[12] In this work, the novel device architecture with face-up anode configuration enabled us to have more options for anode materials, which can be opaque since the anode surface faces the direction of the sun. We used one of the most common anode materials for bacterial-based fuel cells, a carbon-based material, which possesses a large surface area and functional organic groups favoring cell vitality.[28] Biofilms of *Synechocystis sp.* PCC 6803 on the carbon anode appeared dense and compact.

The densely-packed biofilms might be achieved by using technologies for commercial production of algal biomass for biofuels.[41] The non-uniform distribution of light and low transparency in photoreactors are responsible for relatively low biofuel productivity. For better performance within photobioreactors, innovative designs that introduce larger surface area and integrate light guiding structures have been demonstrated.[41,42]

Future work: (1) Bio-solar cells in extreme environments

Nitrogen is an essential element for the earth's ecosystem as well as for humans, considering that the atmosphere consists of approximately 80% nitrogen. Despite the prevalence, atmospheric nitrogen (N_2) has limited availability for biological metabolism. Hence, the nitrogen cycle is driven by photosynthetic plants and microorganisms to reduce nitrogen gas into more pragmatic compounds, such as ammonia (NH_3), nitrite (NO_2^-) and nitrate (NO_3^-) through nitrogen fixation. Nitrate is then released back into the atmosphere through denitrification, which is the reduction of nitrates back into the inert nitrogen gas, completing the nitrogen cycle. Although our conventional devices operated purely on cultures of cyanobacteria capable of nitrogen fixation to ammonia, rapid exhaustion of nitrogen without a regenerating mechanism led to a short duration of the in vitro operation. However, this provides an opportunity for bio-solar cells to be employed in the oceanic environment where nitrogen gas is readily available.

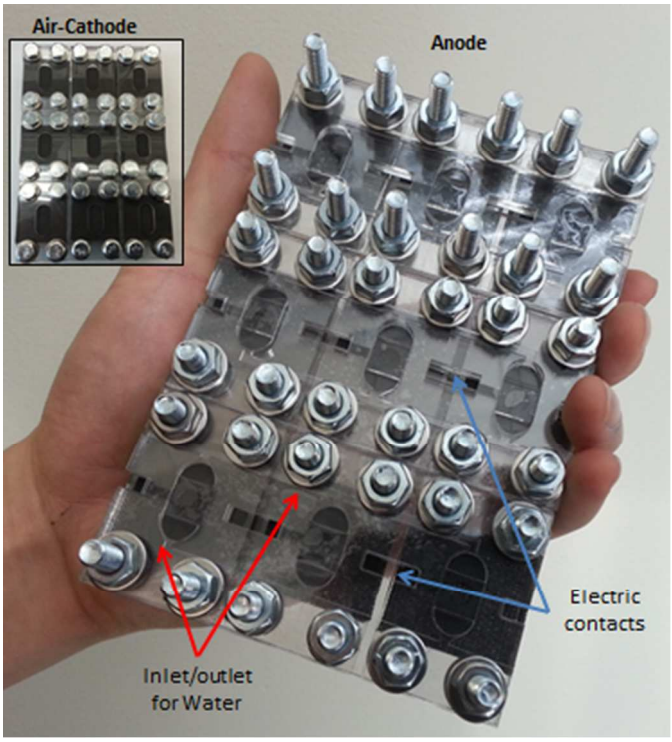

Figure 8. Conceptual 3x3 bio-solar cell array

Bio-solar cells, exposed to the extreme environment where nitrogen and carbon dioxide are abundant while oxygen is scarce, may generate high-density power along with completely matured biofilms on the anode surfaces.

Future work: (2) Bio-solar cell array

The key advantage of miniature bio-solar cells over other types of small-scale energy sources is that their construction, fuel sources, and operation are environmentally friendly and entirely self-sustainable. Their cost of manufacturing is low and the production of electricity has the potential of being continuous over months or years, so long as there are periodic day/night cycles. Their primary disadvantage, however, is the low energy harvesting rates, which currently limits this technology to low power applications. The typical sustainable voltage output from a miniature bio-solar cell is on the order of 0.4~0.6V. To produce sufficient voltage (>1.5V) and/or power (to reside within the operating range of silicon-based circuitry), it is necessary to either scale-up a single unit or connect multiple small units. Fig. 8 shows a proof-of-concept for a 3x3 bio-solar array consisting of an array of single-chambered device structures. This conceptual bio-solar cell array shows how miniature bio-solar cell units can be scalable to collectively generated sufficient power for practical use. Three common inlets and outlets allow for anolyte introduction into nine bio-solar units, which will eventually be sealed using silicone for sustainable field applications.

