# PEDOT:PSS/MnO<sub>2</sub>/CNT Ternary Nanocomposite Anodes for Supercapacitive Energy Storage in Cyanobacterial Biophotovoltaics

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ABSTRACT: A high-performance supercapacitive anode integrated into cyanobacterial biophotovoltaics allows the energy produced by the biophotovoltaics to be capacitively stored and delivered through a significant high-power burst. A ternary nanocomposite of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate, manganese dioxide (MnO<sub>2</sub>), and carbon nanotubes was designed to provide unique and critical functions for the development of a fully light-driven biosupercapacitor or a supercapacitive biophotovoltaic device. The nanocomposite on a carbon cloth exhibited a high specific capacitance of 261 F/g in 1 M sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>). Even with a thick biofilm of *Synechocystis* sp. PCC6803 in a BG-11 cyanobacterial growth



medium having a low-ionic conductivity, the nanocomposite-covered cloth showed great bioelectrochemical activity under illumination, producing an areal capacitance of 105.2 mF·cm<sup>-2</sup> and an energy of 13.2  $\mu$ W h·cm<sup>-2</sup>. This nanocomposite integrated in a cyanobacterial biophotovoltaic device serves as a double-function bioanode concurrently exhibiting light-driven bioelectrocatalytic and charge-storage features. It offers the great energy-harvesting capability of biophotovoltaics and the deep power reservoir of an internal supercapacitor through charging and discharging operations. Our hybrid system produced a maximum power density of 162  $\mu$ W·cm<sup>-2</sup> for a 0.1 s pulse at a discharging current density of 300  $\mu$ A·cm<sup>-2</sup>, which is about 100 times larger than that of the biophotovoltaic device on an unmodified carbon cloth and about 6 times greater than that of our biophotovoltaic device without the charging–discharging operation. The developed supercapacitive biophotovoltaics represent a revolutionary technological breakthrough that offers a potentially viable long-term and powerful energy source for unattended wireless sensor networks.

**KEYWORDS:** supercapacitive biophotovoltaics, self-charging biosupercapacitors, cyanobacteria, light-driven bioelectrocatalytic reactions, solar bioenergy harvesting

## **1. INTRODUCTION**

Biophotovoltaics is an emerging technology that can generate electricity from photosynthetic water splitting by subcellular nonliving proteins (e.g., thylakoid membranes and photosystem II) or cellular living organisms (e.g., cyanobacteria and microalgae).<sup>1-3</sup> Natural photosynthesis uses solar energy and water-the two most abundant resources on Earth-and provided profound inspiration for sustainable energy harvesting and conversion systems.<sup>4-6</sup> Compared with biophotovoltaics based on isolated subcellular proteins, living biophotovoltaics that use whole-cell photosynthetic microorganisms are more attractive as a long-term energy-generating system. The microorganisms are self-maintaining, self-sustaining, stable, and inexpensive and can be processed without purification.<sup>7,8</sup> Prokaryotic cyanobacteria are the most preferable and wellstudied photosynthetic microorganisms used in biophotovoltaic devices because of their metabolic and physiologic simplicity compared to eukaryotic algae.<sup>9-11</sup> While our future will create a fully connected network system that is pervasively and unobtrusively embedded in our environment, named "Smart environment", the cyanobacterial biophotovoltaics can offer the most suitable energy solution because of their selfsustainable and stand-alone operation.<sup>12,13</sup> In a bioelectrochemical system, the cyanobacteria in an anodic compartment liberate electrons, protons, and oxygen during light-induced charge-transfer processes by catalyzing the oxidation of water. The electrons flow to a cathode through an external circuit, while the protons move to the cathode through an ionexchange membrane. The oxygen released as the water molecules split can be used for microbial respiration or move to the cathode for the reduction. The electrons, protons, and oxygen (either from water splitting or from the air) combine to form water at the cathodic compartment and maintain the

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electroneutrality of the system.<sup>3</sup> Cyanobacterial photosynthesis produces carbohydrates, which are subsequently used for their respiratory reaction, re-generating carbon dioxide and water. Therefore, the biophotovoltaic system can be self-sustainable and self-maintainable while supplying long-term power for the smart environment.<sup>14</sup> Despite these strengths and promises, the power generated from the cyanobacterial biophotovoltaics is significantly lower than other bioelectrochemical systems and even the nonliving biophotovoltaics. The main limitation is the slight ability of the cyanobacteria to transfer electrons compared to other heterotrophic exoelectrogens and the isolated photosynthetic proteins that do not impede energy transfer with a membrane. Even the latest cyanobacterial biophotovoltaic devices with revolutionary material and architecture modification suffer from their relatively small power with a sustained power production of only 18.6  $\mu$ W cm<sup>-2</sup> under illumination, and this performance limits widespread practical applications.<sup>15</sup> Furthermore, the mechanisms and metabolic pathways involved in the extracellular electron transfer of cyanobacteria are unclear, and we have not established fundamental knowledge critical for improving their performance.<sup>2,3</sup> Although many strategic plans have been proposed with a large upside potential including device and material breakthroughs and genetic engineering of cyanobacteria,<sup>15–17</sup> their performance remains insufficient to provide a practical and sustainable power supply for real-world applications.

