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Stretchable biofuel cells as wearable textile-based self-powered sensors†

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Highly stretchable textile-based biofuel cells (BFCs), acting as effective self-powered sensors, have been fabricated using screen-printing of customized stress-enduring inks. Due to the synergistic effects of nanomaterial-based engineered inks and the serpentine designs, these printable bioelectronic devices endure severe mechanical deformations, *e.g.*, stretching, indentation, or torsional twisting. Glucose and lactate BFCs with single-enzyme and membrane-free configurations generated the maximum power densities of 160 and 250 $\mu\text{W cm}^{-2}$ with the open circuit voltages of 0.44 and 0.46 V, respectively. The textile-BFCs were able to withstand repeated severe mechanical deformations with minimal impact on its structural integrity, as was indicated from their stable power output after 100 cycles of 100% stretching. By providing power signals proportional to the sweat fuel concentration, these stretchable devices act as highly selective and stable self-powered textile sensors. Their applicability to sock-based BFCs and self-powered biosensors and mechanically compliant operations was demonstrated on human subjects. These stretchable skin-worn "scavenge-sense-display" devices are expected to contribute to the development of skin-worn energy harvesting systems, advanced non-invasive self-powered sensors and wearable electronics on a stretchable garment.

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Introduction

Advanced soft materials for sensors and electronic devices are particularly interesting and used as wearable devices for diverse fitness^{1–3} and biomedical^{4–6} applications. Irrespective of applications, almost all wearable devices mandate viable energy sources, leading to a considerable research activity aimed at advancing wearable energy systems.⁷ Among all the energy storage devices that typically require re-charging and operate under non-physiological conditions, energy bio-harvesting devices, *e.g.*, enzymatic biofuel cells (BFCs), have received considerable attention. Wearable BFCs can scavenge biochemical energy from the wearer, allowing the design of power-harvesting devices for *in vivo* applications and fully integrated miniaturized and self-powered sensors. Since the majority of wearable devices are designed to be integrated with human epidermis, skin-worn BFCs thus have wide applications. Our group demonstrated minimally-invasive microneedles for harvesting energy from subcutaneous glucose⁸ and a non-invasive epidermal tattoo for generating energy from human sweat.⁹ The net power extracted from them is limited due to small contact areas with the body. Textiles have become an important

platform for wearable innovations and can cover a larger surface area. Textile-based BFCs thus have the potential to scavenge significant amounts of energy. Nevertheless, in real scenarios of daily life, multiplexed movements can cause adverse deformations to wearable devices, including both power sources and sensors, leading to one of the major challenges in wearable chemical sensors. Therefore, we herein attempted to overcome these challenges by creating a highly stretchable textile-based BFC as a fully integrated personalized self-powered sensor.

Despite the distinct advantages of textile-based devices, very few reports on textile-based BFCs have tried to address these major mechanical challenges. Nishizawa's group reported fabric-based BFCs that could convert 200–500 mM fructose to energy.^{10,11} In fact, these devices that are based on a biobattery idea showed that stretching 30 cycles at 50% strain provoked a power decrease of 20–30%, indicating key challenges to address both energy and stretchability issues. In addition, unlike the biobattery type, BFC harvesters can operate continuously, as fresh fuels are unceasingly provided by the human body, and more advantageously, they can act as self-powered sensors simultaneously. As will be demonstrated below, our new stretchable textile BFCs can serve as efficient self-powered biosensors. Self-powered biosensors have received considerable attention since the pioneering work of Katz *et al.*¹² Such bioelectronic devices obviate the need for a power source and provide power signals proportional to the level of the fuel

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analyte. Owing to their distinct advantages, including minimal interference effects in complex samples, self-powered sensors have been developed by several groups.^{8,12–16} However, to date, there are no reports on any wearable and stretchable self-powered biosensors.

This article describes the first example of highly stretchable textile-based BFCs as self-powered sensors that extract the electrical power from perspiration for probing the sensing events of sweat metabolites (Fig. 1). The new bioelectronic devices have been fabricated by screen-printing technology that offers simple ink patterning over highly stretchable fabrics or other surfaces of wearable accessories, as well as enables engineering of any extra desirable functionalities to the inks.^{17–19} However, printing electronics on wearable textiles is challenging. For example, it requires viable inks that adhere to substrates and endure high stretchability, while retaining high electrical conductivity and a favorable electrochemical performance.^{20,21} Here, we engineered the printable inks to meet these desired functionalities. Coupling the new ink formulations and serpentine electrode design, the resulting self-powered devices can display the highest stretchability for textile-based bioelectronics and endure a stable performance even upon repeated (>100 times) strains as large as 100%. Such a highly stretchable textile-based BFC has been integrated as a device that can “scavenge” biochemical energy from the wearer’s perspiration, “sense” the biomarker level, and simultaneously “display” to the readout, minimizing the external energy

sources. This “scavenge-sense-display” system is an example of a Stretchable Textile-based Autonomous Sensor (“STAS”) for advancing wearable non-invasive sensors and bioelectronic devices, as demonstrated in the following sections toward the sock-based BFC and the self-powered wearable sensor. Such textile-based stretchable energy harvesters and self-powered sensors thus hold considerable promise for enhancing the functionality of our clothing toward diverse wearable applications.

Experimental section

Chemicals and reagents

Carboxylic acid functionalized multi-walled carbon nanotubes (COOH-CNTs) and hydroxyl functionalized multi-walled carbon nanotubes (OH-CNTs) (purity > 95%, diameter = 10–20 nm, length = 10–30 μm) were purchased from Cheap Tubes Inc. Polyurethane (PU) (Tecoflex® SG-80A) was obtained from Lubrizol Life Sciences. Ecoflex® 00-30 was purchased from Smooth-On, Inc., PA. Lactate oxidase (LOx) was purchased from Toyobo. Potassium ferricyanide(m), mineral oil, *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), chitosan, glucose oxidase (GOx) from *Aspergillus niger*, type X-S (EC 1.1.3.4), 1,4-naphthoquinone (NQ), bovine serum albumin (BSA), glutaraldehyde, D(+)-glucose, L(+)-lactic acid, potassium phosphate dibasic (K₂HPO₄), potassium phosphate monobasic (KH₂PO₄), ethanol, and acetone were purchased from Sigma-Aldrich. All

