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Wearable textile biofuel cells for powering electronics†

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The fabrication and performance of a wearable biofuel cell printed directly onto textile substrates are reported. The textile biofuel cell utilizes physiologically produced sweat lactate as the fuel to generate electrical energy, producing up to 100 μW cm^{-2} at 0.34 V during *in vitro* experimentation, even after repeated bending stress. Furthermore, the wearable and flexible biofuel cell can be easily integrated with a portable energy storage device for on-demand powering of wearable electronics. To validate energy harvesting, the biofuel cell is integrated into a headband and a wristband, and with the help of an on-board DC/DC converter, extracts energy from perspiring human subjects for direct powering of an LED or a digital watch. Convenient incorporation and removal from a variety of garments are achieved by printing the biofuel cell on a detachable care label. Such textile-based non-invasive biofuel cells can be expected to serve in the future as the power unit for wearable electronics and biomedical devices.

Wearable electronics have triggered enormous attention as a promising technology for next-generation portable electronic devices.[1–3] Though tremendous advances have been achieved in this rapidly growing field, further progress has been hampered due to the lack of suitable, anatomically compliant power sources. This roadblock can be overcome by developing flexible and wearable power sources, such as energy storage and energy harvesting devices. Energy storage devices, for example, flexible lithium batteries[4] and wearable supercapacitors,[5] have been reported to serve the needs of wearable electronics, though they still suffer from limited energy density and therefore may require frequent re-charging. Wearable energy harvesting devices, on the other hand, harness energy directly from the wearer's body in a benign fashion, and thus represent an attractive choice to power wearable electronics. In this regard, piezoelectric nanogenerators, that can harvest thermal differential and mechanical energy,[6] endocochlear-potential-based biobatteries based on the inner ear potential difference[7] and biofuel cells (BFCs) that convert chemical energy into electricity[8] have been developed.

As one potential energy harvesting technique, BFCs rely on the use of biocatalytic redox enzymes to convert chemical energy into electrical energy.[9–12] Most of the reported on-body BFCs rely on blood glucose as a fuel and hence require implantation within the wearer.[11,13–15] Incorporating/replacing such BFC devices within the human body requires invasive, strict and complicated procedures, making them less user-friendly and practical. Additionally, while such devices can be used to power implantable devices, their utility as energy sources for externally-worn devices is currently limited. Accordingly, there are urgent needs to develop easy-to-wear non-invasive BFCs that can utilize metabolites present on the epidermis to generate usable energy and power on-body devices.

Herein, we describe the development and performance of a textile BFC, integrated with a printed-circuit board (PCB)-based wearable energy storage device, to power electronic devices. Thick-film printing technology, offering large-scale low-cost mass production of high-fidelity electrodes, is employed to fabricate the textile BFCs. This fabrication technique has recently been applied for printing electrochemical sensors on common textiles,[16,17] but not in connection to fabric-based BFC. The versatility of screen-printing offers facile and modular integration of the BFCs in various series/parallel combinations to tailor output voltages and currents to the desired values. The new textile BFCs have been screen-printed on a detachable care label and hence can be readily incorporated into various garments (Fig. 1A). The resulting flexible textile-based BFCs consume sweat lactate and dissolved oxygen to produce electrical energy.

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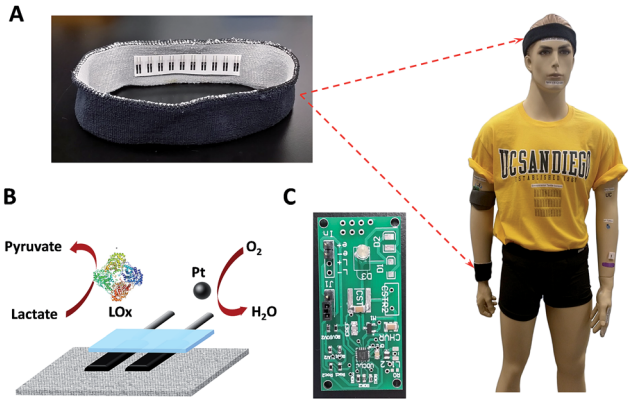

Fig. 1 Wearable textile BFCs. (A) Textile BFCs integrated in various garments such as headbands or wristbands. (B) A scheme of a textile BFC including a bioanode for lactate oxidation and cathode for oxygen reduction. (C) A customized printed circuit board prototype for the conversion, conditioning and temporary storage of extracted energy.