Conclusion

We developed an entirely self-sustainable bio-solar cell in a micro-sized chamber. Using an innovative device architecture, a single-chambered bio-solar cell was constructed in a way that the solar energy can be maximized and bacterial cell attachment and electron coupling can be enhanced. Through these modifications, the cell generated a maximum power density of 0.9 mW/m^2 at a current density of 3.2 mA/m^2, which is the highest power density among all micro-sized bio-solar cells. The development of bio-solar cells is applicable to mobile military and wireless applications, such as perimeter defense networks, environmental protection sensors and micro vehicle applications, where a microsized power source is essential. To take the photosynthetic bio-production to industrial scales, an in-depth understanding of the interplay between miniature device architectures and photosynthetic microorganisms needs to be achieved and the fundamental problems in electron transfer at the microbial and anode interface should be rigorously investigated. Meanwhile, the work done here will undoubtedly help with extracting more information about attaining power density and achieving efficiency high enough to release bio-solar cell technology from its restrictions to conceptual research, advancing its translational potential toward practical, real-world applications.

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References

1 G.K. Singh, *Energy*, 2013, **53**, 1-13.
2 N. Mason, *Nat. Photonics*, 2008, **2**, 281-283.
3 B. Hankamer, F. Lehr, J. Rupprecht, J. H. Mussgnug, C. Posten, and O. Kruse, *Physiol Plant*, 2007, **131**, 10-21.
4 A. Heibenhuber, B. Stefan, and S. Rauh, *Lohmann Information*, 2008, **43**, 24-32.
5 J. Waterbury, S. Watson, R. Guillard, and L. Brand, *Nature*, 1979, **277**, 293-294.
6 M. Rosenbaum, Z. He, and L. T. Angenent, *Current Opinion in Biotechnology*, 2010, **21**, 259-264.
7 D. Strik, R. A. Timmers, M. Helder, K. Steinbusch, H. Hamelers, and C. J. N. Buisman, *Trends in Biotechnology*, 2011, **29**, 41-49.
8 R. W. Bradley, P. Bombelli, S. J. I. Rowden, and C. J. Howe, *Biochemical Society Transactions*, 2012, **40**, 1302-1307.
9 T. Moriuchi, K. Morishima, and Y. Furukawa, *CIRP Annals – Manufacturing Technology*, 2008, **57**, 571-574.
10 A. E. Inglesby, K. Yunus and A. C. Fisher, *Phys. Chem. Chem. Phys.*, 2013, **15**, 6903-6911.
11 S. Yoon, H. Lee, A. Fraiwan, C. Dai, and S. Choi, *Proceedings of the 9th IEEE International Conference on Nano/Micro Engineered and Molecular Systems*, April. 13-16, 2014, Hawaii, USA, pp. 265-268.
12 S. Choi, H. Lee, Y. Yang, P. Parameswaran, C. I. Torres, B. E. Rittmann and J. Chae, *Lab Chip*, 2011, **11**, 1110-1117.
13 A. Fraiwan, S. Mukherjee, S. Sundermier, H. Lee and S. Choi, *Biosensors and Bioelectronics*, 2013, **49**, 410-414.
14 I. Ieropoulos, P. Ledezma, A. Stinchcombe, G. Papaharalabos, C. Melhuish, and J. Greenman, *Phys. Chem. Chem. Phys.*, 2013, **15**, 15312-15316.
15 I. Ieropoulos, J. Greenman, and C. Melhuish, *International Journal of Energy Research*, 2008, **32**, 1228-1240