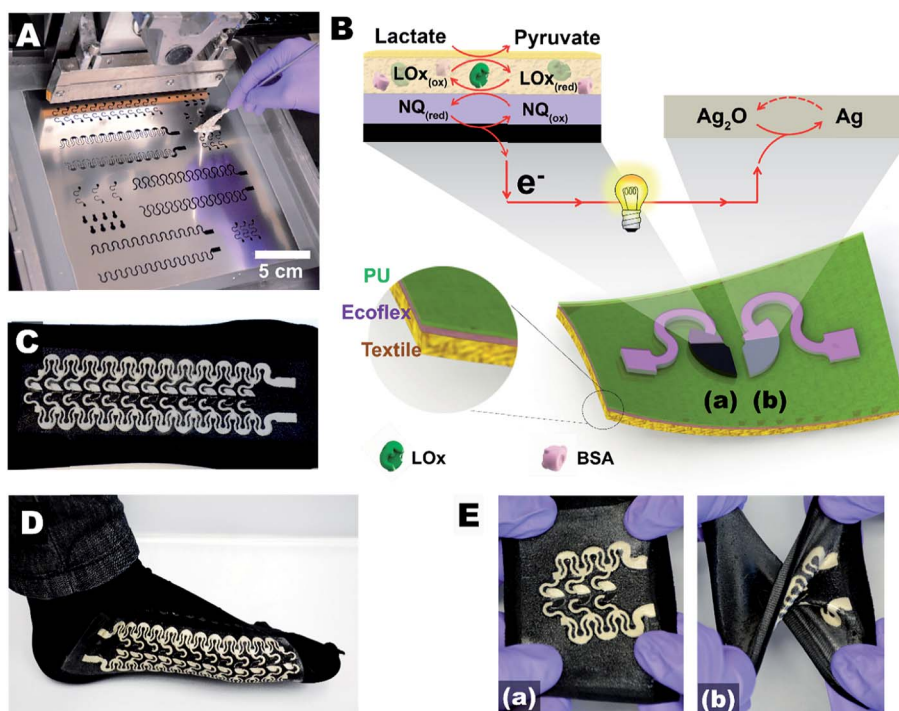


Fig. 1 (A) Photograph of the designed stencil used for printing stretchable devices and the screen-printing process. (B) The components of the stretchable lactate BFC and the redox reactions that occur on the anode (a) and cathode (b). For glucose BFC, lactate, pyruvate and LOx in the reactions are replaced by glucose, gluconolactone and GOx, respectively. (C) Photograph of the stretchable BFC array printed on stretchable textile as wearable sock-based self-powered sensors. (D) A volunteer wearing the sock-based BFC array that can act as self-powered sensors. (E) Mechanical resilience tests on the stress-enduring BFC and self-power sensor printed array. Before (a) and during the multiplex deformations, such as twisting (b).

chemicals were of analytical grade and were used without further purification. Ultra-pure deionized water (18.2 MΩ cm) was used for all of the aqueous electrolyte solutions. Ecoflex® 00-30 was prepared by mixing equal volumes of pre-polymers A and B, provided by the supplier. Ag/AgCl ink (E2414) was purchased from Ercon Inc., Wareham, MA. Glucose stock solution was allowed to mutarotate for at least 24 hours prior to use and stored at 4 °C. Stretchable textile (0.9 mm thickness, 87% nylon, 13% spandex) was purchased from Keyser-Roth Corp., USA.

Preparation of stretchable CNT and silver inks

Stretchable inks were prepared by following our previous report with modifications.²¹ The inks were optimized to suit the stretchable textile-based device. CNT stretchable ink was prepared by mixing 100 mg of COOH-CNTs with 70 mg of mineral oil. This composition was dispersed in THF for one hour in an ultrasonic bath and then homogenized in a shaker for five hours. After that, 91.5 mg of PU was added and the resulting cocktail was shaken overnight. For printing, the solid content was controlled to be the solid-to-solvent ratio of 1 mg : 9 μL. For stretchable silver ink, 90 mg of Ag/AgCl ink were mixed with 10 mg of Ecoflex® to obtain a final weight percentage of 90 : 10, Ag/AgCl ink : Ecoflex®.

Fabrication of stretchable BFC array

The fabrication process was carried out by using an MPM-SPM semi-automatic screen printer (Speedline Technologies, Franklin, MA). Stretchable patterns were designed by the authors in AutoCAD (Autodesk, San Rafael, CA) and chemically etched on a stainless steel 12" × 12" framed stencil of 150 μm thickness (Metal Etch Services, San Marcos, CA). The printing process was carried out as per the following steps. The first step was screen printing a 75 μm thick layer of Ecoflex® on a stretchable textile. The layer was cured at 65 °C for 10 minutes. Then 15% (wt/vol) polyurethane in DMF was screen-printed over the Ecoflex layer and cured in an oven at 50 °C for 20 minutes to obtain a 75 μm thick layer of PU. Afterward, a sequence of stretchable Ag/AgCl and CNT inks were printed to obtain the designed BFC array. These printed patterns of the Ag/AgCl and CNT inks were cured at 90 °C for 4 minutes and at 85 °C for 10 minutes in a conventional oven, respectively. Finally, Ecoflex® was used to define the electrode area and isolate the contact pads, and cured at 65 °C for 10 minutes.

Preparation of enzymatic anodes

The printed CNT anode was first activated by applying a potential of +1.2 V for 100 s in a saturated sodium carbonate solution. Next, the electrode was washed with water and dried in air. After activation, the modification was performed by drop casting the solution, step-by-step, as follows: 6 μL of 5 mg mL⁻¹ OH-CNTs dispersed in 0.2 M NQ in ethanol/acetone (9 : 1 (vol/vol)), 4 μL of 40 mg mL⁻¹ GOx or LOx solution dissolved in 10 mg mL⁻¹ of BSA, 2 μL of 1% glutaraldehyde solution and 2 μL of 1% wt of chitosan in 0.1 M acetic acid. Each step was performed when the

electrode from the previous step had completely dried. Chitosan solution was then added and left to dry overnight.

Preparation of silver oxide/silver (Ag₂O/Ag) cathode

The stretchable Ag₂O/Ag electrode was prepared by using the following procedure. 3% COOH-CNTs : 10% Ecoflex® : 87% pristine Ag/AgCl (by wt) ink was printed over the layer of the stretchable silver ink and then anodized at constant potential of +0.2 V for one hour at room temperature under alkaline conditions (1 M NaOH) in order to generate Ag₂O. Finally, it was rinsed with water and dried in air.

Resistance and electrochemical measurements

The resistance and short circuit current data were measured through an Agilent multimeter (6½ digit model 34411A) and Keysight BenchVue software (version 3.0). Electrochemical experiments were performed using a μAutolab Type II controlled by NOVA software version 1.11. The three-electrode system was carried out. The working electrode was the stretchable electrode. The counter and reference electrodes were platinum and Ag/AgCl (3 M KCl) electrodes, respectively. 10 mM ferricyanide in 0.1 M potassium phosphate buffer solution (PBS, pH 7.0) was used as a probe to evaluate the electrochemical performance. For the BFC characterization, open circuit potentials were obtained in 0.1 M PBS (pH 7.0) before and after the addition of the glucose or lactate solutions. Polarization curves were taken from open circuit potential to 0 V with a scan rate of 1 mV s⁻¹ in 0.1 M PBS (pH 7.0). The autonomous current response was recorded after a 60 min incubation in the sample solution. The biosensor selectivity was evaluated in the presence of relevant constituents of human perspiration in physiological levels, *i.e.*, 84 μM creatinine, 10 μM ascorbic acid, 0.17 mM glucose, and 59 μM uric acid.²² All experiments were carried out at room temperature, unless otherwise indicated. The "scavenge-sense-display" concept was demonstrated by using a dial analog ammeter (uxcell DMiotech Class 2.5 Accuracy DC Analog Panel Meter μA Ammeter). On body measurements were performed by using a compact wireless device with an integrated rechargeable battery (Vernier Go Wireless® Electrode Amplifier) to collect the data *via* Bluetooth in a smart phone.