In the present study, efficient lactate oxidation has been achieved by using lactate oxidase (LOx) enzyme mediated by tetrathiafulvalene 7,7,8,8-tetracyanoquinodimethane (TTF·TCNQ). By incorporating TTF·TCNQ complex, the power density has been increased dramatically compared with our epidermal-tattoo BFC work,[8] hence meeting the requirements of powering common wearable devices. Upon integrating with an energy-processing PCB, the textile BFC was able to power LED or a wrist watch under *in vitro* conditions. Real-time on-body powering of these electronic loads have also been demonstrated when using the textile BFCs in a parallel configuration. The attractive performance and real-life application of the textile BFC thus clearly demonstrate its promise as a viable wearable power source. Such characteristics and applications are reported in the following sections.

Due to their ubiquitous daily use, textiles have been recently utilized for supporting various devices, such as batteries[18] and sensors.[16,17,19] However, textile-based BFCs integrated within garments to harvest energy directly from an individual to power wearable electronics have not yet been demonstrated. Absorption of the fuel by the underlying textile substrate can greatly hamper the performance of the printed BFC. Hence, a non-absorbing textile is desired. A hydrophobic coating of Scotchguard® was thus adopted to prevent adsorption of the solution and to ensure proper functioning of the textile BFCs. Several types of textiles were examined to identify the most suitable substrate, including cotton (T-shirt), polyester/cotton (sock), polytetrafluoroethylene (Gore-Tex®), and polyester (care label) (Fig. S1†). Initial characterization of BFC electrodes printed on these substrates revealed that the care label offers the best print quality as well as BFC operation due to its smooth and densely woven texture. Additionally, care labels are widely used in clothing apparels and hence care label-based BFC can be easily incorporated into (and removed from) different types of garments using detachable fastener tape. Accordingly, care labels were employed throughout this work as the substrate for the fabrication of textile BFCs. Fig. 1A shows an array of textile BFCs, attached to a headband, using Velcro® sticky-back hook and loop fastener tape.

A continuous and high concentration of fuel supply is desirable for using BFCs to generate energy sufficient for powering electronics. Fortunately, human perspiration contains high levels of lactate fuel.[20,21] Therefore, the textile BFC was prepared using LOx as the biocatalyst at the bioanode for sweat lactate oxidation and platinum black at the cathode for oxygen reduction, as shown in Fig. 1B. Efficient electron mediation from the enzyme to the electrode is greatly desired for fabricating high performance BFCs. TTF·TCNQ has been widely used as a mediator for biosensor applications and *in vivo* glucose measurements due to its low toxicity and low redox potential.[22,23] In addition, TTF·TCNQ was selected as the mediator to minimize oxygen competition in the lactate oxidation by LOx. The bioanode was thus first modified with TTF·TCNQ and carbon nanotube (CNTs) and subsequently with LOx. The final biocompatible chitosan overlayer enhances the stability of the enzyme and prevents direct contact of the bioanode reagents and materials with the skin. Similarly, the platinum-black modified cathode was further coated with Nafion®. Platinum has been well recognized as a catalyst for oxygen reduction, and the platinum-black was selected due to its high shelf-life stability.

From a system perspective, extraction of the maximum possible energy requires co-design between the BFC electrodes and the energy harvesting microelectronics. Specifically, the power generated by the BFC must be conditioned in some manner to match the voltage and current requirements of an electronic load. Unfortunately, only a few emerging implantable BFC studies have discussed this co-design in detail.[13,24–27] Since the output voltage and current of a single BFC are rarely perfectly matched to the voltage and current required by electronic loads, energy conditioning thus becomes mandatory and this is typically performed by: (1) arranging individual BFC in series or parallel configurations to stack output voltage (series) or increase the current capability (parallel); and/or (2) employing a DC/DC converter that transforms the voltage and current from the BFC to a different output voltage and current more suited for the electronic load. Since the loaded BFC output voltages are typically lower than required for most electronic devices (which often require voltages greater than 1 V), series stacking of individual BFC elements can be used to increase the effective output voltage. However, as in photovoltaic applications,[28] the overall energy harvesting performance of the series stack is limited by the instantaneous current generation of the weakest BFC in the stack. Thus, while a promising, low-complexity technique for voltage matching between the BFC and the load, series stacking does not offer a means to regulate this voltage, and is difficult to employ *in vivo*; as a result, series stacking has primarily been used for *in vitro* experimentation, or between independent living creatures.[13,24,29] Instead, employing a DC/DC converter that boosts the BFC output voltage to a higher level is the generally preferred solution.[25,30] As illustrated in Fig. 1C and S2,† a PCB, featuring a DC/DC boost converter, has been designed in this work, which includes a maximum power point tracking (MPPT) circuit that can dynamically change the input impedance matching conditions to extract the maximum possible energy from the BFC. The PCB is sufficiently