Recent studies described the capability of microbial charge stored in a cell membrane or through redox mediators, demonstrating output pulses of stronger power when the bioelectrochemical systems operate in alternate charging and discharging modes.<sup>18-20</sup> Lovley's group demonstrated that microbial biofilms can function as supercapacitors with good charging and discharging reversibility.<sup>18</sup> Saar et al. achieved a 2.5-fold power improvement from the wild-type cyanobacterial biophotovoltaics by decoupling charge storage in the redox electron carrier,  $K_3[Fe(CN)_6]$ , and power delivery from the charged carrier.<sup>20</sup> This supercapacitive behavior can allow innovative charge-storage features offering high-power operation even from the low-performance biophotovoltaics. Recent advances have sought to revolutionize biophotovoltaics by integrating additional capacitive materials in the anode, forming a dual-function photobioanode and capacitively storing more charges produced by the biological metabolism.<sup>21-23</sup> Many supercapacitive biophotovoltaics using the isolated photosynthetic proteins have been demonstrated. Ravi et al. developed photoprotein-based biophotovoltaics in which charge-storage processes were integrated within a single, multifunctional material.<sup>24</sup> Gorton's group combined photosynthetic thylakoid membranes with pseudocapacitive polymers to enable simultaneous generation and storage of electric power.<sup>25</sup> They attained a current density of 282  $\mu$ A cm<sup>-2</sup> and a power density of 56  $\mu$ W cm<sup>-2</sup>. However, the biophotovoltaics based on those isolated proteins are limited for long-term power generation because they lack internal stability and selfmaintainable photosynthetic machinery.<sup>2,26</sup> Recently, our group for the first time demonstrated a supercapacitive biophotovoltaic device relying on living whole cells.<sup>13</sup> The cyanobacterial system exhibited far more resilient and significantly more robust features than systems using subcellular proteins, while the supercapacitance of the cells and additional redox polymers on the carbon cloth effectively stored charges obtained from the irreversible faradaic reaction

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of the cyanobacteria (i.e., photosynthesis and respiration). Our system generated a current density of 120  $\mu$ A cm<sup>-2</sup> and a power density of 38  $\mu$ W cm<sup>-2</sup> with the charging and discharging operation, which were 5-fold and 16-fold larger, respectively, than the devices without the charging mode. Given that this exciting performance was obtained by a simple integration of a nonoptimized low-capacitive material, remarkable power enhancement can be achieved by improving the specific capacitance and conductivity of the anode. While biophotovoltaics produce a small number of electrons, addition of supercapacitance allows the anode to store electrons and energy and the device to generate powerful pulses during short discharges. The improved performance of biophotovoltaics can represent a major technological breakthrough that offers a potentially viable power solution for the unattended smart environment. In this work, a high-performance supercapacitive anode was prepared by designing a ternary nanocomposite of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PE-DOT:PSS), manganese dioxide (MnO<sub>2</sub>), and carbon nanotubes (CNTs). The nanocomposite was used as a dualfunction photobioanode with the whole-cell cyanobacteria comprising the biophotovoltaics and the internal supercapacitor. The specific capacitance of the anode can reach 261 F/g and exhibit excellent charge and discharge rates with good cycle stability. The supercapacitive anode in the presence of Synechocystis sp. PCC6803 achieved significant power enhancement with the charging-discharging operation. The device attained a maximum power density of 160  $\mu$ W cm<sup>-2</sup> and a maximum current density of 450  $\mu$ A cm<sup>-2</sup> at a pulse time of 0.1 s. The output is the greatest value of any previously described cyanobacterial biophotovoltaic device. The combination of the nanocomposite and the biophotovoltaics produced unacceptably strong output during pulse discharges.