Mechanical resiliency studies

Initially, the two-probe method for resistance measurements was employed to observe the mechanical resiliency. The printed designs (Fig. 2C and S2, ESI†) were connected with the probes, multimeter, and computer. The external force was applied to stretch the device until reaching the input strains. Afterward, it was unconstrained to its original location. During the procedure, the resistance was measured. Cyclic voltammetry (CV) was also used to monitor the resilient ability of the stretchable device. CV was first recorded on the non-stretched device. Subsequently, various forms of mechanical deformations were applied to the device and then the device was allowed to relax to its original form. Afterward, CV was recorded again to monitor the changes in the electrochemical behavior of the textile-based

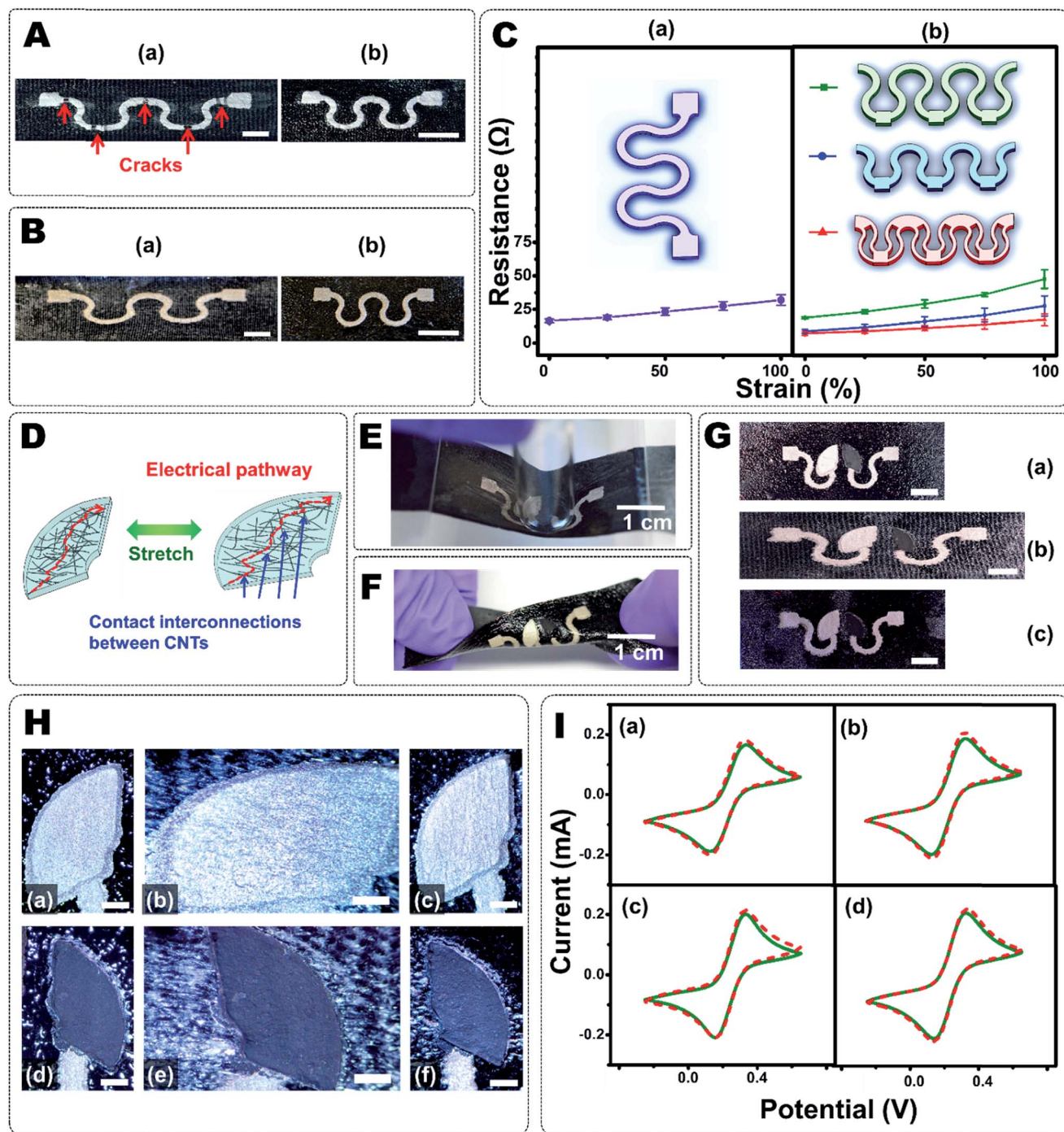


Fig. 2 Mechanical stretching study performed on the serpentine patterns printed by using (A) pristine and (B) modified Ag/AgCl inks with 10% (wt) Ecoflex®. During stretching at 100% (a) and after stretching (b). Scale bar: 5 mm. (C) Resistance study of the printed serpentine patterns. Legends show pictorial representation of the serpentine interconnect designs. Corresponding details of the designs are shown in Fig. S2 and S3, ESI.† (D) Illustration showing the percolation structure of the electrode with the nanofiller of CNTs embedded within an elastomeric matrix offering stretchability. Photographs of the stretchable device showing the mechanical robustness: (E) 5 mm indentation; (F) 180° twisting; (G) (a) before stretching, (b) during stretching and maintaining at 100% strain and (c) after repeated stretching at 100% strain for 100 times. Scale bar: 5 mm. (H) Microscopic images from the cathode (before (a), during 100% strain (b), and after 100 repeated 100% strain cycles (c)), and from the anode (before (d), during 100% stretching (e), and after 100 repeated 100% stretching cycles (f)). Scale bar: 1 mm. (I) CVs recorded before (green solid lines) and after (red dash lines) (a) applying increasing levels of strain from 0 to 100% with increments of 25%; (b) applying 100% stretching cycles for a total of 100 iterations; (c) indentations (5 mm) for a total of 100 repetitions; (d) 180° twisting cycles for a total of 100 iterations. Complementary CVs are shown in Fig. S5, ESI.†

electrodes. Power characterization and mechanical resiliency tests were carried out in a similar way.