miniaturized to be easily integrated in garments, such as headbands or wristbands, and contains representative load circuits for demonstration purposes.

The developed textile BFC was first examined in phosphate buffer solutions containing different lactate concentrations. As expected and illustrated in Fig. 2A and B, the power density of the BFC was dependent on the fuel concentration. The maximum power density increased linearly with the lactate concentration up to 9 mM, and then began to level off from 12 mM. With 15 mM lactate, the textile BFC displayed an open circuit potential of 0.67 V, along with power density of up to 100 $\mu W\ cm^{-2}$ (electrode area: $3 \times 1.5\ mm^2$) at the voltage of 0.36 V. Such dependence indicates considerable promise of using the textile BFC as self-powered biosensors as well, although such potential sensing applications would benefit from a wider dynamic range. In addition, the textile BFC displayed a stable power output over a prolonged operation, as was illustrated over a 6 h period with 8 mM lactate (Fig. 2C and D). The power density of the textile BFC demonstrated an initial decrease of 20% over the first hour and maintained high stability for up to 6 h, thus underscoring its ability to operate over extended period. Whenever needed, the energy device can be easily replaced by the wearer in connection to the detachable care-label support. Such convenient removal is attractive also for laundry applications.

Normal wear and daily human activities may affect the energy harvesting efficiency of the printable BFCs on textile substrate, and hence we examined the influence of repetitive mechanical stress upon the performance of the device. During routine use of the textile BFC, the care-label will be incorporated into garments (*e.g.*, the headband/wristband used in this work). These garments (containing the care-label BFC) undergo deformations, such as bending and stretching. Note that while the care-label itself is not fully stretchable, the corresponding headband support is greatly stretched, and the overall operation mimics real-life scenarios. The experiments shown in Fig. 3 were thus conducted to examine the overall effects of bending/stretching of these garments, containing the textile BFC under relevant daily operation. The headband containing the BFC was stretched for 40% and bended at 270° up to 100 iterations and the power density was examined after each 20 stress cycles (Fig. 3). The textile BFC with Velcro® remained mechanically robust and was able to withstand such repeated stress that closely associated with the usual wear and tear. Such repeated bending/stretching resulted in negligible effect on the power output of the textile BFC, reflecting its tolerance and flexibility.

In order to increase the total power produced by the textile BFC to levels sufficient for operating typical electronics, multiple BFCs were connected in a parallel configuration. For example, two BFCs were able to generate 6 μW at 0.376 V, as opposed to 3 μW at 0.358 V for a single BFC. Since 0.376 V is insufficient to directly power most electronic devices, we employed a BQ25504 boost converter integrated circuit to step-up the voltage to upwards of 3.2 V. Specifically, the boost converter is used in an energy-buffering topology,[7] where an energy-storing capacitor is periodically charged until it stores sufficient energy to briefly power a load that has a higher instantaneous power requirement than is available directly from the BFC. To verify system functionality, a blue LED requiring 2.5 V and 0.5 mA, was periodically illuminated by the converter output after sufficient energy was buffered. During *in vitro* experiments the blue LED flashes upwards of 5 times when powered from two parallel textile BFCs operating with a 14 mM lactate fuel solution (Fig. 4A). To further study the long term