# 2. RESULTS AND DISCUSSION

2.1. Characterization of the PEDOT:PSS/MnO<sub>2</sub>/CNT Ternary Nanocomposite. PEDOT:PSS has been widely used as an anodic material for bioelectrochemical systems and biophotovoltaics because its water-soluble property can make fabrication easy through spraying, dipping, screen-printing, or spin-coating.<sup>26–28</sup> Furthermore, its great biocompatibility and bioaffinity can improve the initial microbial adhesion and subsequent biofilm formation, leading to great power enhancement.<sup>28,29</sup> Its conducting and excellent electrochemical performance can mediate the extracellular electron transfer from microorganisms and enhance the electricity generation.<sup>30</sup> Above all, PEDOT:PSS can be used as an active supercapacitive material to store charges through a faradaic electron charge transfer (i.e., pseudocapacitance).<sup>31</sup> Therefore, PE-DOT:PSS can be an excellent material for biophotovoltaics and supercapacitors, thus leading to the realization of supercapacitive biophotovoltaics. Previously, our group constructed the supercapacitive biophotovoltaics by using this redox polymer in which electrons recovered through microbial photosynthesis and respiration were stored for power pulse generation.<sup>13</sup> However, the supercapacitive biophotovoltaics exhibited a relatively low power which was comparable to the device without the supercapacitive layer because of the limited capacitance (69 F/g) and poor cyclic stability of PE-DOT:PSS.<sup>31</sup> To dramatically improve the performance, MnO<sub>2</sub> for high specific capacitance and rate capability and CNTs for mechanical stability and good conductivity were added to PEDOT:PSS creating a ternary nanocomposite.<sup>32-34</sup>



Figure 1. SEM images of (a,b) the bare carbon cloth without cyanobacteria, (c,d) the PEDOT:PSS/MnO<sub>2</sub>/CNT ternary nanocomposite on a carbon cloth without cyanobacteria, (e,f) the bare carbon cloth with cyanobacteria, and (g,h) the PEDOT:PSS/MnO<sub>2</sub>/CNT ternary nanocomposite on a carbon cloth without cyanobacteria.

MnO<sub>2</sub> metal oxides have attracted much attention for pseudocapacitive materials because of their high specific capacitance, low-cost, environmental friendliness, and fast charging-discharging processes via faradaic redox reactions.<sup>35</sup> Their low conductivity can be overcome by adding carbonaceous materials such as CNTs and graphene.<sup>31,36,37</sup> Because these carbonaceous materials offer a large surface area, high conductivity, long-term operational stability, and strong mechanical strength, they have been widely used as an electric double-layer capacitive material and as an added material for the supercapacitors based on the metal oxides and the conductive polymers. In particular, binary or ternary composites can dramatically improve the supercapacitive performance by providing a unique and critical function and compensating for the weakness of each component.<sup>31</sup> The ternary nanocomposite of PEDOT:PSS, MnO<sub>2</sub>, and CNTs was prepared by mechanical mixing. Because PEDOT:PSS is watersoluble and can disperse the metal oxides and carbon-based materials, it can be a good binder material to mix these materials, which improves the nanocomposite stability. The CNTs and MnO<sub>2</sub> powders were dispersed well in aqueous

PEDOT:PSS through ultrasonification. The aqueous ternary nanocomposite solution was coated on the carbon cloth using an airbrushing technique, which allowed simple and quick deposition of the supercapacitive material with high homogeneity. Figures 1 and S1 show the scanning electron microscopy (SEM) images of the bare carbon cloth and the PEDOT:PSS/ MnO<sub>2</sub>/CNT ternary nanocomposite on the carbon cloth with and without cyanobacteria. The nanocomposite was conformally and tightly deposited on the carbon cloth fibers providing a large surface area by forming a 3-D porous structure (Figures 1a-d and S1). The SEM images with greater magnification clearly shows the morphology of the ternary nanocomposite on the carbon cloth. The 3D porous structure of the electrode is critical to improving the performance of the supercapacitance and the efficiency of the cyanobacterial extracellular electron transfer. In particular, a macroporous structure with a large and accessible surface area can enable internal bacterial biofilm growth and efficient nutrient exchange. Furthermore, the polymer-based nanocomposite improved the bioaffinity, while the carbon nanomaterials increased the mechanical properties of the electrode

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Figure 2. (a) Cyclic voltammograms (50 mV/s scanned from 0 to 1 V), (b) GCD curves of PEDOT:PSS, PEDOT:PSS/MnO<sub>2</sub>/CNTs, and PEDOT:PSS/MnO<sub>2</sub>/graphene oxide, and (c) GCD cycle curves of PEDOT:PSS/MnO<sub>2</sub>/CNTs obtained at a current density of 10 mA·cm<sup>-2</sup>.

and bacterial electrocatalytic activities, which ultimately led to a higher bacterial density than the bare carbon cloth electrode (Figure 1e-h). The XPS spectrum obtained from the nanocomposite on the carbon cloth shows signals from Mn, C, and O (Figure S2).

