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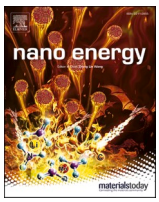

A wearable, disposable paper-based self-charging power system integrating sweat-driven microbial energy harvesting and energy storage devices

Yang Gao [a], Maryam Rezaie [a], Seokheun Choi [a,b,*]

[a] Bioelectronics & Microsystems Laboratory, Department of Electrical & Computer Engineering, State University of New York at Binghamton, Binghamton, NY 13902, USA

[b] Center for Research in Advanced Sensing Technologies & Environmental Sustainability, State University of New York at Binghamton, Binghamton, NY 13902, USA

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ABSTRACT

Microbial fuel cell (MFC) technology is constantly pushing its boundaries and advancing in unexpected ways. Integrating non-toxic, storable, spore-forming bacterial cells into a flexible, disposable paper-based MFC platform provides a new route for powering single-use, sweat-based, wearable devices. Even for one-time or short-term operations, however, the MFC performance remains insufficient as an integrated wearable power source that is reliable and practical. This work demonstrates the first example of wearable, sweat-based, disposable self-charging power paper integrating three MFCs as an energy harvester and a solid-state supercapacitor (SC) as an energy storage device. By printing energy harvesting and storing functionalizes on the same piece of paper, the design and fabrication of the system can be revolutionarily simplified while its flexible, wearable, all-in-one papertronic platform will conform to the skin. Horizontal MFC and planar interdigitated SC devices are easily integrated into a single sheet of paper. This hybrid self-powered system generates an outstanding 4 μW/cm^2 and 37 μA/cm^2 from sweat, stores an excellent 9.81 mF of energy, demonstrates stable capacitive behavior for more than 100 cycles, and possesses superior self-charging characteristics as it can produce a constant discharge of 5.53 μAh. As a proof of concept, the system successfully powered an on-chip light-emitting diode (LED).

1. Introduction

Wearable, flexible electronic devices have received tremendous attention in recent years because of their in situ and real-time monitoring capabilities of human health parameters and mobile activities in a non-invasive or minimally invasive manner [1,2]. Recent advances in micro- and nano-manufacturing, materials science, and biotechnology have created various unconventional wearable applications in healthcare, wound healing, drug delivery, and human-machine interface [3]. However, the immaturity of the technique for seamless and intimate integration of electronics with the human body hampers prolonged device wearing. Wearables provoke discomfort, distraction, and burden [4]. Existing commercial wearable products such as smart watches, patches, wristbands, and healthcare monitoring tools are being worn at most for 12 h and then are taken off to recharge batteries and eliminate the growing feeling of uncomfortableness. Even with the reduced discomfort from emerging electronic skin technology [5], wearable devices are only suitable for short-term missions or must be replaced intermittently because of human perception of the presence of the devices. Practically, many wearable diagnostic sensors are designed for one-time or short-term applications and then thrown away [6,7]. As those single-use wearables are increasingly pervasive and updated frequently, there is increasing demand for disposable, low-cost wearable platforms. Their disposability is a critical development requirement to avoid potential infections or the possible release of toxic substances after use [8].

Paper-based device platforms offer great opportunities for single-use wearable applications because of their disposability, flexibility, biocompatibility, breathability, wickability, porosity, and low-cost [9]. Moreover, paper's rich tunability with many other functional materials enables facile engineering and manufacturing possibilities [10–12]. In particular, all-printed paper-based electronics can be readily realized with functional inks. Many paper-based flexible devices have been proposed for wearable applications with large upside potential [13]. A significant challenge in realizing self-sustainable and self-powered wearable paper-based devices is the development of an integrated

* Corresponding author at: Bioelectronics & Microsystems Laboratory, Department of Electrical & Computer Engineering, State University of New York at Binghamton, Binghamton, NY 13902, USA.
E-mail address: sechoi@binghamton.edu (S. Choi).

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power source [14]. The paper-based power sources should have the same characteristics as the wearable paper devices so the fully integrated paper system can be disposable, eco-friendly, and cost-effective. If the system can be constructed by an all-printing technique, wearable components can be readily and cost-effectively integrated onto flexible, single piece of paper substrate [15]. Moreover, low-power and low-energy sources should be sufficient to run that disposable and single-use operation for a short period because they are more economical both from performance and cost perspectives [16]. Among many other potential paper-based power sources for wearable applications, biofuel cells have drawn enormous attention because of their easy integration into the paper and reliable power production from energy-rich biochemical compounds readily available in human sweat [17,18]. Enzymatic fuel cells are being actively pursued for sweat-based wearable applications, but excitement about microbial fuel cell (MFC) technology is building because biocatalytic bacteria are more versatile and resilient than enzymes and possess superior self-sustaining and stable features [19]. The latest wearable MFC demonstrated excellent stability by using spore-forming bacteria as a storable biocatalyst [20,21]. The dormant and robust nature of bacterial spores offered prolonged storage capability but readily produced on-demand power with nutrient-rich sweat by returning to vegetative bacterial cells through germination. Given the fact that millions of microorganisms inhabit the environment as well as human skin, by using bacteria as a fuel cell catalyst in wearables, we can minimize the requirement of maintaining cell viability with continuous feedstocks and suitable conditions. After the short-term use of the paper-based MFCs, they can be safely disposed of by incineration, which will prevent potential contamination or infection concerns [22,23]. However, the miniaturized MFC technique is in its early stage of development as a wearable supply. Even the latest paper-based MFCs cannot be the sole power source; they require booster circuits because of their low energy-conversion efficiency and low power performance [19]. Moreover, as MFCs typically are based on a vertical configuration of individual components with an anode, an ion-exchange membrane, and a cathode, the device requires several layers of paper and an attaching step for the functional layers [23]. This additional process causes problems such as vertical discontinuity, misalignment, and increases resistance to the transfer of ions, which ultimately hampers batch fabrication and decreases overall power performance [12]. The use of multiple layers will require a large amount of sweat to ionically connect each component and activate the MFC.

