

Generating Electricity from Biofluid with a Nanowire-Based Biofuel Cell for Self-Powered Nanodevices

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The goal of nanotechnology is to build nanodevices that are intelligent, multifunctional, exceptionally small, extremely sensitive and have low power consumption. When the nanodevice is required for applications such as in vivo biomedical sensors, a nanoscale power source is required. Although a battery or energy storage unit is a choice for powering nanodevices, harvesting energy from the environment is an essential solution for building a “self-powered” nanodevice/nanosystem,^[1,2] which is an integration of nanodevice(s) and nano-enabled energy scavenging technologies.^[3] Previously, nanogenerators (NGs) have been demonstrated that can convert mechanical energy of low (order of Hz) and high (around 50 kHz) frequencies into electricity by means of piezoelectric zinc oxide nanowires (NWs).^[4–6] A single silicon NW-based heterostructure has been used to fabricate solar cells that are effective for driving an NW-based pH sensor or logic gate.^[2] Still, the most abundant energy available in biosystems is chemical and biochemical energy, such as glucose. In this paper, we report an NW-based biofuel cell (NBFC) based on a single proton conductive polymer NW for converting chemical energy from biofluids, such as glucose/blood, into electricity, using glucose oxidase (GOx) and laccase as catalyst. The glucose is supplied from the biofluid and the NW serves as the proton conductor. Although the electrolyte solution is a choice for transferring proton, it is essential to develop a proton conductive NW in some cases, such as the case in Figure S3c (see Section III of the Supporting Information (SI)), in which the anode and cathode solution are separated. A net current is generated

due to the chemical potential difference between the anode and cathode as a result of the respective chemical reactions at those electrodes. The NBFC of a single NW generates an output power as high as 0.5–3 μW , and has been integrated with NW-based pH, glucose or photon sensors for performing self-powered sensing. This study shows the feasibility of building self-powered nanodevices for biological sciences, environmental monitoring, defense technology and even personal electronics.

Our nano biofuel cell is based on an electrochemical process of converting glucose into gluconolactone (Figure 1a). GOx and laccase are used as catalysts at the anode and cathode, respectively. GOx is an enzyme that catalyses the oxidation of β -D-glucose by molecular oxygen. However, in the absence of mediating small molecules, the well-defined direct electrochemical action of GOx systems is rendered extremely difficult, as its active center-flavin adenine dinucleotide (FAD) is deeply embedded within a protective protein shell. GOx immobilized on the surface of carbon nanotubes (CNTs) was reported to have a direct electron transfer and retain its

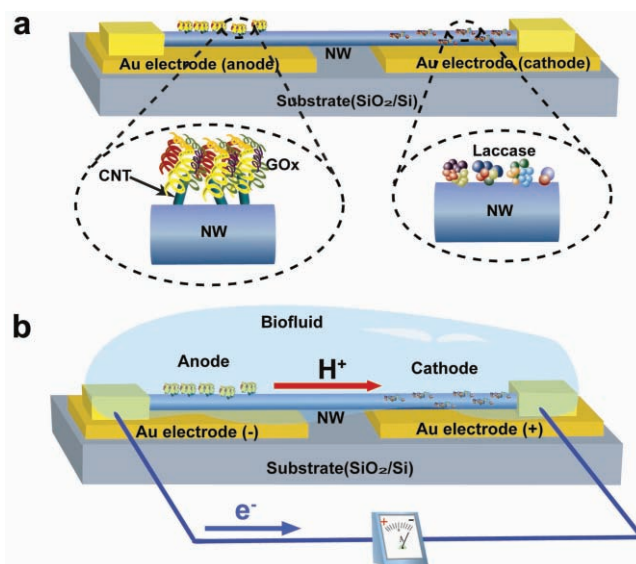


Figure 1. Design of a single Nafion/poly(vinyl pyrrolidone) compound nanowire (NPNW)-based biofuel cell. a) The NW lies on a substrate (of any kind), with both ends tightly bonded to the substrate and outlet interconnects. GOx and laccase are used as catalysts in the anode and cathode region, respectively. b) The NBFC is immersed into a biofluid solution, two chemical reactions occur in the anode and cathode regions, creating a corresponding chemical potential drop along the NW, which drives the flow of protons in the NW and electrons through the external load.

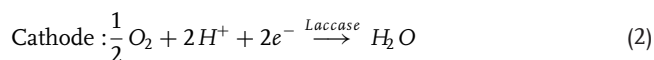
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bioelectrocatalytic activity for the oxidation of glucose, with the bioelectrocatalytic activity also being stable.^[7,8] Thus, to assist direct electron transfer to and from GOx, CNTs are dispersed on the NW and anode electrode surface, and then GOx is immobilized on the surface of the CNT layer. A proton conductive polymer nanowire is used for transporting protons, which lies flat on a substrate (of any kind) as electrolyte and is affixed to two electrodes at both ends (see Section I in the SI). The typical contact resistance between the NW and gold electrodes is approximately $10^4 \Omega$ (Figure 1c).