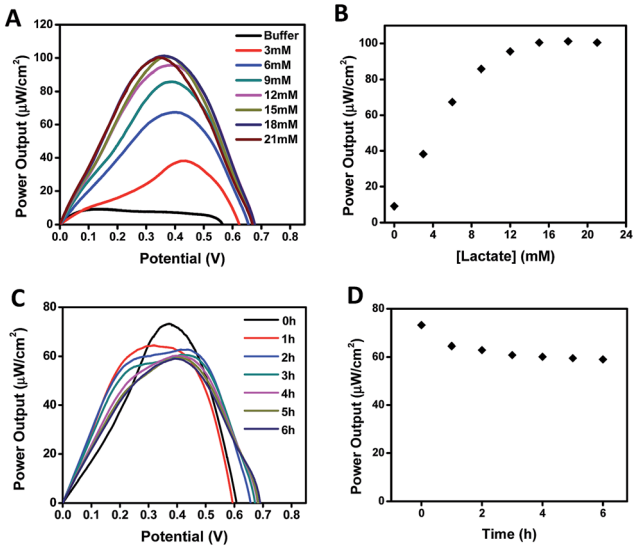

Fig. 2 (A) Power density of a textile BFC at varying lactate fuel concentrations (3–21 mM) in 0.1 M phosphate buffer. (B) Corresponding power–concentration (calibration) plot. (C) Stability of the power output of the textile BFC with a 8 mM lactate fuel solution over 6 hours. (D) Corresponding maximum power *vs.* time plot.

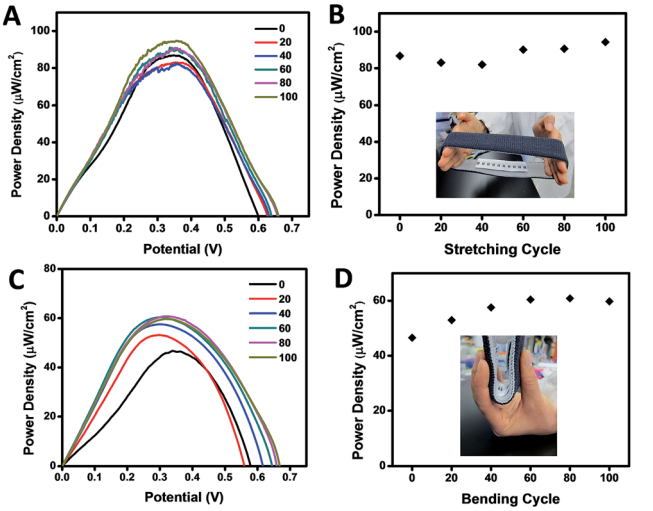

Fig. 3 Effect of mechanical deformations upon the power output of the textile BFC. (A) Power output after repeated stretching ($n = 20$–100); (B) stability of the power output during these 100 stretching iterations. (C) Power output after repeated bending; (D) stability of the power output during these 100 bending iterations. Inset images of (B and D) illustrate the stretching and bending deformation of the textile BFC, respectively.

operation of the textile BFC, two BFCs were connected in series and five such pairs were connected in parallel to power the LED. When exposed to a 14 mM lactate solution, the LED flashed 9 times initially when the energy buffering capacitor reached a voltage of 3.2 V. Subsequently, the LED turned off for 1.5 min, restricted by the large instantaneous load power requirements, limited converter efficiency at low input voltage, and slow diffusion of the fuel towards the electrode surface.[31] When the capacitor voltage dropped to 2.4 V, the output switch was disabled, and the load was shut-off. At this point, the capacitor voltage began to slowly replenish based on incoming energy harvested by the BFCs, and then the LED flashed again. This ON–OFF cycle lasted for 46 min. At the end, the LED was turned off, most likely due to depletion of the lactate fuel. When replaced with new lactate solution, the LED began flashing again.

To demonstrate system functionality under a realistic environment, a consented subject was asked to perform a stationary bike exercise while wearing a headband integrated with four BFCs connected in parallel. As shown in Fig. 4B, the integrated device was able to flash the LED seven times shortly after the subject started perspiring. This result demonstrated the ability of the integrated device to scavenge energy directly from the wearer and convert the biochemical energy to electricity. The enhanced power generation of the textile BFC enables it to power wearable electronic devices. To further demonstrate this on-body capability, the textile BFCs were incorporated into a wristband garment and used to power a digital watch. The watch, which requires a minimum of 10 μW from a 3 V supply, was powered from four parallel-configured textile BFCs connected with the PCB. During both the experiments the PCB was housed between the two layers of the underlying garment. Fig. 4C displays the watch – mounted with wristband – before and after it was turned ON by the energy harvested from the wearer's sweat by the textile BFCs. The watch remained ON for up to 50 seconds. Limited converter efficiency at low input voltage and slow diffusion of the fuel towards the electrodes may be the limiting factors for the intermittent operation of the devices. The present work describes textile BFC harvesting energy directly from human sweat by using lactate as the fuel. In most of the reported BFCs, a constant flow of the fuel supply (commonly glucose) of fixed and higher concentration is