In this work, we developed an all-printed paper-based self-charging power patch that integrated sweat-activated three MFCs and one interdigitated energy-storing supercapacitor (SC). This hybrid fully system was flexible, wearable, and completely disposable. The SC was printed on a piece of paper with an interdigitated planar-type structure, demonstrating good capacitance behavior and electrochemical stability. The revolutionary integrated MFCs have a horizontal configuration that allows individual components to be placed on a single paper layer so the MFCs and SC devices can be manufactured simultaneously by all-printing, batch-fabricable processes. The single-sheet paper-based MFC required much less sweat for operation than its vertical multilayer counterpart. Moreover, the cathode can be easily designed to be larger than the anode so that the anodic activity cannot be impaired by the cathodic reaction limitation. In addition, several MFCs can be readily linked in series without complicated wire connections. Consequently, the integrated self-charging power source harvested microbial energy from sweat and simultaneously stored the energy in the SC. The stored energy can be delivered on-demand with higher and longer power output. As a proof-of-concept, an on-chip light-emitting diode (LED) was powered by our all-in-one paper-based self-charging power patch.

2. Results and discussion

2.1. Horizontally structured MFCs on paper

Usually, paper-based MFCs have a vertical configuration where an ion-exchange membrane layer is sandwiched between the anodic and the cathodic layers [24]. When bacterial cells oxidize organic substrates in the anodic part, protons and electrons are metabolically produced. The protons move through the ion-exchange membrane and reach the cathode while the electrons flow through the external circuit from the anode to the cathode, which ultimately maintains electroneutrality in both areas and completes an electrical circuit. Finally, the electrons and the protons that traveled from the anode are combined at the cathode through reduction reactions. An early version of the device used five separate paper layers for individual components, i.e., an anode, an anodic chamber, an ion-exchange membrane, a cathodic chamber, and a cathode [16,24,25]. As the technique advanced, four-, three- and two-layer MFCs were developed minimizing the process flows, the materials, and consequently the cost [10,26]. A single-layer paper device was created where all the components were vertically integrated into a single sheet of paper [10,12]. However, the device required complicated fabrication processes that compromised the performance; the limited vertical space within the single layer needed to be shared by several necessary components decreasing the anodic volume. Moreover, a serial stacking of individual MFCs (e.g., the anode of MFC #1 to the cathode of MFC #2) requires vertical through-holes for electrical connections, which prevents all-printing fabrication methods [20]. Above all, the vertical configuration limits the cathode-to-anode surface ratio to 1:1 even though a larger cathodic surface area than the anode is preferable for greater performance. Typically, the cathodic reduction process is much slower than the anodic oxidation process, leading to a significant power decrease [27,28]. To avoid those critical issues, we develop, *for the first time*, a horizontally structured MFC on a single sheet of paper. This horizontal configuration allows the development of all-printed, batch-fabricated MFCs on a single layer that can enable simple device connections in series with metallic traces prepared only on one side of the layer and provide versatile designs with a larger cathodic to anodic area ratio providing a relatively faster as well as more stable response compared to the vertical configuration (Fig. S1). Fig. 1.

As a prototype demonstration, we designed a horizontal MFC on a single sheet of paper having about a 3:1 (cathode:anode) ratio (Fig. 2a). First, hydrophobic wax was printed, followed by a heat treatment to define the anodic and cathodic regions. Also, the wax patterned between two parts was used as an ion-exchange membrane [10]. These wax patterns penetrated through the entire paper thickness to completely separate individual components. Then, the bottom cathodic part that faces the skin was patterned with wax that partially penetrated the paper so the upper hydrophilic part defined the cathodic region (Fig. 2b). That wax boundary prevents the sweat from soaking into the cathode while the entirely hydrophilic anodic part contacts the human skin and absorbs the sweat. To effectively harvest metabolically produced bacterial electricity, we engineered the pristine anodic part of the paper to be conductive by introducing an water-based poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) polymer ink [10,11]. This polymer was conformally and tightly deposited on individual paper fibers to maintain the paper's porous structure. To improve the conductivity of the polymer, dimethyl sulfoxide (DMSO) was added [10,11]. Moreover, 3-glycidoxypropy-trimethoxysilane (3-GLYMO) was additionally introduced to increase the paper's hydrophilicity [11]. For the cathodic paper part the PEDOT:PSS was supplemented with Ag_2O to improve cathodic reduction [10]. Typically, Ag_2O has been widely used as a cathodic catalyst because of its stable and high performance [29]. Like other consuming types of catalysts (e.g., Prussian blue and MnO_2), Ag_2O can be an excellent choice for short-term applications [29,30]. As an electrical contact (i.e., current collector) and a metallic trace, a graphite paste was screen-printed. Finally, the anodic part was