Results and discussion

Fabrication of the stretchable BFC self-powered sensors

We demonstrated a scalable, facile, and low-cost method to fabricate highly stretchable textile-based BFC devices by utilizing the screen printing process, based on stretchable tailored inks, along with the customized stencil and electrode design (Fig. 1A). The membrane-less BFC was employed to obtain the wearable stretchable textile-based device (Fig. 1B). The bioanode was functionalized with a single enzyme (*i.e.* GOx or LOx) and NQ as a redox mediator for the biocatalytic oxidation of biofuels and increase of power density, respectively²³ (Fig. 1B(a)). A silver(i) oxide/silver ($\text{Ag}_2\text{O}/\text{Ag}$) redox couple electrode was chosen as the cathode because of several advantages, such as integration as the cathode for the BFC under anaerobic conditions²⁴ (Fig. 1B(b)). Upon adding a biofuel (*e.g.*, glucose or lactate), the biochemical fuel is enzymatically oxidized on the anode and releases electrons. On the cathode compartment, silver oxide accepts those electrons to complete the power circuit. Therefore, this BFC does not rely on the oxygen reduction reaction (ORR) and can thus operate on human-body sweat to harvest energy or provide a self-powered response without errors associated with the limited or fluctuated oxygen concentrations. With this approach, we could obtain a printable electronic array on stretchable fabrics, such as socks, that can be worn comfortably on human bodies, *e.g.*, a foot, as shown in Fig. 1C and D. Compared with other fabrication methods, this approach guarantees mechanical resilience, accommodating stress such as multiaxial stretching, bending, wrinkling, stretching (Fig. 1E), besides being simple, scalable, and free from complex transferring steps, vacuum, clean room, high temperature, and time-consuming processes.^{17,18}

Substrate modification, rationale for the stretchable connection design and engineering of stretchable inks

As a solely straight pattern cannot endure high strains, we had to employ a serpentine shaped pattern for printing the stretch-enduring traces.²⁵ Hence, preliminary efforts relied on our reported design to print the conductive traces. Additionally, the textile substrate was modified by printing elastomers in order to ensure mechanical robustness of the devices and smooth down the fabric hair in order to achieve decent printing quality (Fig. S1, ESI†). The modification was carried out by a simple low-cost process. First, a layer of highly stretchable Ecoflex® was printed on the fabric surface, filling the empty spaces of the textile's mash, offering an improvement in the fabric stretchability and also generating a smooth surface by trapping down the textile hair. As the engineered inks are typically hydrophilic in order to obtain desirable electrochemical characteristics, they are not compatible with the elastomeric under layer. Thus, in the second step, an interface layer of PU was printed over the Ecoflex® in order to overcome the ink compatibility issue with the substrate. 15% (wt/vol) polyurethane in DMF was the

optimum composition to ensure printability, stretchability, and compatibility with ink materials (Table S1, ESI†). After printing the PU layer, the substrate was cured at 60 °C for 20 minutes, this process allows time for the PU to anchor into the Ecoflex® layer, promoting good adhesion.

Conductive Ag/AgCl patterns were printed on the modified textiles. Ag/AgCl ink was used to demonstrate the stretchable conductive ink as it is compatible with the elastomer and can be further integrated with electrochemical sensors as pseudo-reference⁴ or iontophoretic²⁶ electrodes. Fig. 2A and B show optical images comparing the pristine and modified Ag/AgCl inks with 10% (wt) Ecoflex®. Fig. 2A shows the poor interfacial adhesion and cracking problems of the normal commercial ink, when it was printed on the modified textile. These issues have been addressed by adding an elastomer into the pristine ink. Note that adding Ecoflex® leads to a decreased conductivity and hence requires careful tuning of the ink composition. The optimum composition that ensures both favorable stretchability and conductive properties of the engineered ink was found to be 90% (wt) Ag/AgCl ink : 10% (wt) Ecoflex®. Compared with the pristine ink pattern in Fig. 2A at 0% strain, the Ecoflex® addition resulted in an increased electrical resistance of $\sim 14\ \Omega$ (*vs.* the $2.5\ \Omega$ original resistance of the pristine ink). As shown in Fig. 2B, it is evident that this approach enabled us to achieve a stretch-enduring ink that was compatible with the mechanically stretchable textile. No fractures were found under microscopic observation. Accordingly, these optimum conditions were applied for realization of the connection design.

Recently, we described a design that induces additional stretchability.²¹ The change in electrical resistance from this pattern (Fig. 2C(a)) indicates that this printed serpentine remained a good conductor ($\sim 32\ \Omega$) even under 100% strain. The resistance increased slightly with increasing 100% tensile strain. To further explore and accomplish superior patterns, we systematically designed a new stencil and elucidated different printed patterns (Fig. S2, ESI†). The combination patterns are also designed to accommodate the bidirections of external strains. In order to obtain the same device size, the array-to-array distance was fixed at 10.5 mm. The important parameters including the connecting angle (θ), width (W), and inner radius (r) are defined in Fig. S3, ESI†. As we proved in the previous report, a wider angle θ is preferable. Therefore, we focused on $\theta = 30^\circ$ and 45° . Three new different patterns were designed and their stretchable silver patterns were printed on the textiles to explore the best pattern. From a mechanical point of view, W should be decreased, while r should be wider to reduce an actual maximum strain on serpentine structures.^{25,27} On the other hand, Pouillet's law suggests that the resistance of interconnects will also unwillingly increase with the length and increase with decreasing W . Hence, we demonstrated the designs by keeping W constant (at 1.5 mm). One approach to reduce W is by splitting the curvature, whereas the overall size of W is still the same. The connecting lines between the small separated traces were intended to ensure lower resistance. The details are illustrated in Fig. S2, ESI†. When comparing the effect of the applied strain on the electrical resistance

(Fig. 2C(b)) and performing two-way analysis of variance (ANOVA), we find that the designs are statistically different with 95% confidence. The separated traces exhibited superior durability and conductivity than 30° and 45° designs, respectively. This separated trace design showed that applying 100% tensile strain causes a slight increase in the resistance by less than 10 Ω . With this separated trace design and aforementioned reasons, this stretchable interconnect can withstand the applied stress better. This attractive ability to relax the stresses is supported by earlier simulations.^{27,28} The experimental results fulfill the stretch-enduring electronics realization, because the consequences of two real parameters (*i.e.* conductivity and stress) were evaluated.

Regarding the BFC, more special materials are required for the anode and the cathode. The developed CNT-based ink was used in the printed anode since the CNTs provide favorable conductivity properties and play an important role in the bio-electronic processes. In addition, the high surface area of CNT leads to high and stable adsorption of the enzyme and mediator. We observed that the maximum ratio of CNT–mineral oil composite : PU was 65 : 35 (wt/wt) to achieve a highly porous surface, favorable electrochemical properties and mechanical durability.

Moreover, regarding the cathode, the Ag₂O/Ag couple was used in order to improve the performance of the BFC and mitigate the effect from environmental oxygen fluctuations. It is shown that the Ag₂O cathode has superior advantages over the common Pt, laccase, or bilirubin oxidase cathodes. Most of the existing BFCs rely on precious metals or enzymes to catalyze the ORR at the cathode. Besides high cost (*e.g.*, Pt) and instability (*e.g.*, enzymes), these BFCs have a relatively low power output, because they are limited by the low concentration of dissolved oxygen and sluggish kinetics.^{11,29,30} In this work we achieved a significantly higher power density using the Ag₂O-based cathode, compared with the Pt-based one (Fig. S4, ESI and Table S2, ESI†). However, our preliminary effort on using anodization synthesis of Ag₂O merely obtained from a scarified silver ink showed a significant loss of conductivity of the electrode.^{31,32} Therefore, COOH-CNTs were added to the ink in order to enhance the conductivity and further improve its mechanical properties. This high-aspect-ratio (~1300) CNT filler promotes sufficient percolation within the ink matrix (Fig. 2D). We suggest that dispersed CNT percolation is useful to facilitate the electron transport and the reduction on the Ag₂O cathode, as well as to enhance the mechanical resilience.^{33–35} The nanometer-scale of the CNT filler enables sufficient pathways to allow electrons to complete the electrochemical reaction. It should be noted that the simple addition of CNTs resulted in the significantly inferior mechanical performance of the cathode due to the limited binder content for holding the CNT filler. This stretchable issue could be overcome by carefully tailoring the amount of CNTs and adding an elastomeric binder. Here, highly stretchable Ecoflex®, plasticized at a mild curing process, was used to offer mechanical compliance. After having CNTs, Ecoflex®, and electrochemically generating Ag₂O, the desirable electrochemical performance was obtained. Nevertheless, considering the trade-off of three critical factors:

mechanical, electrical, and chemical properties, we had to judiciously optimize the mixing ratio of the three components, namely CNTs, Ecoflex®, and silver. The optimum weight percentage was observed using 3 : 10 : 87 (COOH-CNTs/Ecoflex®/pristine silver ink). While the electrode potential was controlled at +0.2 V in the anodization process, the outermost silver layer was first oxidized. Immediately, under alkaline aqueous solution (pH ~ 13), the generated silver ions reacted with hydroxide ions to form Ag₂O.^{36,37} The nanometer-scale of the CNT filler allows favorable electrical transport during such electrochemical synthesis as well as favorable power generation processes. Advantageously, the stretchable Ag₂O material offers potential applications in diverse energy-related applications, *e.g.*, catalytic reactions,^{38,39} fuel cells,⁴⁰ batteries,⁴¹ and photo-voltaic cells.⁴²

Mechanical resiliency study

The integration of the BFCs with wearable textiles requires resilience to harsh mechanical deformations. Therefore, mechanical resiliency was extensively tested. Fig. 2E–G shows the photographs of the poked, twisted and stretched devices. The highly stretchable serpentine interconnect helps in distributing the applied strain, reducing the actual strain on the BFC part.^{4,21} After performing these multiple deformations, we observed that the devices were mechanically rugged and maintained good adhesion with the textile substrate. Moreover, the active surface morphology of the device was also analyzed by light microscopy in reflection mode. The resulting images in Fig. 2H reveal no major cracks or major effect on the surface even though the device was stretched repeatedly for 100 times at 100% stretching. Cyclic voltammetry (CV) was used to examine the electrochemical characteristic and mechanical resiliency of the active electrode surface. First, a series of increasing strains was applied repeatedly. CVs were recorded with successive increments of tensile strain from 0 to 100% (repeated 20 times for each), as shown in Fig. 2I(a). We observed reversible CVs, as the ratio of cathodic (I_{pc}) to anodic peak (I_{pa}) currents is unity. The device maintained good functionality even under this repeated stretching, as the peak separation (ΔE_p) and peak currents were negligibly affected by such deformations (indicated from RSD for ΔE_p = 2.53%; for I_{pc}/I_{pa} = 1.31%). Furthermore, to emulate the intermittent strains of a large stretching level, the device was stretched repeatedly at strain as extremely high as 100% for 100 times. The CVs in Fig. 2I(b) confirms again the robustness of the printed device (RSD for ΔE_p = 3.93%; for I_{pc}/I_{pa} = 1.50%). Other types of strains can be anticipated for on-body applications. For instance, indentation force of 5 mm depth was applied repeatedly for 100 times. No obvious variation in the electrochemical functionalities was observed in Fig. 2I(c) (RSD for ΔE_p = 4.96%; for I_{pc}/I_{pa} = 2.61%). Additionally, as the wearable device may wrinkle, repeated torsional twisting was also emulated and tested. After applying a torque to cause 180° twisting for 100 repetitions, there was a minimal effect on the electrochemical performance (RSD for ΔE_p = 4.20%; for I_{pc}/I_{pa} = 0.76%), as shown in Fig. 2I(d). For clarity, only the

first and the last CVs are displayed in Fig. 2I. The corresponding midway CVs are shown in Fig. S5, ESI†

SEM was also used to characterize the microscopic morphology (Fig. S6, ESI†). The SEM images reveal that the printed-CNT electrode possesses homogeneous distribution and high density of CNTs within the matrix, showing good nanoscale percolation networks with numerous contact connections between CNTs, which result in excellent electrical pathways. Furthermore, the porosity exposes an internal surface area toward enhanced electrochemical properties. SEM images that were obtained after applying a large strain at 100% for 100 cycles to the device indicate a negligible effect of these mechanical deformations (Fig. S6B, ESI†), indicating an outstanding mechanical resiliency of the printed device.

The remarkable mechanical durability of the textile-based devices toward extreme external strains is illustrated in Videos 1 and 2, ESI†. A variety of severe strains were demonstrated, ranging from linear and biaxial stretching, twisting, bending, and indentation. These data indicate that the new textile-based printed BFC devices can accommodate extremely large, multi-axial and repeated multi-forms of strains. These observations

suggest that the textile-printed devices allow several degrees of freedom relevant to the wearer's movement, and can be conformably utilized in diverse real-life situations.

BFC power and stretchability

The power from the textile-based glucose BFC was primarily tested using different glucose concentrations. Fig. 3A shows that the power density increases proportionally with the glucose concentration. The maximum power density achieved was $160 \mu\text{W cm}^{-2}$ with potential showing maximum power around 0.3 V and an open circuit voltage of 0.44 V. The high power density was achieved due to the attractive conductive properties of CNTs in the tailored inks, which facilitate the electron flow from the anode to the cathode.⁴³ The power density increases linearly with the glucose concentration in the 0–50 mM range, with good sensitivity ($3.14 \pm 0.20 \mu\text{W cm}^{-2} \text{ mM}^{-1}$) and correlation coefficient ($R^2 = 0.980$), as displayed in Fig. 3B. Deviation from linearity was observed when concentrations were higher than 50 mM. Such behavior indicates that the textile BFC holds considerable promise as a self-powered biosensor.