2.2. Electrochemical Performance of the Supercapacitive Anode. The electrochemical and energy storage performance of the PEDOT:PSS/MnO<sub>2</sub>/CNT ternary nanocomposite-based supercapacitive anode were characterized in a standard three-electrode system using a potentiostat (Squidstat Plus, Admiral Instruments), where the anodic material on the carbon cloth was used as a working electrode, Ag/AgCl (in saturated KCl) was used as a reference electrode, and a platinum foil was used as a counter electrode. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) were performed in a 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte to compare the capacitive behavior of the pure PEDOT:PSS with the PEDOT:PSS/MnO<sub>2</sub>/graphene oxide materials (Figure 2). The PEDOT:PSS/MnO<sub>2</sub>/graphene oxide nanocomposite was prepared in the same way with the same concentration as the PEDOT:PSS/MnO<sub>2</sub>/CNT ternary nanocomposite. All anodic materials were airbrushed on a carbon cloth and served as the working electrode for the electrochemical measurements. The CV analyses were performed at a scan rate of 50 mV/s for a potential window of 1.0 V. The greater current response of PEDOT:PSS/MnO<sub>2</sub>/CNTs indicates a higher capacitance than those of the pure PEDOT:PSS and PEDOT:PSS/  $MnO_2$ /graphene oxide (Figure 2a). All CV curves exhibit quasirectangular shapes, indicating the excellent capacitive behavior that comes from combining the electric double layer capacitance with pseudocapacitance. The PEDOT:PSS/

 $MnO_2/CNT$  nanocomposite exhibits a larger enclosed CV area compared with the others, indicating a greater specific capacitance and a larger charge capacity. The specific capacitance of 261 F/g was estimated from the CV curve based on eq 1.

$$C_{\rm SP} = \int I dV / (m \times \Delta V \times R) \tag{1}$$

where  $\Delta V$  is the range of voltage scan, R is the scan rate, m is the mass of the nanocomposite, and I is the measured current.<sup>38</sup> Its dramatic enhancement compared with the pure PEDOT:PSS is attributed to the excellent synergetic effect of the three supercapacitive components. The poor performance of another ternary nanocomposite, PEDOT:PSS/MnO<sub>2</sub>/ graphene oxide, is likely because the graphene oxide powder is not easily dispersed in the polymer solution. Graphene sheets normally aggregate because of their high attractive van der Waals forces.<sup>39,40</sup> The GCD characteristics of the materials were measured at the current density of 10 mA·cm<sup>-2</sup> in the potential range between 0 and 1 V (Figure 2b). The linear discharge characteristics and triangular shapes of the three materials are ascribed to their highly capacitive nature, which is consistent with those seen in the CV curves. All capacitive materials exhibit asymmetric charge-discharge curves, indicating that their capacitances mainly originate from the combination of both electric double-layer capacitance and pseudocapacitance behaviors. A noticeable IR drop in the initial part of the discharging curves indicates the internal resistance of the anode and between the anode and the electrolyte at the charge-discharge current. The IR drop  $(\Delta V_{\rm IR})$  quantifies the equivalent series resistance (ESR) of a

capacitor, which is an important quantity that appears in series with the capacitance. The ESR can be calculated at a given constant discharge current  $I_{\text{dis}}$  using eq 2<sup>41</sup>

$$ESR = \Delta V_{IR} / (2 \times I_{dis})$$
<sup>(2)</sup>

The ESR values calculated at 10 mA·cm<sup>-2</sup> is 7.5  $\Omega$ ·cm<sup>-2</sup>. The maximum capacitance and power performance can decrease because of the potential loss caused by the ESR. The PEDOT:PSS/MnO<sub>2</sub>/CNT nanocomposite displays a longer discharge time than the others, demonstrating its larger areal capacitance and better charge–discharge properties. The areal capacitance ( $C_A$ ) can be calculated according to the following equation<sup>41</sup>

$$C_{\rm A} = (I_{\rm dis} \times \Delta t) / (A \times (\Delta V - \Delta V_{\rm IR}))$$
(3)

where  $\Delta t$  (s) is the discharging time,  $\Delta V$  (V) is the voltage drop during the discharging time, and A (cm<sup>2</sup>) is the area of the anode. The areal capacitance of PEDOT:PSS/MnO<sub>2</sub>/ CNTs reached 294 F·cm<sup>-2</sup>, while much lower specific capacitance was measured from PEDOT:PSS (80.4 F·cm<sup>-2</sup>) and PEDOT:PSS/MnO<sub>2</sub>/graphene oxide (116.3 F·cm<sup>-2</sup>). From the GCD curves, the areal energy ( $E_A$ ) and power ( $P_A$ ) were calculated based on the following equations.<sup>41</sup>