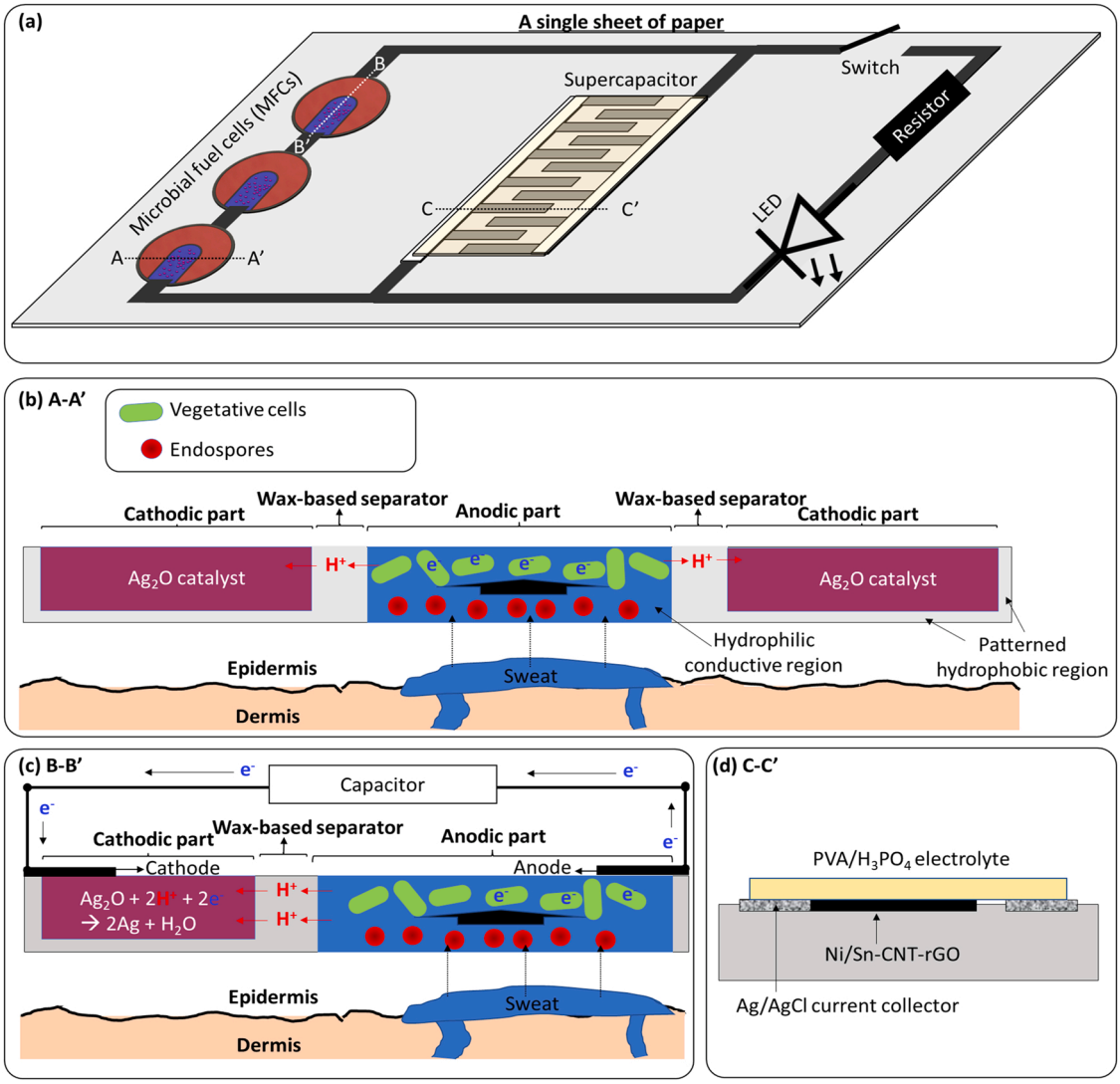

Fig. 1. (a) Schematic illustration of the self-charging power system integrating three microbial fuel cells and a supercapacitor on a single sheet of paper, (b) A-A‘ and (c) B-B‘ cross sectional illustrations of the microbial fuel cell. The cell inoculats with *B. subtilis* spores which will be germinated with sweat, generating electricity. (d) C-C‘ cross sectional illustration of the supercapacitor.

pre-inoculated with *Bacillus subtilis* endospores as a storable, dormant biocatalyst. Previously, we successfully demonstrated the spore-forming bacterial fuel cells on paper for wearable applications [20,21]. However, their configuration was limited to the vertical structure, leading to many fabrication issues, integration incompatibility with other on-chip components, and design challenges in providing various cathodic to the anodic area ratios. Our horizontal device generated a maximum power density of 4 μW/cm^2 (Actual output: 0.74 μW) and a maximum current density of 37 μA/cm^2 (Actual output: 6.945 μA) with human sweat voluntarily obtained from our group members (Fig. 2c). A control device without the spores produced negligible power, indicating that the electrical output from the device originated from the bacterial metabolism. In addition to the single MFC operation, serial assembly of the MFCs was explored (Fig. S2). It should be noted that the output voltage of the 5-MFC stack was approximately 4 times higher than that of the single unit because of additional resistances from the graphite ink traces, variability in the individual MFCs, and shunt resistance from fluidic shorting in the germinant layer [31]. However, five devices were readily designed on a single sheet of paper for a serial connection that successfully powered an electrical calculator with the sweat (Fig. 2d).

An additional paper layer pre-loaded with a nutrient germinant promoted spore germination and improved the power performance. The germinant layer fabricated on a filter paper having smaller pore sizes than *B. subtilis* spores could efficiently prevent any potential leakage (Fig. S3). However, the additional layer will require more preparation steps, hampering the batch fabrication using a single sheet of paper. Given that bacterial spore germination can be triggered by just human sweat alone [21], removing the germinant layer will be preferable for an all-in-one hybrid system development.