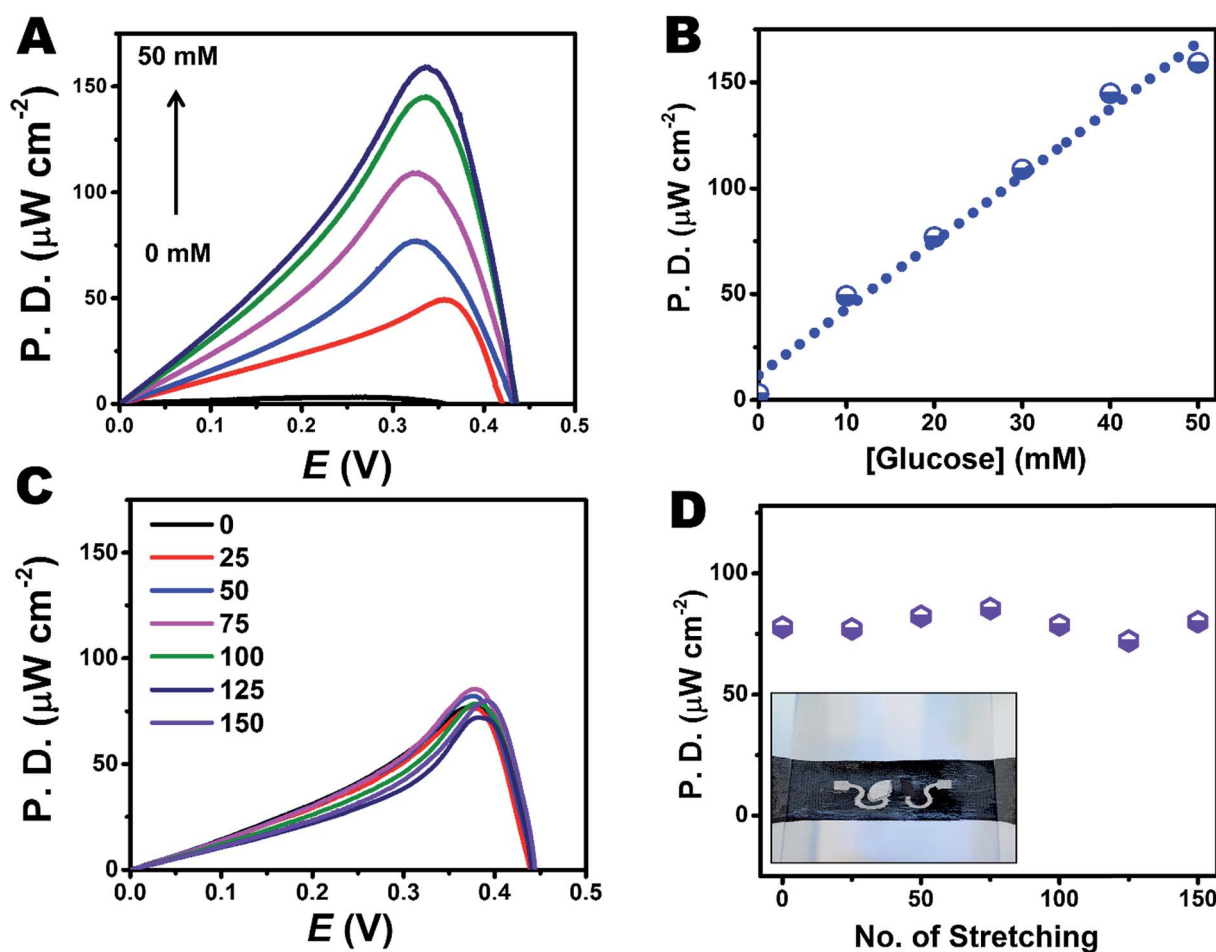


Fig. 3 (A) Power density vs. potential plots of the stretchable glucose BFC when varying the glucose concentration (0, 10, 20, 30, 40, and 50 mM) in 0.1 M PBS (pH 7.0). (B) Corresponding power–concentration calibration plot. (C) Power density vs. potential plots obtained from 20 mM glucose after every 25 cycles of 100% stretching for a total of 100 iterations. (D) Stability of the power output during these 100 stretching iterations. Inset: photograph of the stretchable BFC under 100% strain.

The stability and efficiency of the prepared BFC toward real on-body applications were examined using stretching deformation tests. For example, the durability of the generated power was monitored while applying repeated cycles of 100% stretching for many times. As shown in Fig. 3C and D, no significant variation was observed in the shape and power density after every 25 cycles of 100% stretching up to 150 iterations, with high stability (RSD = 5.37%) even after these iterations of harsh deformations. Such results illustrate the attractive performance after stretching of the present textile-based BFC against any other stretchable BFCs reported.¹¹ One of the keys for the high stretchability is our customized stretchable inks used to print the cathode and anode arrays. For the cathode, the stretchable character of the ink was improved *via* elastomeric properties of Ecoflex® and the high-aspect-ratio CNT nanofiller. For the anode, the stretchable feature of the ink was achieved through the PU elastomeric properties and the good interfacial formation of hydrogen bonds between carboxyl groups on CNTs and functional groups of PU. Besides, the layers of elastomers used as a supporting layer onto textile are essential to maintain the BFC device firmly attached to the fabric, preventing cracks on the printed array and enabling favorable stretchability to the bioelectronic printed device. This

route for fabricating mechanically robust and power-efficient devices is thus attractive for creating a variety of wearable textile-based electrochemical devices.

Demonstration of wearable BFC energy harvesting and self-powered biosensing during on-body applications

We demonstrated the versatility of our approach by patterning arrays on several commercially available flexible and stretchable substrates, as shown in Fig. S7, ESI.† This route can meet the demands of printing electronic technology for the commercial viability, as general substrates should be manufactured only under a mild processing temperature and in a scalable, rapid and inexpensive fashion. This approach, thereby, enables mass fabrication and commercialization. To illustrate the potential practical green-energy applications in personalized medicine, we fabricated the BFC devices on mechanically soft substrates of commercial accessories, such as socks, underwear, textile straps, and flexible watches that ensure the appropriate conformability between the sensor and the wearer. Six BFCs were printed on a sock (inner bottom) and connected in series to demonstrate the direct powering of six LEDs (Fig. 4A), and illustrate its potential as a feasible wearable power source.