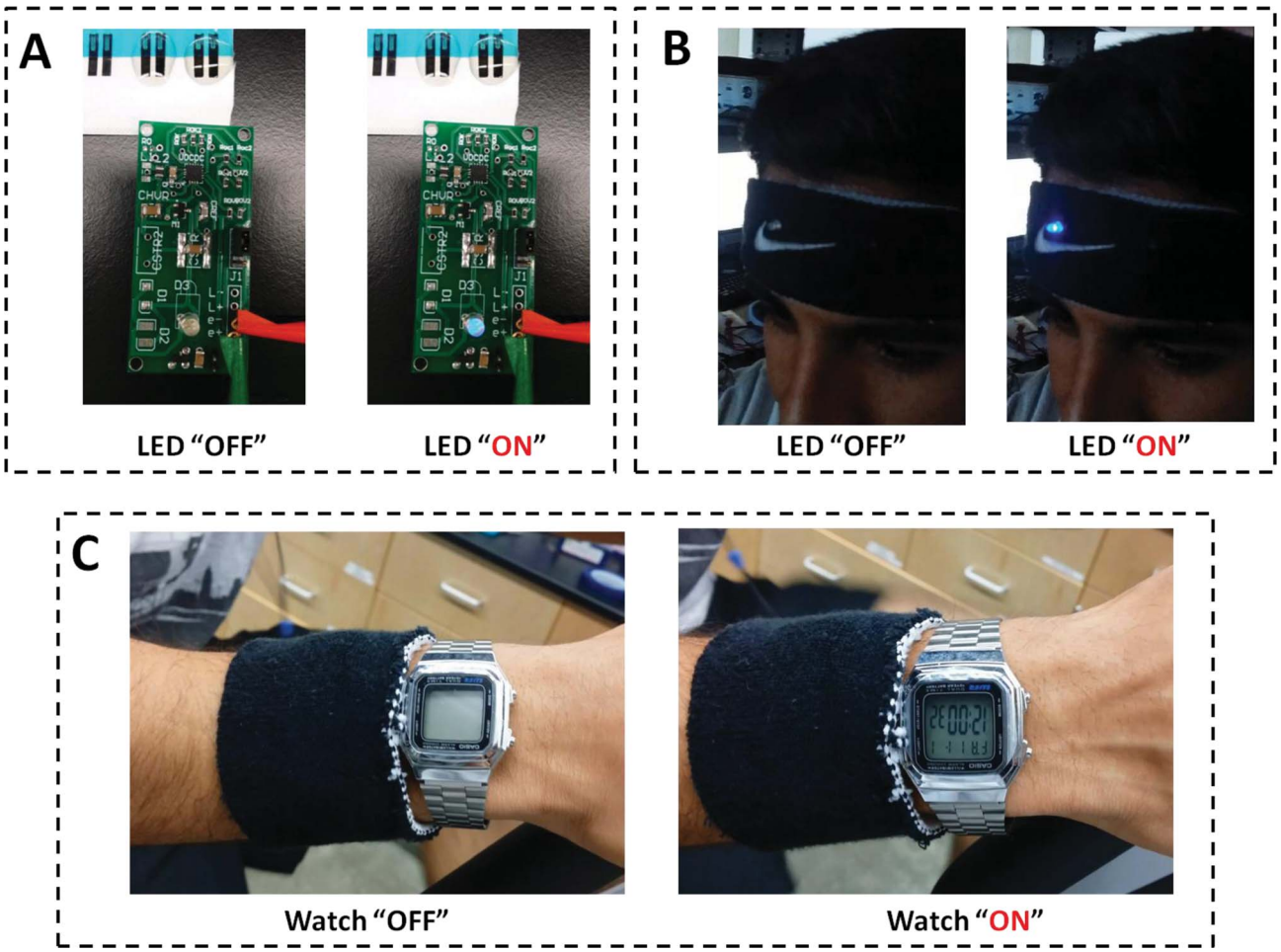

Fig. 4 (A) Photographs demonstrating operation of an LED powered by two textile BFCs connected in parallel in a 14 mM lactate solution; (B) Photographs of LED operation powered by four parallel BFCs, integrated into a headband, before and after a stationary bicycle exercise; (C) Photographs of a watch powered by four parallel BFCs integrated into a wristband before and after a stationary bicycle exercise.

provided, leading to continuous high power densities. However, in our case, the fuel (lactate) concentration in sweat changes dynamically. A major factor affecting the lactate concentration is the dilution effect occurring due to increasing sweat rate with time. The sweat rate also affects the convection of both lactate and oxygen to the respective electrode surface, and thus the overall power output. Despite of these unfavorable physiological conditions, the new textile BFC was shown useful in powering commonly used devices. The energy-buffering architecture, coupled with MPPT algorithm enabled sufficient collection of energy during concentration peaks to sustain operation for a longer time than normally possible. Future work will focus on the improvement of the working time of the system. Further improvement of the textile BFC can be achieved by using the biscrolled carbon nanotube yarns as shown very recently upon the completion of present work.[32] Enhancing the oxygen reduction at the cathode by leveraging multi-copper oxidases, optimizing the relative areas of the two electrodes for maximizing power output, and building a lower power boost converter further optimized to operate under varying input power conditions.

In conclusion, we have described a wearable textile BFC based on direct screen printing of BFC electrodes onto fabrics, and realized its integration with a PCB to power electronic devices. The textile BFC, which relies on the oxidation of sweat lactate at the bioanode and oxygen reduction at the cathode, can harvest energy directly from the wearer's to generate electricity. The generated power of the parallel BFCs, in connection to the PCB, was able to light a blue LED when integrated in a headband, and to power a watch integrated in a wristband. The favorable behavior of such fabric-based flexible BFC and the new integrated customized electronic device holds considerable promise as a power source for wearable electronics.