2.2. An interdigitated SC on paper

Energy harvesting from the human body is the best power solution for wearable devices, but their low power density and output instability limit their ability to power useful applications in practice. In particular, wearable MFCs cannot provide any power when sweat is not available or may not produce sufficient power even with much sweat because of their intrinsically low power-producing capability. Combining the energy harvesting device of the MFC and the energy storage device of the SC can be the ideal strategy to address this issue, named “a supercapacitive bioenergy harvester” or “a self-charging biopower system.” The harvested energy from the bacteria can be charged and discharged by the SC for more constant and higher power generation. Many previous reports successfully demonstrated the hybrid power system by combining SCs

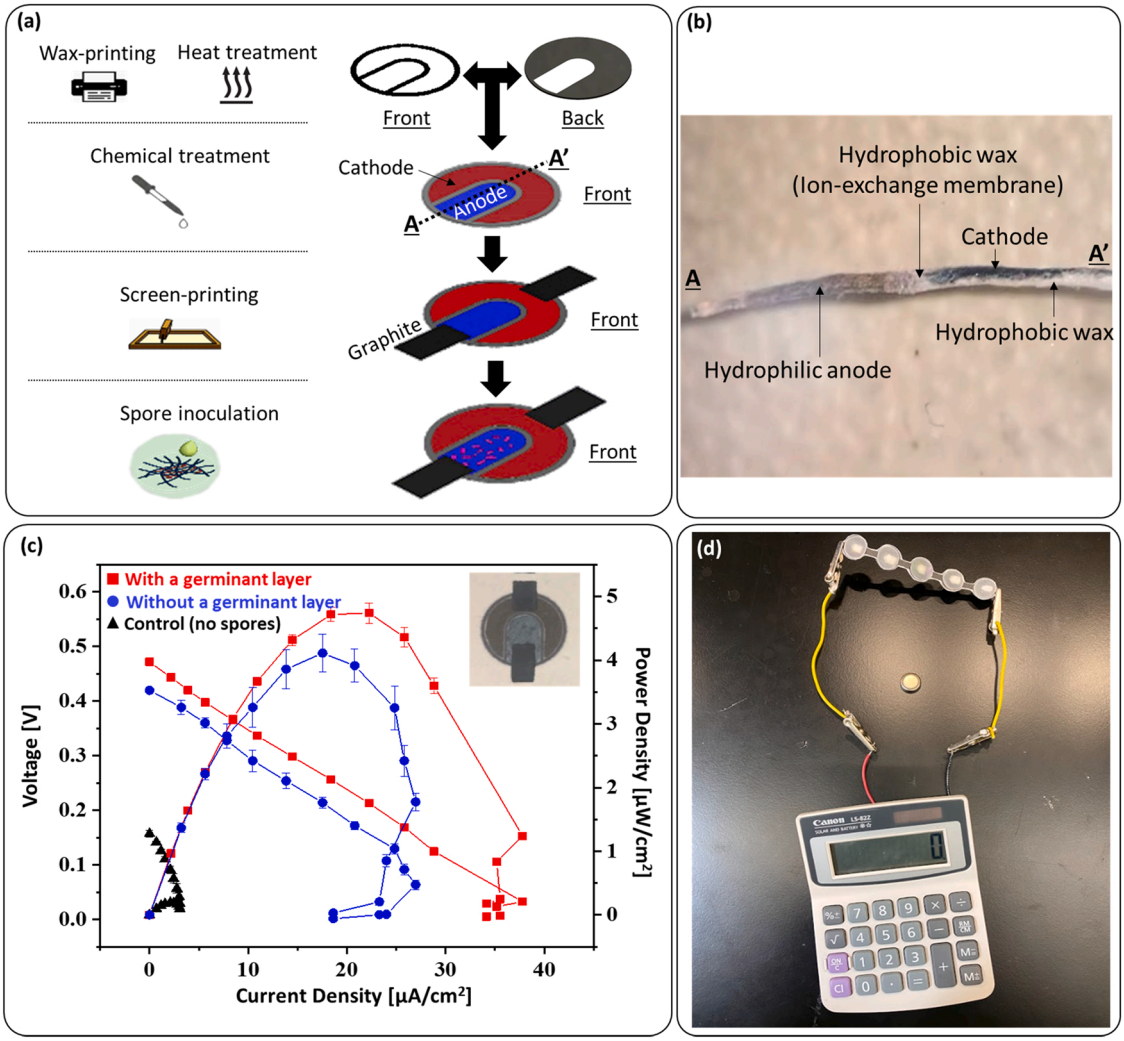

Fig. 2. (a) Schematic illustration of the fabrication process of the horizontally structured microbial fuel cell, (b) a microscopic image of the cross section of the device, (c) polarization curves and power outputs of the device with and without a germinant layer, and (d) a photo of the five serially-connected devices powering an electrical calculator.

and biological fuel cells such as enzymatic fuel cells, biophotovoltaics, and MFCs. However, reported work on the self-charging bacteria-driven power system constructed on paper was unavailable or quite limited because of a critical challenge in integrating both devices into a single sheet of paper. Recently, Liu et al. proposed a new technique to create solid-state supercapacitors on paper by using simple inkjet printing. They successfully printed a PEDOT:PSS-carbon nanotube (CNT)/Ag film on paper and then drop-cast polyvinyl alcohol–phosphoric acid (PVA/H_3PO_4) polymer electrolyte on the film to form the SC. Their paper-based SC generated high capacitance and cycle stability, which will be part of the best-fit solution for our paper-based hybrid power system with the MFCs. To improve the performance of their SC, we created a printable ink of CNT, reduced graphene oxide (rGO), and PEDOT:PSS in the form of hydrogel along with nickel/tin nanoparticles (Ni/Sn-NPs). While the rGO significantly improves the electrocatalytic interactions, Ni/Sn-NPs are added to prevent aggregation and stacking interactions of graphene in the composite. Moreover, the NPs increase the catalytic activity of the hydrogel. The roughness of the electrode surface was measured under a microscope (Fig. S4). The chemical and molecular structure of the prepared ink was characterized by the Fourier-transform infrared spectroscopy (FTIR, Nicolet 8700) (Fig. S5). Peaks of the FTIR observed at 3507 cm^{-1} and 1500 cm^{-1} correspond to the -COOH where O-H is stretching in the rGO structure. Meanwhile, C-O (epoxy or alkoxy) and C═O (carbonyl) in -COOH, along with the carbonyl groups of rGO contribute to peaks at 1054 cm^{-1}, 1515 cm^{-1}, and 1737 cm^{-1}, respectively. Subsequently, peaks at 916 cm^{-1} and 764 cm^{-1} are assigned to the Sn-O, and O-Sn-O stretching and bending movements of SnO_2, respectively. The detected peak at 1037 cm^{-1} represents the existence of nickel-oxide (Ni-O). Furthermore, the absolute black CNT network produces a very low signal-to-noise ratio in its corresponding curve of some kind of peaks as the CNT absorbs all of light's visible colors. The above facts announce the presence of all the functional groups desired and possible compact chemical bonding among SnO_2 and NiO nanoparticles, and the rGO and CNT structures, which may give rise to synergic effects. The 8-finger interdigitated electrodes were constructed by screen-printing the prepared ink and then a silver/silver-chloride (Ag/AgCl) current collector on paper. Finally, a PVA/H_3PO_4 electrolyte was cast, followed by air-drying to form a solid-state SC.