16 H. Wang, A. Bernarda, C. Huang, D. Lee, J. Chang, , *Bioresource Technology*, 2011, **102**, 235-243.
17 S. Choi and J. Chae, *Sensors and Actuators: A. Physical*, 2012, **177**, 10-15.
18 M. Chiao, K.B. Lam, and L. Lin, *Journal of Micromechanics and Microengineering*, 2006, **16**, 2547-2553.
19 K.B. Lam, E.A. Johnson, M. Chiao, and L. Lin, *Journal of Microelectromechanical Systems*, 2006, **15**, 1243-1250.
20 A.J. McCormick, P. Bombelli, A.M. Scott, A.J. Philips, A.G. Smith, A.C. Fisher, and C. J. Howe, *Energy & Environmental Science*, 2011, **4**, 4699-4709.
21 P. Bombelli, M. Zarrouati, R.J. Thorne, K. Schneider, S.J.L. Rowden, A. Alik, K. Yunus, P.J. Cameron, A.C. Fisher, D.I. Wilson, C. J. Howe, and A.J. McCormick, *Phys. Chem. Chem. Phys.*, 2012, **14**, 12221-12229.
22 P. Bombelli, R.W. Bradley, A.M. Scott, A.J. Philips, A.J. McCormick, S.M. Cruz, A. Anderson, K. Yunus, D.S. Bendall, P.J. Cameron, J.M. Davies, A.G. Smith, C.J. Howe, and A.C. Fisher, *Energy & Environmental Science*, 2011, **4**, 4690-4698.
23 A. Fraiwan, S. Sundermier, D. Han, A.J. Steckl, D.J. Hasseett, and S. Choi, *Fuel cells*, 2013, **13**, 336-341.
24 J. H. Sung and M. L. Shuler, *Biomedical Microdevices*, 2009, **11**, 731-738.
25 C. Liu, J. A. Thompson, and H. H. Bau, *Lab Chip*, 2011, **11**, 1688-1693.
26 H. Liu and B. E. Logan, *Environmental Science & Technology*, 2004, **38**, 4040-4046.
27 Y. Zou, J. Pisciotta, R. B. Billmyre, I. V. Baskakov, *Biotechnology and Bioengineering*, 2009, **104**, 939-946.
28 F. Qian and D. E. Morse, *Trends in Biotechnology*, 2011, **29**, 62-69.
29 Y. Fan, E. Sharbrough, and H. Liu, *Environ. Sci. Technol.*, 2008, **42**, 8101-8107
30 A. P. Borole, G. Reguera, B. Ringeisen, Z. Wang, Y. Feng, and B. H. Kim, *Energy & Environmental Science*, 2011, **4**, 4813-4834.
31 D. Davila, J. P. Esquivel, N. Sabate, and J. Mas, *Biosens Bioelectron.,* 2011, **26**, 2426-2430.
32 J. Y. Nam, H. W. Kim, K. H. Lim, and H. S. Shin, *Environ Eng Res.*, 2010, **15**, 71-78.
33 Y. Yu, L. You, D. Liu, W. Hollinshead, Y. Tang, and F. Zhang, *Marine Drugs*, 2013, **11**, 2894-2916.
34 J. D. Young, A. A. Shastri, G. Stephanopoulos, and J. A. Morgan, *Metabolic Engineering*, 2011, **13**, 656-665

35 J. G. K. Williams, *Methods in Enzymology*,1988, **167**, 766-778.
36 V. Krasikov, E. A. V. Wobeser, H. L. Dekker, J. Huisman, and H. C. P. Matthijs, *Physiol. Plant*, 2012, **145**, 426-439.
37 M. Gorl, J. Sauer, T. Baier, and K. Forchhammer, *Microbiology*, 1998, **144**, 2449-2458.
38 V. Flexer, J. Chen, B. C. Donose, P. Sherrell, G. G. Wallace and J. Keller, *Energy & Environmental Science*, 2013, **6**, 1291-1298.
39 R. Thorne, H. Hu, K. Schneider, P. Bombelli, A. Fisher, L. M. Peter, A. Dent and P. J. Cameron, *Journal of Materials Chemistry*, 2011, **21**, 18055-18060.
40 Y. Zou, J. Pisciotta, I. V. Baskakov, *Bioelectrochemistry*, 2010, **79**, 50-56.
41 E.E. Jung, M. Kalontarov, D.F.R. Doud, M.D. Ooms, L.T. Angenent, D. Sinton, and D. Erickson, *Lab Chip*, 2012, **12**, 3740-3745.
42 E.E. Jung, A. Jain, N. Voulis, D.F.R. Doud, L.T. Angenent, D. Erickson, *Bioresource Technology*, 2014, **171**, 495-499.