The key component, a proton-conductive NW, used in our experiment was a Nafion®/poly(vinyl pyrrolidone) composite NW of typical diameter of 200–800 nm, which was obtained via electrospinning^[9] (see Section II of the SI). This component has been found to exhibit good proton conductivity, with the large surface-to-volume ratio of the NWs improving the efficiency of the energy conversion.^[10] This approach is unique in comparison to the NW fuel cells that was originally demonstrated based on PtRu and Pt as catalysts and methanol as fuel, following the design for conventional fuel cells,^[10] here, we use enzymes as catalysts and biofluid containing glucose as fuel, aiming to generate electricity from biochemical energy for in vivo biological applications.

When the NBFC is in contact with a biofluid that contains glucose, the corresponding chemical processes occurring at the two ends of the NW are (Figure 1b): glucose is electrooxidized to gluconolactone at the anode, Equation (1),^[11,12] and dissolved O_2 is electroreduced to water at the cathode, Equation (2).^[13,14]



The performance of the NBFCs was characterized by measuring the short circuit current I_{sc} and open circuit voltage V_{oc} . The output of the NBFCs is in the microampere and hundreds of millivolt range (Figure 2). In measuring electric signal at such a small scale, artifacts may occur in the measurements due to system induced bias and/or environmental interference, such as system capacitance, thermal/instability drifting and so on. In order to make sure the measured signals are generated by the NBFC other than the measurement system, we applied the switching polarity and linear superposition criteria to verify the received signals.^[15,16] When the current meter was forward connected to a single-wire NBFC (Figure 2a), a positive voltage/

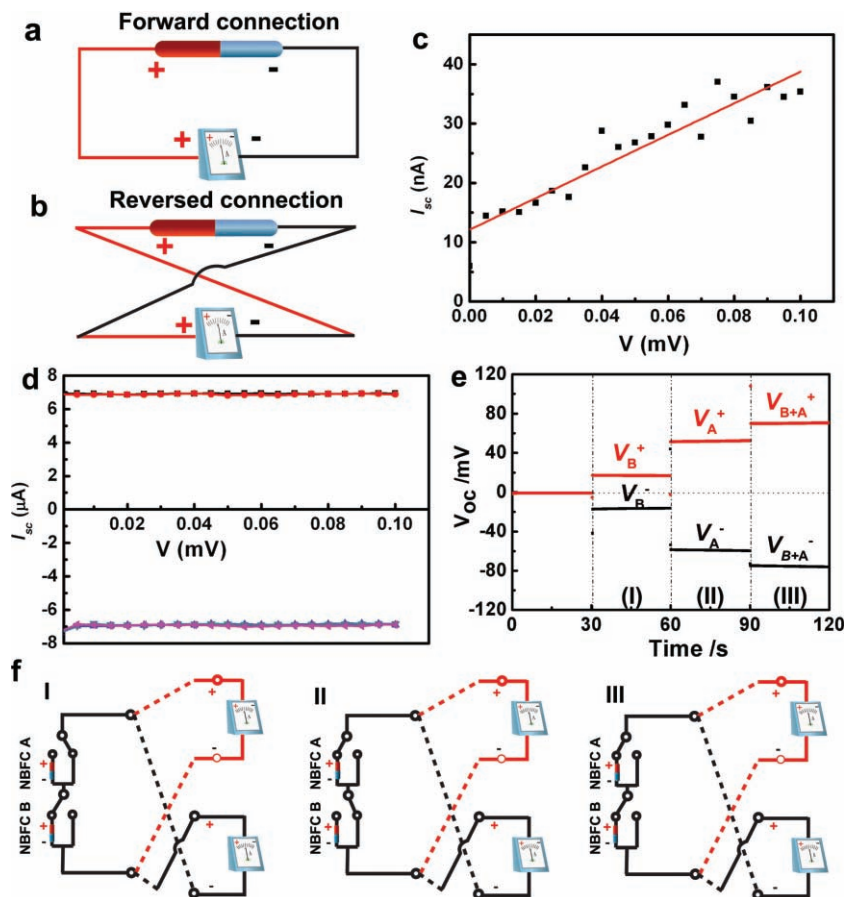


Figure 2. Electrical performance of single-wire biofuel cell. a,b) Definition of the switching-polarity test: forward connection means the positive probe of the current meter is connected to the positive electrode of the NBFC; in contrast, reversed connection means the positive probe of the current meter is connected to the negative electrode of the NBFC in the measurement circuit. c) I - V characteristics of an as-prepared single-wire NBFC before filling fuel, showing a typical resistant of the NBFC is about 25 000 ohm. d) Switching-polarity test of a NBFC. The I_{sc} is about $6.9 \mu\text{A}$ when forward-connected (up region) and about $-6.9 \mu\text{A}$ when reverse-connected (down region). The measurement of I_{sc} is repeated several times, showing a good stability of the NBFC. e) Superposition of open-circuit voltage of two NBFCs by connecting them in series, respectively, following the configurations shown in (f). The measurement demonstrates NBFC's ability to "add up" or "cancel out." Switching-polarity test is proved once again.

current was recorded. For this NBFC, the short-circuit current was $6.9 \mu\text{A}$ (Figure 2d). When the current meter was reversely connected (Figure 2b), the voltage and current signals were reversed in sign but kept respectively the same magnitudes (Figure 2d). The performance of our single wire NBFC was stable and repeatable as indicated by the five sets of I_{sc} data shown in Figure 2d.