Cyclic voltammetry (CV) at scan rates of 10 mV/s, 30 mV/s, 50 mV/s, 100 mV/s, 200 mV/s, and 300 mV/s evaluated the capacitive behavior of the SC. All the CV profiles show near-rectangular shapes with small redox current peaks, indicating that the electric double-layer capacitance (i.e., CNT) and the pseudocapacitance (i.e., PEDOT:PSS) contribute to charge storage. The current response increases with the increasing scan rate, which demonstrates a good rate capability of the SC. A maximum capacitance value of 9.81 mF was achieved at the scan rate of 10 mV/s (See Supporting Information). Electrochemical impedance spectroscopy (EIS) testing was performed to evaluate the

electrochemical properties of the SC. A Nyquist plot of the frequency range of 0.1–10 kHz is shown in Fig. S6 and is analyzed by the plot to an equivalent circuit model. The plot consists of a very low semicircle in the high-frequency region and a linear part toward lower frequencies, representing a supercapacitive behavior with fast electron transfer. The model is composed of equivalent series resistance (ESR), charge transfer resistance (R_{ct}), and concomitant equivalent capacitance (C). Based on the model, ESR, R_{ct}, and C were estimated to be 83 Ω, 3.2 Ω, and 9.8 mF, respectively, implying a favorable charge transport on the electrode, in the electrolyte, and at the interface with the electrolyte. Galvanostatic charge and discharging (GCD) curves measured at a constant current at 0.2 mA are shown in Fig. 3b. The GCD curves exhibit a triangular profile with some curved shapes, indicating a dominant electric double-layer capacitance with a partial faradaic activity. The results obtained from the GCD measurement are consistent with those from the CV analysis. A cycling life test for 100 cycles was performed. Figs. 3c and 3d show very stable GCD cycles with less than 5% decay after 100 cycles. As revealed by the CV and GCD measurements, the solid-state SC built on a single sheet of paper exhibits good capacitance behavior and electrochemical stability for 100 cycles, suggesting that its performance will be enough for the short-term operation of disposable wearable applications. However, it should be noted that the CV peak current shifts towards positive potentials or negative potentials due to incomplete intercalation and deintercalations of electrolyte ion on the electrode. A linear plot of anodic and cathodic peak current versus square root of scan rates reveals the diffusion-controlled reaction (Figs. 3e and 3f).

2.3. An all-in-one self-charging power paper

A wearable and disposable self-charging power system consisting of MFCs and an SC can be fabricated on a piece of commercial filter paper. Three MFCs and one 8-finger interdigitated SC are readily aligned and integrated into the same paper substrate by all printable and potentially automatable batch-fabrication technique (Fig. 4a). To demonstrate the practicability of the system, we dropped sweat samples to activate the MFCs. The three MFCs in series charged the SC to about 1.2 V in 51 s, which can fully meet the power requirement of low-power, single-use applications (Fig. 4b). Through the subsequent galvanostatic discharging at a constant current of 0.1 mA, the capacity of the SC was obtained as 5.53 μAh. To test the cyclic performance, the SC was continuously charged by the MFCs and then discharged for 20 cycles, after which the capacitance retention of 96% was obtained (Fig. 4c).

The self-charging power system can power an on-chip light-emitting diode (LED) with orange diffused light (1.2 V, 0.2 mA) through a switch and a resistor mounted on the same paper substrate (Fig. 5a, Fig. S7, and Fig. S8). The entire paper-based system was flexible and wearable, making conformal contact with the skin through 3 M Tegaderm medical transparent tape (Figs. 5b and 5c). The self-powered paper system was disposed of by incineration after the non-combustible switch, resistor, LED, and tape were removed. Fig. 5d shows the self-powered paper was completely decomposed in 22 s. Disposability is a critical requirement for one-time use applications. This must be a priority for bacteria-containing devices because of potential bacterial infection risks if they are not properly treated after use. Fig. 5 demonstrates the potential of our paper-based self-charging power system as a wearable and disposable application. Because humidity may degrade the performance and shelf life of the paper device, additional packaging will be required in the future [32].

3. Conclusion

Here, we developed an all-in-one self-charging power paper integrating microbial energy harvesting and storage. Horizontally structured MFCs were readily printed on paper and easily connected in series through planar metallic traces. With human sweat, bacterial spores serving as a dormant, storable biocatalyst in the MFC began germination