$$E_{\rm SP} = C_{\rm A} (\Delta V - \Delta V_{\rm IR})^2 / 2 \tag{4}$$

$$P_{\rm SP} = E_{\rm SP} / \Delta t \tag{5}$$

The  $E_A$  and  $P_A$  of PEDOT:PSS/MnO<sub>2</sub>/CNTs were 40.1  $\mu$ W h·cm<sup>-2</sup> and 5.8 mW·cm<sup>-2</sup>, respectively. The long-cycling life is a critical parameter to characterize supercapacitors. A cycling life test for 14,000 cycles for PEDOT:PSS/MnO<sub>2</sub>/CNTs was performed. Figure 2c demonstrates the very stable charge–discharge cycles.

2.3. Electrochemical Performance of the Supercapacitive Anode with a Cyanobacterial Biofilm. The electrochemical performance of the PEDOT:PSS/MnO<sub>2</sub>/CNT anode with cyanobacteria was evaluated by CV and GCD measurements. A supercapacitor can maximize its performance in a chemical electrolyte that has good ionic conductivity, such as 1 M Na<sub>2</sub>SO<sub>4</sub>. Our supercapacitive anode, however, should perform similarly well in a physiological fluid with the living whole-cell cyanobacteria with very small ionic conductivity. The high ionic strength can inhibit the growth and metabolism of microorganisms,<sup>42</sup> and the low ionic conductivity can significantly reduce the performance of the supercapacitor.43 While the 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte exhibited a high ionic conductivity of 85 mS/cm, BG-11 media for cyanobacteria had a very low ionic conductivity of 2.33 mS/cm (Figure S3). Therefore, the evaluation of the capacitive behavior in BG-11 with cyanobacteria is critical to characterize its capability in cyanobacterial biophotovoltaics. The CV measurements were first performed between -0.2 and -0.4 V in BG-11 aqueous media without illuminated cyanobacteria, increasing the potential scan rate from 1 to 20 mV/s (Figure 3a). The shapes of the CV curves change from quasirectangular to fusiform as the scan rate increases. The CV area increased with the scanning speed for the PEDOT:PSS/MnO<sub>2</sub>/CNT anode, indicating a good rate capability. However, the nanocomposite anode exhibits a low capacitance in this BG-11 medium, which demonstrates very limited access to the electrolyte's ions. On the other hand, the CV curves with cyanobacteria dramatically increased the capacitance because the ions can be produced from the irreversible photosynthetic and respiratory reaction of



**Figure 3.** Electrochemical properties of the PEDOT:PSS/MnO<sub>2</sub>/ CNTs on a carbon cloth in BG-11 media. Cyclic voltammograms (a) without and (b) with cyanobacteria at various scan rates (1-20 mV/s). (c) GCD curve with cyanobacteria at 0.25 mA·cm<sup>-2</sup>.

the cyanobacteria (Figure 3b). The GCD curve with cyanobacteria is triangular and corresponds to the optimum capacitance behavior, generating an areal capacitance of 105 mF·cm<sup>-2</sup>, an energy of 13.2  $\mu$ W h·cm<sup>-2</sup>, and a power of 118  $\mu$ W·cm<sup>-2</sup>, respectively (Figure 3c). While the nanocomposite supercapacitive anode loses its capacitive behavior in the lowionic conductive electrolyte, its performance can be enhanced

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Figure 4. Operating principle of our supercapacitive cyanobacterial biophotovoltaics. In open-circuit conditions, charges produced from cyanobacterial photosynthesis and respiration are stored. In a short-circuit mode, the electrons stored are discharged with a high-power output.

when integrated with other charge-producing components such as energy-harvesting techniques including biophotovoltaics and bioelectrochemical systems. The biophotovoltaics continuously supply active ions, which can be used to charge the supercapacitor.