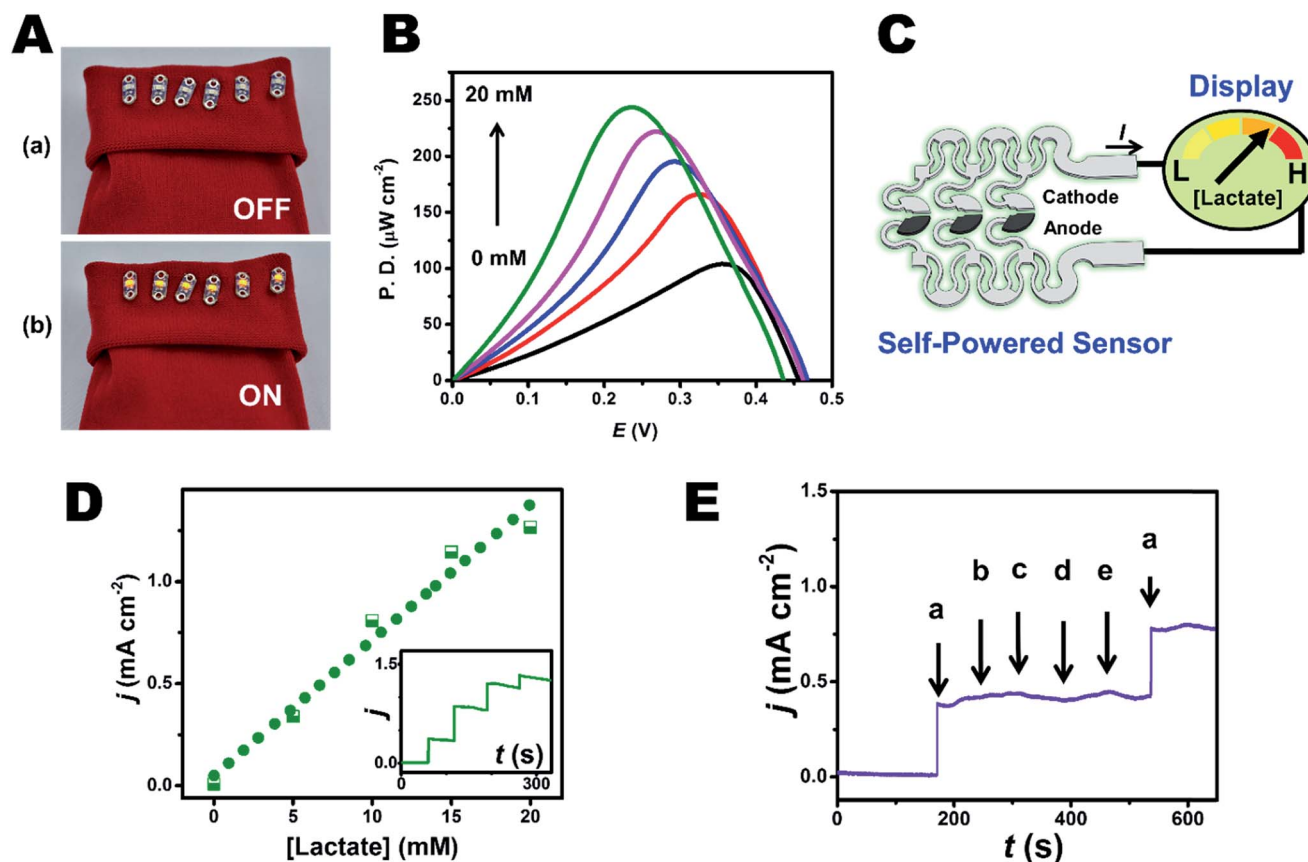


Fig. 4 (A) Photographs demonstrating the operation of six LEDs powered by six equivalent textile BFCs that were connected in series in a 14 mM lactate solution. (B) Power density vs. potential plots of the stretchable nylon-spandex textile-based lactate BFC at varying lactate concentrations (0, 5, 10, 15, and 20 mM). (C) Schematic diagram of the integrated "scavenge-sense-display" system. (D) The self-generated current response, obtained from the stretchable lactate BFC, is plotted against the concentration of lactate, with no applied potential. The inset depicts the current response upon increasing the lactate concentrations (0, 5, 10, 15, and 20 mM). (E) Response of the stretchable self-powered BFC sensor to (a) 5 mM lactate, (b) 84 μM creatinine, (c) 10 μM ascorbic acid, (d) 0.17 mM glucose, and (e) 59 μM uric acid, with no applied potential.

Herein, we introduce the Stretchable Textile-based Autonomous Sensor ("STAS") where the electrical power is extracted for probing sensing events. Lactate, as a health indicator of pressure ischaemia, physiological metabolism, or pathological disorders, was selected for demonstration.^{44–46} As illustrated in Fig. 4B, the LOx bioanode/Ag₂O cathode BFC displays well defined lactate power signals in the presence of different lactate concentrations. The open circuit voltage of the cell is assessed to be 0.46 V. The maximum power density of $250 \mu\text{W cm}^{-2}$ was obtained in the presence of 20 mM lactate. Such a power density is sufficient to power electronic devices.⁴⁷ We also found a linear relationship between the power output and the lactate concentration up to 20 mM ($R^2 = 0.974$) with the sensitivity of $6.71 \pm 0.90 \mu\text{W cm}^{-2} \text{ mM}^{-1}$. The potential shift for the power curve upon increasing fuel concentration is slightly larger for the lactate BFC (Fig. 4B) compared with the glucose one (Fig. 3A). The slightly different behavior may be attributed to the enzymatic reaction of LOx, which has much smaller Michaelis

constant (K_m). Apparently, LOx has a higher affinity for lactate, with smaller amounts of the biofuel needed to saturate the active sites of the enzyme, leading to common performance losses in BFCs.^{48–50} To demonstrate the fully autonomous sensing system in the mechanically compliant wearable platform, short circuit current responses, generated by the sensor itself, were recorded when no voltage was applied (Fig. 4C and D). This approach proves that our wearable self-powered sensor can display a real-time signal of lactate levels without any amplification, filtering, and applied energy from external energy sources, to greatly simplify such lab-on-a-textile operation (inset of Fig. 4D). The calibration curve of the autonomous signals in Fig. 4D shows good linearity ($R^2 = 0.985$) up to 20 mM lactate and a limit of detection of 0.3 mM ($3 \times \text{SD}/\text{sensitivity}$) with enhanced sensitivity ($66.5 \pm 6.8 \mu\text{A cm}^{-2} \text{ mM}^{-1}$), compared to early lactate sensors.^{51,52} The high sensitivity, along with mechanical stretchability, reflects the combination of several factors, including the customized nanomaterial-based inks, the