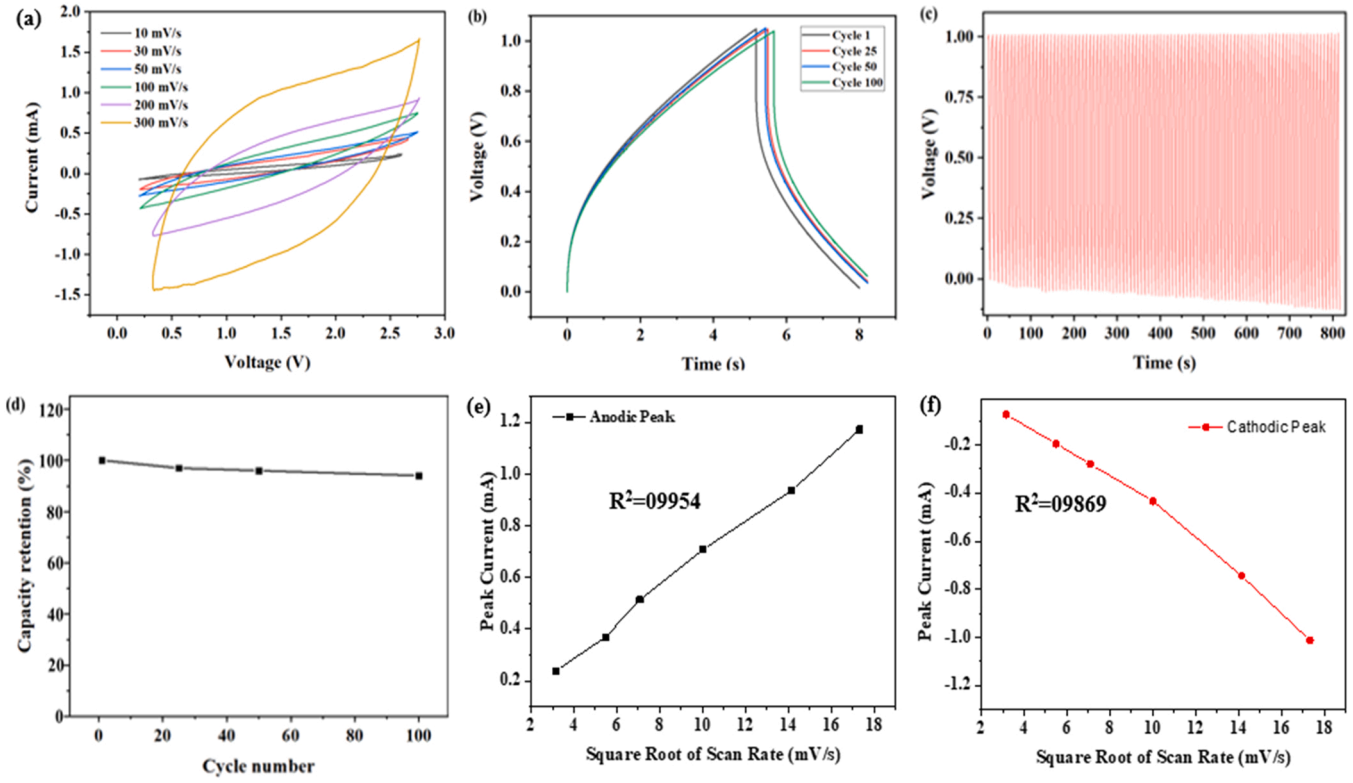

Fig. 3. Characteristics for the paper-based sucpercapacitor. (a) CV curves for voltage window of 0 V ~ 1.5 V at scan rates of 10 mV/s, 30 mV/s, 50 mV/s, 100 mV/s, 200 mV/s, and 300 mV/s. (b) GCD curves at constant current of 2 mA after different degrees of cycling. (c) GCD curves of 100 cycles. (d) Cyclic stability test for 100 cycles. (e) Plot of anodic peak current vs. square root of scan rates. (f) Plot of cathodic peak current vs. square root of scan rates.

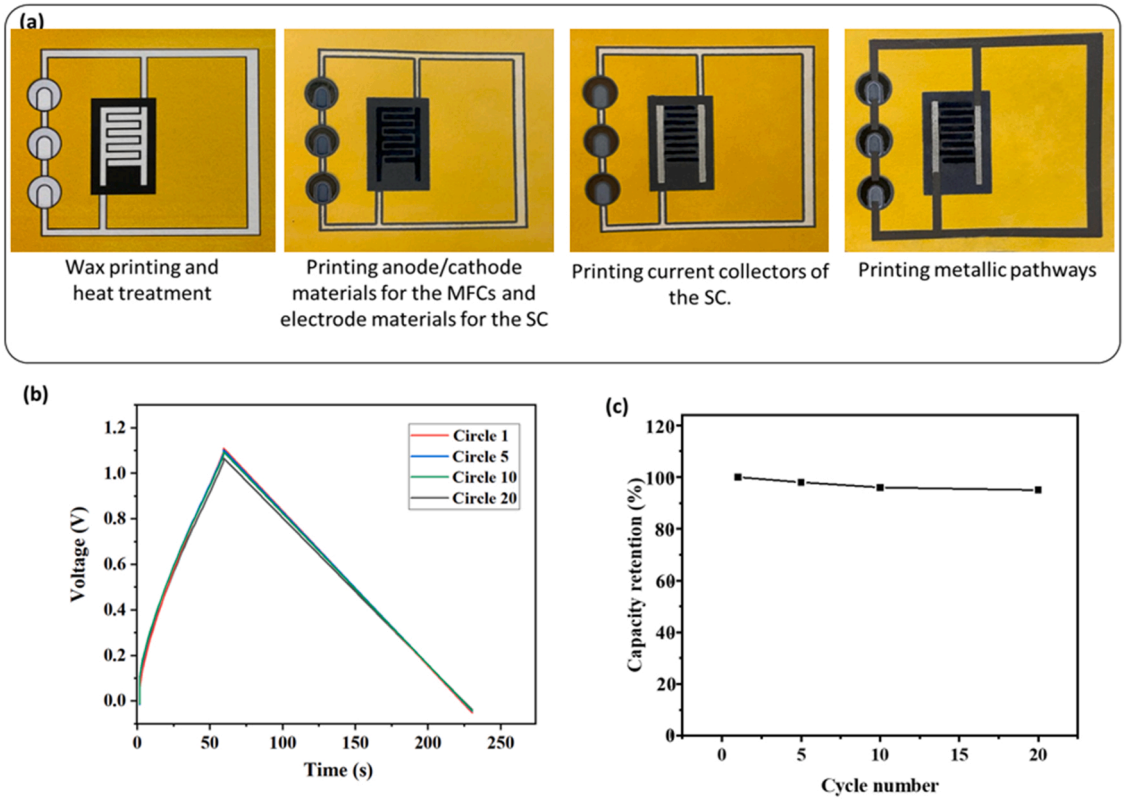

Fig. 4. (a) Fabrication steps required for making an all-in-one paper-based self-charging power system that includes three MFCs and one SC. (b) Voltage profile of the SC charged by the MFCs and discharge curve of the SC after different degrees of cycling. (c) Charging/discharging cyclic stability test for 20 cycles.