2.4. Supercapacitive Biophotovoltaics. After we confirmed that the PEDOT:PSS/MnO2/CNT anode with the cyanobacteria exhibited great performance in the threeelectrode experimental setting, it actually integrated into a practical cyanobacterial biophotovoltaic device with a twoelectrode configuration, an anode and a cathode. PE-DOT:PSS/MnO<sub>2</sub>/CNTs on a carbon cloth acted as a dualfunctional anode with the cyanobacterial biofilm, capacitively storing electrons generated by microbial photosynthesis and respiration. The integration of the internal supercapacitor within the cyanobacterial biophotovoltaics allows the device to simultaneously store charges and harvest energy. The cyanobacteria perform photosynthesis and produce charges as byproducts from the light-driven water splitting, while they produce their own energy by respiration, generating charges through the electron transport chain. They functionally overlap the photosynthetic and respiratory systems, where the electrons released during the respiratory reaction can be boosted to higher energies by photosynthesis.<sup>44</sup> In the open circuit mode, those excess negative and positive charges are stored in the supercapacitive anode faradaically by electron charge transfer (i.e., pseudocapacitance) and non-faradaically by counterions (i.e., electric double layer capacitance) (Figure 4).<sup>45</sup> At the cathode, positive charges are balanced by negative ions from the electrolyte while an oxygen reduction reaction occurs. Under the short circuit conditions, the stored charges are discharged with strong but short pulses, so that a highpower output can be achieved. Ideally, because water and carbon dioxide are used for photosynthesis, producing oxygen and carbohydrates that will be reused for respiration, this system is self-sustainable.<sup>14</sup> Furthermore, as photodamaged photosynthetic proteins can be repaired by the cell, it can be self-maintainable and self-healing,<sup>44</sup> which can be a perfect power supply for the unattended smart environment. A microliter-scale biophotovoltaic device containing the supercapacitive anode was constructed by micromachining transparent poly(methyl methacrylate) (PMMA) and parafilm thin

layers (Figure 5). The device consisted of four functional components: the anode, anodic chamber, ion-exchange membrane, and air-cathode. The ion-exchange membrane allows efficient ionic transport between the anode and the cathode for supercapacitive charge–discharge performance,



**Figure 5.** (a) Schematic illustration and (b) photo of individual layers of the supercapacitive biophotovoltaic device. (c,d) Photos of the assembled device. (e) Polarization curve and power output of the device without charging and discharging operations.



Figure 6. (a) Discharging characteristics of the supercapacitive biophotovoltaics with different external resistors (1, 10, and 100 k $\Omega$ ). (b) Charging–discharging voltage curves with different external resistors. (c) Pulse power densities and current densities with different discharging times.

while it physically separates the electrodes. For initial biofilm formation on the supercapacitive anode, the bacterial inoculum was continuously introduced through a microfluidic inlet at 30 °C in 12 h light and 12 h dark cycles for 5 days. When the thick green biofilm was observed, the microfluidic inlet and outlet were sealed using silicone to test sustainable operation. Under the light conditions without charging–discharging operation, this cyanobacterial biophotovoltaic device produced an OCV of 0.47 V, a maximum power density of 25.3  $\mu$ W·cm<sup>-2</sup>, and a maximum current density of 144  $\mu$ A·cm<sup>-2</sup>, respectively. These electrical outputs originated only from cyanobacterial photosynthesis and respiration.

To characterize the supercapacitive function, the device was operated by intermittently connecting individual resistors of different ohms (Figure 6). After the device was fully charged for 28 min, it was discharged for 2 min by connecting external resistors, 1, 10, and 100 k $\Omega$ , and then the self-charging process was followed in the open circuit mode. All voltage drops were measured every 1 min and recorded via a customized LabVIEW interface. At 1 and 10 k $\Omega$ , the voltage rapidly dropped within 1 min, while 100 k $\Omega$  required a relatively long discharging time. The external loads modulated the discharging rate of the charged energy during the discharging mode. A lower resistance enabled a more rapid discharge of the stored energy and a greater power delivery, while a higher resistance could not discharge all the stored energy. The operational stability of the device with a specific external resistor was characterized by repeating 28 min charging and 2 min discharging operations. The stability of the device with 1 and 10 k $\Omega$  gradually degraded, while 100 k $\Omega$  exhibited the most stable and durable properties. However, this relatively long

discharging time allowed the power delivery of the charges stored in the supercapacitive anode (i.e., stored energy) and charges produced by the cyanobacterial metabolism (i.e., irreversible faradaic energy), so that we cannot maximize the power delivery only from the stored energy in the supercapacitive anode. Furthermore, our 1 min recording system could not measure the transient power pulse generated from the stored energy in the anode, failing to exactly characterize the supercapacitive behavior. The electrical outputs we measured can be more noncapacitive faradaic electricity from cyanobacterial biophotovoltaics because the stored capacitive energy is expected to be delivered with a sharp and short current peak at the beginning of the discharging period. To address this issue, the power pulses at a fixed discharging time were delivered galvanostatically. The power densities during discharges of 0.1, 0.25, 0.5, and 60 s were measured as a function of current densities. Generally, a shorter discharge time provided greater power and current pulses. For example, the power pulse of 88  $\mu$ W·cm<sup>-2</sup> for 0.25 s discharging time was achieved, which is 3 times higher than the power pulse of 28  $\mu$ W·cm<sup>-2</sup> for 60 s. The maximum power density of 162  $\mu$ W·  $\text{cm}^{-2}$  for 0.1 s pulse at a discharging current density of 300  $\mu$ A·  $cm^{-2}$  was produced, leading to a rapid release of the stored power. This value is about 6 times greater than that of the biophotovoltaic device without supercapacitive operation and about 100 times higher than that of the biophotovoltaic device on the unmodified carbon cloth.<sup>15</sup>