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Notes and references

1 A. J. Bandodkar and J. Wang, *Trends Biotechnol.*, 2014, **32**, 363–371.
2 D. H. Kim, R. Ghaffari, N. S. Lu and J. A. Rogers, *Annu. Rev. Biomed. Eng.*, 2012, **14**, 113–128.
3 D. H. Kim, N. S. Lu, R. Ma, Y. S. Kim, R. H. Kim, S. D. Wang, J. Wu, S. M. Won, H. Tao, A. Islam, K. J. Yu, T. I. Kim, R. Chowdhury, M. Ying, L. Z. Xu, M. Li, H. J. Chung, H. Keum, M. McCormick, P. Liu, Y. W. Zhang, F. G. Omenetto, Y. G. Huang, T. Coleman and J. A. Rogers, *Science*, 2011, **333**, 838–843.
4 G. M. Zhou, F. Li and H. M. Cheng, *Energy Environ. Sci.*, 2014, **7**, 1307–1338.
5 K. Jost, C. R. Perez, J. K. McDonough, V. Presser, M. Heon, G. Dion and Y. Gogotsi, *Energy Environ. Sci.*, 2011, **4**, 5060–5067.
6 J. H. Lee, K. Y. Lee, M. K. Gupta, T. Y. Kim, D. Y. Lee, J. Oh, C. Ryu, W. J. Yoo, C. Y. Kang, S. J. Yoon, J. B. Yoo and S. W. Kim, *Adv. Mater.*, 2014, **26**, 765–769.
7 P. P. Mercier, A. C. Lysaght, S. Bandyopadhyay, A. P. Chandrakasan and K. M. Stankovic, *Nat. Biotechnol.*, 2012, **30**, 1240–1243.
8 W. Z. Jia, G. Valdes-Ramirez, A. J. Bandodkar, J. R. Windmiller and J. Wang, *Angew. Chem., Int. Ed.*, 2013, **52**, 7233–7236.
9 I. Willner and E. Katz, *Angew. Chem., Int. Ed.*, 2000, **39**, 1180–1218.
10 M. T. Meredith and S. D. Minteer, *Annu. Rev. Anal. Chem.*, 2012, **5**, 157–179.
11 L. Halamkova, J. Halamek, V. Bocharova, A. Szczupak, L. Alfonta and E. Katz, *J. Am. Chem. Soc.*, 2012, **134**, 5040–5043.
12 F. Davis and S. P. J. Higson, *Biosens. Bioelectron.*, 2007, **22**, 1224–1235.
13 K. MacVittie, J. Halamek, L. Halamkova, M. Southcott, W. D. Jemison, R. Lobeld and E. Katz, *Energy Environ. Sci.*, 2013, **6**, 81–86.
14 A. Zebda, C. Gondran, A. Le Goff, M. Holzinger, P. Cinquin and S. Cosnier, *Nat. Commun.*, 2011, **2**, 370.
15 C. Agnes, M. Holzinger, A. Le Goff, B. Reuillard, K. Elouarzaki, S. Tingry and S. Cosnier, *Energy Environ. Sci.*, 2014, **7**, 1884–1888.