and produced electricity. An interdigitated planar-type SC was simply built on paper and exhibited good capacitance behavior and electrochemical stability. Three MFCs and the SC were successfully incorporated on a single piece of paper while all were connected on a paper circuit board, resulting in simplified design and fabrication for an all-in-one integrated system with flexible and wearable characteristics. The hybrid system produced more than enough power to light up an on-chip LED as a proof-of-concept demonstration. After use, the paper system was readily disposed of by incineration which would eventually eliminate potential risks of bacterial infections. Our work offers a promising direction for the research of paper-based wearable applications, as well as a new prospect for the development of the self-charging biopower system.

4. Materials and methods

4.1. Materials

PEDOT:PSS (Clevios PH1000) was obtained from Heraeus. Whatman™ Filter Paper (Grade 1), hydrolyzed polyvinyl alcohol (PVA), (3-Glycidyloxypropyl) trimethoxy silane (3-GLYMO), graphene oxide powder (GO), multi-walled carbon nanotubes (MWCNT), Nickel (II) sulfate ($NiSO_4.6H_2O$), Tin (II) chloride ($SnCl_2$), ethylene glycol (EG), Ammonium chloride (NH_4Cl), and sodium hydroxide (NaOH) were all purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) was obtained from EMD Millipore Corp. Phosphoric acid (H_3PO_4) was purchased from Consolidated Chemical & Solvents LLC. Graphite ink (E3449) and silver/silver-chloride (Ag/AgCl, E2414) ink were acquired from Ercon Inc.

4.2. Cultivation and sporulation of Bacillus subtilis

We purchased *Bacillus subtilis* strain 168 from the American Type Culture Collection (ATCC) and cultivated them in Luria Broth (LB) medium on a shaker at 50 rpm at 37 °C for 24 h. Then, the cultured bacterial cells were induced to sporulate by nutrient exhaustion on agar plates [20,21,23]. The spores were collected and pelleted by centrifugation at 4000 rpm for 4 min. The spores were resuspended in distilled water and heated at 80 °C for 30 min to kill all the remaining vegetative cells. The spores were stored in 15 mL air-tight tubes at 4 °C before use.

4.3. Fabrication of the microbial fuel cells

All device boundaries and ion-exchange membranes were defined on paper by printing the hydrophobic wax with a commercial printer (Xerox Phaser, ColorQube 8570) and penetrating it through the paper with heat treatment at 150 °C for 30 s. The hydrophilic regions were defined for the anodic (0.185 cm^2) and the cathodic (0.599 cm^2) compartments. Additional wax was printed on the bottom of the cathodic compartment and partially penetrated the paper leaving the hydrophilic region for the cathode preparation. The anode was prepared by introducing a mixture of 2 mL PEDOT:PSS and 10 μL DMSO, followed by dropping 20 μL of 3-GLYMO. The cathode was prepared by introducing 300 mg of Ag_2O in a 10 mL PEDOT:PSS solution. The graphite ink was screen-printed as current collectors for the anode and the cathode and as metallic traces to connect the devices. Finally, the endospores were pre-inoculated in the anodic compartment and air-dried.

4.4. Fabrication of the supercapacitor

Eight interdigitated fingers were hydrophilically defined for the paper supercapacitor. The gap between fingers is 0.5 mm and each finger is 12 mm long and 2.5 mm wide. The Ni/Sn-CNT-rGO/PEDOT:PSS ink was introduced to the finger regions and then dried for 20 min at 120 °C. The Ni/Sn-CNT-rGO hydrogel was synthesized through a one-step hydrothermal synthetic method in a Teflon autoclave