**2.5.** Future Work. The total capacitance of the biophotovoltaics can be determined by the series connection of both the capacitive anode and cathode based on eq 6,

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resulting in a lower overall capacitance and power performance compared with those of individual electrodes.

$$C_{\text{device}} = \left(\frac{1}{C_{\text{anode}}} + \frac{1}{C_{\text{cathode}}}\right)^{-1}$$
(6)

While we focused on developing the high-performance of supercapacitive anode in this work, the overall performance of the biophotovoltaic device may not be maximized because of the nonoptimized cathode. In particular, the air-breathing cathode in the absence of an electrolyte may not have a high specific capacitance. Further studies to characterize and optimize the cathodic capacitance will be performed in the future to revolutionize the biophotovoltaic performance to attain higher power density and longer-term operational capability which then provide a practical and sustainable power supply for the environmental sensing applications.

# 3. CONCLUSIONS

The cyanobacterial biophotovoltaics can be the most suitable energy-harvesting technique for wireless sensor networks in our environment because it can self-sustainably and selfmaintainably harvest the most abundant natural energy sources, solar energy and water, to produce electricity. However, its performance remains insufficient to power those applications. The integration of the high-performance supercapacitive anode into the biophotovoltaic device can be a revolutionary solution to improve its low-power limitation. In this work, the PEDOT:PSS/MnO<sub>2</sub>/CNT ternary nanocomposite on a carbon cloth was prepared as a supercapacitive anode. Each component in the nanocomposite had an important influence on the electrochemical and energy storage properties of the material. CNTs improved the mechanical stability and the electrical conductivity of the composite, while MnO<sub>2</sub> achieved the high specific capacitance and PEDOT:PSS can work as a binder solution. The nanocomposite exhibited a very high specific capacitance of 261 F/g and stable chargedischarge reversibility for 14,000 cycles. Even with the cyanobacterial biofilm, the anode showed a high areal capacitance of 294 mF·cm<sup>-2</sup> under illumination. The biophotovoltaic device with this ternary nanocomposite demonstrated solar energy harvesting and charge-storage functions, producing a maximum power density of 162  $\mu$ W·  $\text{cm}^{-2}$  for 0.1 s pulse at a discharging current density of 300  $\mu$ A·  $cm^{-2}$ , which is the greatest performance among all the reported biophotovoltaic devices that use whole-cell cyanobacteria as a biocatalyst.

## 4. EXPERIMENTAL METHODS

**4.1. Materials.** Untreated carbon cloth (CCCP10), 30% wetproofed carbon cloth (CCWP), carbon black powder (XC-72), and 10% Pt on carbon were purchased from Fuel Cell Earth. MnO<sub>2</sub> (99% pure fine powder, CAS #1313-13-9) was obtained from Loudwolf Industrial & Scientific. CNTs (multiwalled, 698849), graphene oxide (powder, 796034, 15–20 sheets, 4–10% edge-oxidized), polytetra-fluoroethylene (PTFE), parafilm-sealing films, Nafion solution, Nafion 117 membrane, glutaraldehyde, hexamethyldisilazane, phosphate-buffered saline (PBS), isopropanol, and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich. Thin-film PMMA plastics (1/16-inch clear scratch- and UV-resistant cast acrylic sheet) were obtained from McMaster-Carr. Microfluidic tubes (0.35 mL volume) and PEDOT:PSS powder (Clevios PH1000) were purchased from CODAN and Heraeus, respectively.

**4.2.** Supercapacitive Anode Fabrication. The anode was constructed on the untreated carbon cloth by air-brushing a mixture of 100 mg of CNTs and 100 mg of  $MnO_2$  in 2 mL PEDOT:PSS solution (1 wt % PEDOT:PSS and 5 wt % DMSO) with a subsequent heat-treatment at 120 °C in an oven for 2 h. Then, the anode was microwave-sintered for 4 min to improve its porosity.<sup>46</sup> For comparison, two other supercapacitive anodes were prepared: PEDOT:PSS only (1 wt % PEDOT:PSS and 5 wt % DMSO) and PEDOT:PSS/MnO<sub>2</sub>/graphene oxide (100 mg of graphene oxide and 100 mg of  $MnO_2$  in 2 mL PEDOT:PSS solution). All mixtures were sonicated in an ultrasonic bath for 1 h, followed by a further stirring process for 30 min at 60 °C.