16 Y. L. Yang, M. C. Chuang, S. L. Lou and J. Wang, *Analyst*, 2010, **135**, 1230–1234.
17 M. C. Chuang, J. R. Windmiller, P. Santhosh, G. V. Ramirez, M. Galik, T. Y. Chou and J. Wang, *Electroanalysis*, 2010, **22**, 2511–2518.
18 L. B. Hu and Y. Cui, *Energy Environ. Sci.*, 2012, **5**, 6423–6435.
19 L. M. Castano and A. B. Flatau, *Smart Mater. Struct.*, 2014, **23**, 053001.
20 C. J. Harvey, R. F. LeBouf and A. B. Stefaniak, *Toxicol. In Vitro*, 2010, **24**, 1790–1796.
21 W. Jia, A. J. Bandodkar, G. Valdes-Ramirez, J. R. Windmiller, Z. Yang, J. Ramirez, G. Chan and J. Wang, *Anal. Chem.*, 2013, **85**, 6553–6560.
22 R. Pauliukaite, A. Malinauskas, G. Zhylyak and U. E. Spichiger-Keller, *Electroanalysis*, 2007, **19**, 2491–2498.
23 J. Kulys, V. Simkeviciene and I. J. Higgins, *Biosens. Bioelectron.*, 1992, **7**, 495–501.
24 A. Szczupak, J. Halamek, L. Halamkova, V. Bocharova, L. Alfonta and E. Katz, *Energy Environ. Sci.*, 2012, **5**, 8891–8895.
25 A. Zebda, S. Cosnier, J. P. Alcaraz, M. Holzinger, A. Le Goff, C. Gondran, F. Boucher, F. Giroud, K. Gorgy, H. Lamraoui and P. Cinquin, *Sci. Rep.*, 2013, **3**, 1516.
26 E. Katz and K. MacVittie, *Energy Environ. Sci.*, 2013, **6**, 2791–2803.
27 T. Hanashi, T. Yamazaki, W. Tsugawa, S. Ferri, D. Nakayama, M. Tomiyama, K. Ikebukuro and K. Sode, *Biosens. Bioelectron.*, 2009, **24**, 1837–1842.

28 S. B. Kjaer, J. K. Pedersen and F. Blaabjerg, *IEEE Trans. Ind. Appl.*, 2005, **41**, 1292–1306.
29 M. Holzinger, A. Le Goff and S. Cosnier, *Electrochim. Acta*, 2012, **82**, 179–190.
30 M. Southcott, K. MacVittie, J. Halamek, L. Halamkova, W. D. Jemison, R. Lobel and E. Katz, *Phys. Chem. Chem. Phys.*, 2013, **15**, 6278–6283.
31 M. J. Cooney, V. Svoboda, C. Lau, G. Martin and S. D. Minteer, *Energy Environ. Sci.*, 2008, **1**, 320–337.
32 C. H. Kwon, S. H. Lee, Y. B. Choi, J. A. Lee, S. H. Kim, G. M. Spinks, G. G. Wallace, M. D. Lima, M. E. Kozlov, R. H. Baughman and S. J. Kim, *Nat. Commun.*, 2014, **5**, 3928.