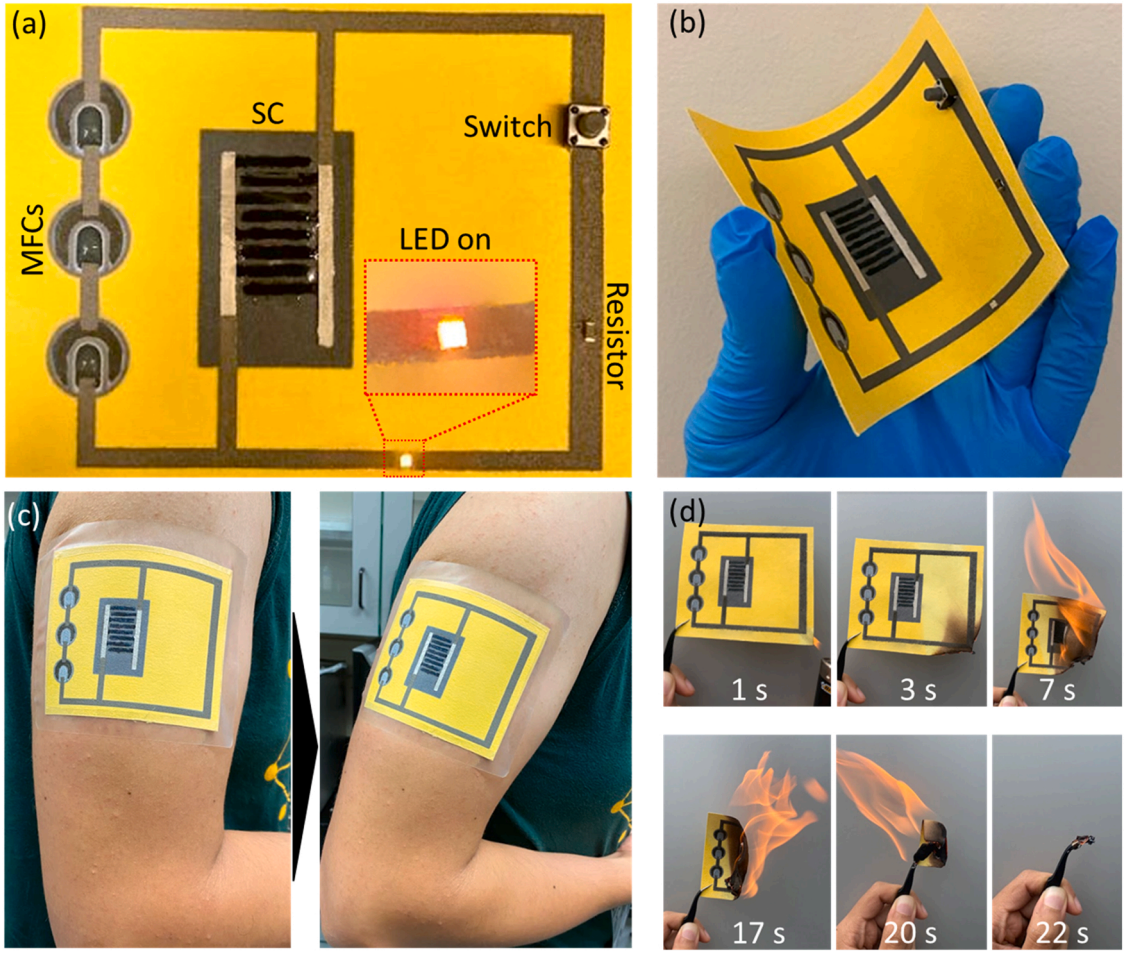

Fig. 5. (a) Screenshot of an electronic circuit integrated with our self-charging power paper. An LED was lighted up by the power system. Photos demonstrating (b) flexible and (c) wearable features of the power paper. (d) Disposal of the paper-based power system by incineration.

at 160 °C for 20 h. First, 20 mg MWCNTs and 20 mL of GO solution were mixed and sonicated for 1 h, followed by the slow addition of nickel (II) sulfate and tin (II) chloride under constant stirring. During the hydrothermal process, the graphene oxide was reduced and the CNTs were distributed between the graphene layers while Ni/Sn nanoparticles were grown on the surface of the CNT-rGO. After rinsing, centrifuging, and freeze-drying the suspension, a purified Ni/Sn-CNT-rGO powder was obtained. Finally, the powder was dissolved in a 2 mL PEDOT:PSS solution with 5 wt% DMSO and 1 wt% 3-GLYMO as a supercapacitive ink. After the finger electrodes were formed, the Ag/AgCl ink was screen-printed on the fingers as the current collector. Then, the PVA/H_3PO_4 gel electrolyte was cast all over the figures. The gel was prepared by introducing 1 g PVA to 10 mL boiling water and 0.475 mL H_3PO_4 after cooling the water to room temperature.

4.5. Preparation of the germinant layer

As a germinant solution, we prepared a mixture of L-Valine (10 mM) and AGFK (10 mM L-Asparagine, 33.6 mM D-Glucose, 33.6 mM D-Fructose, 60 mM KCl) in an LB medium. Then, the germinant paper layer was prepared by wicking the mixture. In *B. subtilis,* three germinant receptors, GerA, GerB, and GerK, were discovered, that can trigger germination in their endospores [20,23]. L-Valine targets GerA while AGFK is recognized by GerB and GerK.

4.6. Characterization

CV, EIS, and GCD measurements were performed using a potentiostat (Squidstat Plus, Admiral Instruments). ZView® 4.0 software was used to obtain the EIS data and model equivalent circuits. The electrical outputs of the MFCs were obtained by using a data acquisition system (DATAQ Instruments) through various external resistors. Their polarization curves and power outputs were obtained by measuring the voltage drops across the resistors and calculating the current and the power. Power and current densities were normalized to the anodic surface area (0.185 cm^2).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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CRediT authorship contribution statement

Yang Gao: Investigation; Methodology; Data curation; Formal analysis; Validation; Writing – review & editing;, **Maryam Rezaie**:

Investigation; Methodology; Data curation;, **Seokheun Choi**: Conceptualization; Supervision; Project administration; Funding acquisition; Writing – original draft; Writing – review, editing, and finalization.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2022.107923.

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Yang Gao is currently an electrical engineering Ph.D. student under the supervision of Dr. Seokheun Choi at SUNY Binghamton. She received her M.S. from Chinese Academy of Sciences in 2020. Her current research focuses on wearable and flexible biobatteries

Maryam Rezaie is currently an electrical engineering Ph.D. student under the supervision of Dr. Seokheun Choi at SUNY Binghamton. She received her M.S. from the University of Tehran in 2020. Her current research focuses on ingestible and small-scale biobatteries

Seokheun Choi received his B.Sc. and M.Sc. degrees in electrical engineering from Sungkyunkwan University, Korea, in 2003 and 2004, respectively. He received his Ph.D. degree in electrical engineering from Arizona State University, USA, in 2011. He was a research engineer with LG Chem, Ltd., Korea, from 2004 to 2006. From 2011–2012, he was a research professor at the University of Cincinnati, USA. He is currently a Professor in the Department of Electrical & Computer Engineering at SUNY-Binghamton. Also, he is serving as a Director of the Center for Research in Advanced Sensing Technologies and Environmental Sustainability at SUNY-Binghamton.