**4.3. Air-Cathode Fabrication.** The air-cathode was constructed by applying four layers of a mixture of XC-72 and PTFE solution on the air-facing side of the 30% CCWP as an oxygen-diffusive layer and coating a mixture of 10% Pt including carbon powder and a binder solution (Nafion solution, isopropanol, and DI water) on the other side of the cloth.<sup>47</sup>

4.4. Biofilm Formation on a Supercapacitive Anode for Electrochemical Characterization. After the anodes were sterilized with 70% ethanol and ultraviolet light for 24 h, they were placed in the bacterial cultured container, allowing biofilm formation under static conditions for 8 days in the light-controlled chamber that operated under 12 h light and 12 h dark cycles. When the thick and mature biofilm was observed, the anode samples were taken out of the container and placed on the working electrode in a three-electrode cell to characterize their electrochemical properties. The beaker-type three-electrode cell was prepared with the working electrode having the anodic samples of interest, the platinum foil as the counter electrode, and Ag/AgCl as the reference electrode. 1 M Na<sub>2</sub>SO<sub>4</sub> was used as the electrolyte having a high ionic conductivity. All electrochemical experiments were performed on an electrochemical workstation (Squidstat Plus, Admiral Instruments) under 12 h light and 12 h dark cycles.

**4.5. Bacterial Inoculum.** Synechocystis sp. PCC 6803 were procured from ATCC and grown in 25 mL shake flask cultures using BG-11 medium for 2 weeks inside the fluorescent lamp-controlled chamber (VWR Signature Diurnal Growth Chamber) at 30 °C in 12 h light and 12 h dark cycles. The BG-11 medium contained 6 mg of citric acid, 40 mg of  $K_2$ HPO<sub>4</sub>, 75 mg of MgSO<sub>4</sub>, 1.5 g of NaNO<sub>3</sub>, 36 mg of CaCl<sub>2</sub>, 1 mg of EDTA, and 6 mg of ferric ammonium citrate per 1 L distilled water. Bacterial growth was monitored by measuring the optical density at 730 nm (OD<sub>730</sub>), and the inoculum reached an OD<sub>730</sub> of 1.5.

**4.6. Biophotovoltaic Device Fabrication.** The device is composed of five substrate layers: the 1st PMMA top layer with an inlet and an outlet, the 1st parafilm gasket layer, the 2nd PMMA layer to define the anodic chamber and contain the supercapacitive anode, the 2nd and 3rd parafilm gasket layers to hold the ion-exchange membrane (Nafion 117), and the 3rd PMMA layer to contain the aircathode. The individual layers were well designed by AutoCAD software and were micromachined by a laser cutter (Universal Laser System, VLS3.5). To form a 3-D biophotovoltaic device, all layers were carefully aligned and assembled by melting the parafilm layers between the PMMA layers through hot-pressing. The anodic volume of the device was 200  $\mu$ L (Figure S4).

**4.7. Biofilm Formation in Biophotovoltaic Devices for Power Generation.** The biophotovoltaic device was first sterilized by introducing 70% ethanol through the microfluidic inlet and being placed under the ultraviolet light for 24 h. Then, the cyanobacterial inoculum in the BG-11 medium was continuously introduced to allow the cell attachment and biofilm formation under the 12 h light and 12 h dark cycles for 5 days. After an obvious green biofilm was observed, the biophotovoltaic device was operated in either of the two ways: by intermittently connecting a specific external resistor or by galvanostatically discharging at different current pulses for different times. For the intermittent connection of the circuit with the resistor, electrical potentials between the anode and the cathode were monitored through the resistor by a data acquisition system (NI, USB-6212), while the charging–discharging cycles were performed

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using a customized electric relay circuit with Arduino software. For the galvanostatic discharging operation, the electrochemical workstation was used where the working electrode was connected to the anode and the reference and counter electrodes were connected to the cathode.

**4.8. Cyanobacterial Fixation and SEM Imaging.** The anode samples were treated with 4% glutaraldehyde solution for 24 h at 4  $^{\circ}$ C and rinsed two times with PBS. Then, they were dehydrated by serial transfers through 35, 50, 70, 80, 90, 95, and 100% ethanol. The anode samples were placed in hexamethyldisilazane for 10 min and then placed in a desiccator to air-dry for 24 h. The samples were examined using a field-emission scanning electron microscope (Supra 55 VP, Zeiss).

## ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.0c02054.

SEM images of the nanocomposite; XPS spectrum; EIS data; and design and dimensions of the device (PDF)

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### Notes

The authors declare no competing financial interest.

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