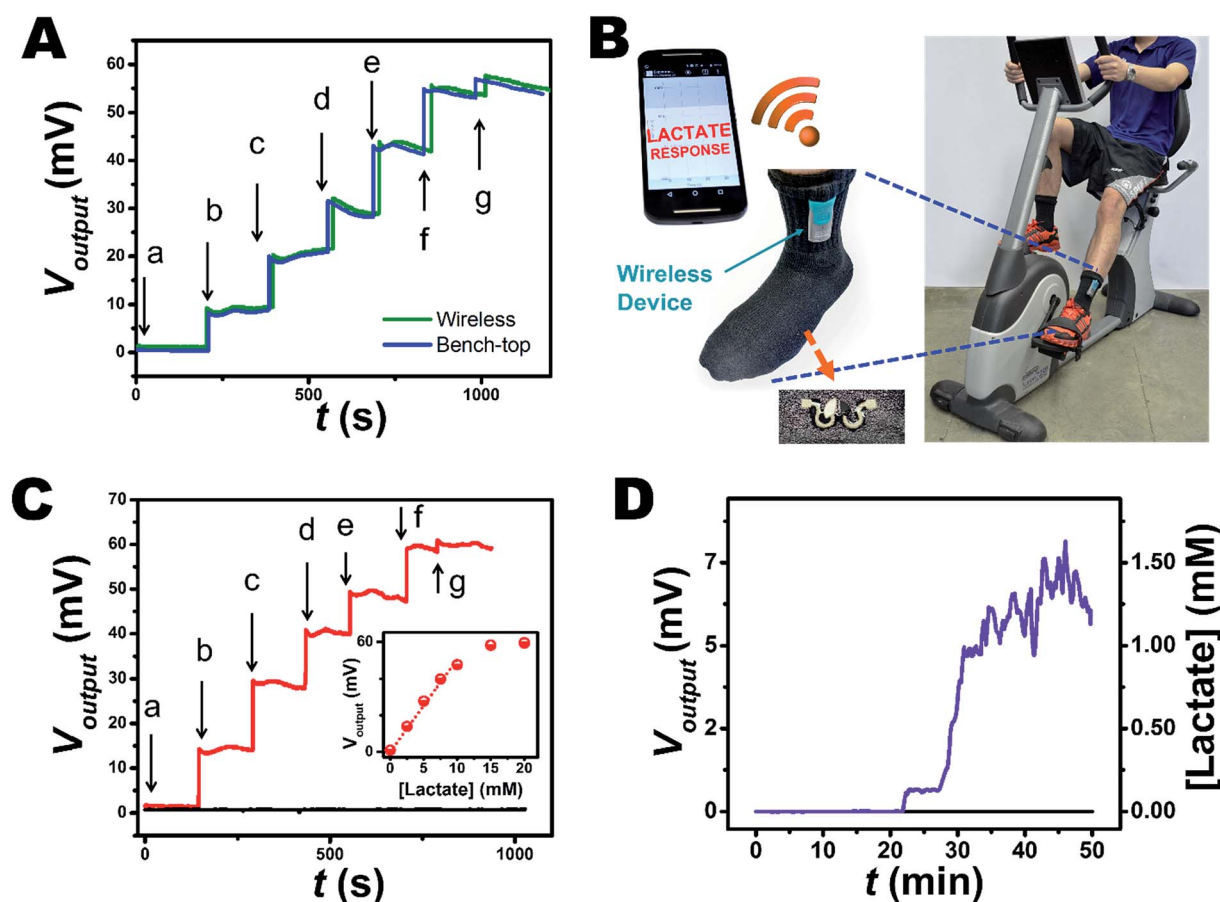


Fig. 5 Self-powered lactate sensing. (A) Comparison of calibration obtained from a bench-top multimeter (blue plot) and a compact wireless device (green plot). (a–g: 0, 2.5, 5.0, 7.5, 10, 15, and 20 mM). No potential was applied. (B) The lactate STAS on the sock applied to a volunteer's foot. (The device was printed inside the sock.) The self-generated real-time signal obtained from the sock-based biosensor can be read and recorded wirelessly using a smartphone and a compact wireless device. The corresponding circuit is shown in Fig. S8, ESI.† (C) Self-generated voltage output obtained from the lactate STAS and a compact wireless device at 37 °C (a–g: 0, 2.5, 5.0, 7.5, 10, 15, and 20 mM). Response of the LOx- (red plot) and enzyme-free (black plot) sensors. No potential was applied. Inset: corresponding *in vitro* calibration curve of the lactate STAS at 37 °C, autonomous response to different lactate concentrations up to 20 mM. (D) Real-time lactate response obtained from the on-body test during the cycling exercise. The subject maintained a constant cycling rate for 50 min. Response of the LOx- (purple plot) and enzyme-free (black plot) STASs on the sock, with no applied potential.

effective single-enzyme immobilization and electron shuttle, and the electrical communication associated with the simplified BFC configuration.⁴⁸ The selectivity was examined in the presence of common interference at physiological levels expected in real sweat.²² As illustrated in Fig. 4E, the STAS offers high selectivity in the presence of common co-existing interference. Such an analytical selectivity of the self-power sensor is attractive compared with traditional amperometric biosensors that are subjected to interference from these co-existing electroactive species. The STAS thus enables monitoring of the analyte (fuel) in the real complex matrix without interference.^{12,13}

Fig. 4C, S7, and Video 3, ESI† demonstrate the “scavenger-sense-display” concept using the totally integrated system in connection with the biosensing of lactate. The system consists of the stretchable biofuel cell and the analog ammeter display, without any external power sources. The current signal from the sensor is extracted by the BFC (an energy bio-harvester that converts biochemical inputs into electricity), and is quantitatively monitored by the dial display due to the relationship of magnetic and electric fields in the ammeter. This results in a quantitative response as the electricity generated by the BFC is proportional to the biofuel concentration. As shown in Fig S7,† the device has been printed on a variety of textiles, ranging from stretchable headbands, straps and socks. The real-time change in the autonomous current output upon increasing the lactate concentration is clearly illustrated in Video 3.† This concept involves scavenging bio-energy from human perspiration while simultaneously monitoring the health status by the autonomous power output and using this energy itself to show the response. In order to further demonstrate the on-body performance of the new stretchable self-powered biosensing concept and obtain the real-time data, we adapted the compact wireless device to record the lactate signal on a smart phone. The system includes a STAS, a resistor as a load, the compact wireless device, and a smart phone. The voltage output between the cathode and anode was measured by the compact device and transmitted to the smart phone *via* Bluetooth (Fig. S8, ESI†). The response of this wireless system compares favorably with that of a bench-top equipment (Fig. 5A). Our STAS can eliminate concerns about external applied potentials as well as bulky and complex instrumentation, as illustrated in Fig. 5B for integrating it with the sock-based biosensor and applying them on the volunteer's foot. As illustrated in Video 4,† placing the sock-based STAT on the foot involves extreme mechanical strain. In order to monitor the real-time lactate concentration for the on-body test, the STAS was calibrated at 37 °C, reflecting the enzyme's activity in the physiological temperature. The volunteer wearing the sock-based STAT was asked to cycle at a constant level and the real-time voltage output was recorded during the cycling exercise (Fig. 5D, left y-axis). The corresponding lactate concentration was obtained from the correlated calibration (Fig. 5D, right y-axis). The output of the LOx-immobilized (purple plot) and the control “LOx-free” (black plot) of the sock-based STASs is shown for comparison. The real-time signal that was self-generated from the LOx-immobilized STAS clearly indicates the well-defined lactate response

(different from the control one). Such a negligible background signal represents an attractive feature of the self-powered biosensing system, compared to common controlled-potential amperometric measurements. From the real-time lactate profile, no self-generated output is detected during the first stage of cycling. After the subject secreted the lactate-containing sweat, the self-generated signal output can be observed due to the power harvested from the lactate biofuel in the wearer's sweat. After operating the device under physiological conditions for 50 minutes, the device was successfully rechecked to evaluate the operational stability, which indicated that it was still functional. This proof-of-concept demonstration can be further developed as a self-powered logic for manipulating bio-computing systems and could greatly simplify the design of intelligent miniaturized wearable electronics wherein mechanical compliance is also mandatory.^{16,53,54}

Conclusions

We demonstrated the fabrication and operation of stretchable textile-based printed biochemical energy harvesters and self-powered sensors. Tailored stretch-enduring inks and judicious design patterns were used for screen-printing these bio-electronic devices onto the corresponding textile substrates. Nanocomposite materials were carefully engineered to enhance the electrical, electrochemical, and mechanical properties. The resulting devices displayed remarkable mechanical resiliency without compromising their functionalities. To advance further understanding of the system behavior, future work will focus on strain distribution analysis to evaluate the combinational effects on the devices from intrinsic and design-induced stretchability using strain mapping analysis and theoretical mechanical simulations. By addressing the limitations of traditional textile-based electrochemical devices, the new devices can readily conform to the body and are thus ideal for epidermal energy harvesting in diverse real-life situations. These capabilities offer considerable promise toward potential on-body, non-invasive self-powered sensing and energy-harvesting operations. The versatile fabrication approach could be applied to a wide range of soft commercial garments. The new bioelectronic socks can incorporate additional sensors (*e.g.*, pressure sensors for monitoring the foot pressure for athletes or diabetics) and can be integrated with mobility sport tracking devices to collect vital-sign data *via* wireless communication. The new textile-based stretchable devices thus hold considerable promise for next-generation of smart clothes for monitoring personal health and performance.

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