In a general linear superposition experiment, when the two NBFCs are connected in parallel following the same polarity, the short circuit current is apparently increased, and the output is close to the sum of the short circuit current of the individual NBFCs. In contrast, when the two NBFCs are connected in parallel but in reversed polarity, the average output magnitude of the short circuit current was approximately the difference of the two. For the V_{oc} , a typical superposition result is demonstrated in Figure 2e, and the corresponding circuit configurations are shown in Figure 2f. For NBFC A,

note V_A^+ is the measured voltage for positive connection, and V_A^- that for negative connection (in an ideal case, $V_A^- = -V_A^+$, following the switching polarity rule). Similar symbols are used for NBFC B. Thus, we have $V_{A+B}^+ = V_A^+ + V_B^+$ (red line (up region) in Figure 2e), and $V_{A+B}^- = V_A^- + V_B^-$ (black line (down region) in Figure 2e), which agree well with the linear superposition rule. In addition, we also determined $V_A^- = -V_A^+$, $V_B^- = -V_B^+$ and $V_{A+B}^- = -V_{A+B}^+$ from this experiment, which agree well with the switching polarity rule. In the other configurations (see Section IV in the SI), the apparent enhancement with the same polarity connection and the decrease with reverse polarity connection indicate clearly a linear superposition of I_{sc} and V_{oc} of the two NBFCs, and these measurements clearly eliminate the effects from measurement system error. Above all, the switching polarity test and linear superposition tests, together with the comparative experiments, confirm that the output was indeed generated by the NBFC.

Studying the performance of NBFC when directly interfacing with the biofuel in human body is necessary for exploring its potential applications in powering in vivo wireless nanodevices. However, there are only a few reports describing the performance of a mediator-, cofactor- and membrane-less BFC operating in human physiological liquids.^[17] The performance of our mediator-, cofactor- and membrane-less nano biofuel cell operating in neutral glucose-containing phosphate buffer (PBS, pH = 7.0) and human blood are recorded in Figure 3a and Figure 3b. It can be seen that the V_{oc} is about 0.23 V, which is lower than the ideal V_{oc} of a biofuel cell (0.7 V). This can be attributed to two reasons: firstly, the oxidant used for our NBFC is O_2 dissolved in water, which concentration is very low, only about 1.5×10^{-4} M, not an oxygen saturated solution; and, secondly, the oxygen dissolved maybe partially react with glucose at the anode directly (isolating the anode and cathode fluid,

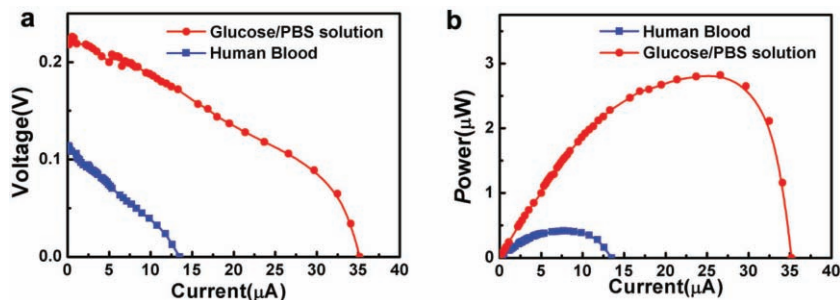


Figure 3. Studying the adaptability and flexibility of NBFC for potential in vivo applications. a,b) The performance of NBFC in glucose-containing PBS buffer solution and human blood, respectively.

and removing the oxygen from anode fluid will improve the V_{oc} , but this is difficult to achieve in implanted nanodevices, using both oxygen and glucose from the same biofluid). Fortunately, our NBFC is strong enough for powering those nanowatts-consuming nanodevices, since the power output in glucose-containing PBS is about $2.7 \mu\text{W}$. The corresponding power output density is around $30 \mu\text{W cm}^{-2}$, which is comparable to that of membrane-less miniature biofuel cells, see Table 1. The performance of the NBFC driven by blood glucose was $0.5 \mu\text{W}$ (35 ~ 40% of that driven by glucose/PBS solution). The proton flux through the NW can meet the requirement to get 0.5–3 μW of power due to its diameter-dependent and high proton conductivity^[15] (see Section VII in the SI). The decrease is attributed to partial enzyme inhibition by several compounds presented in human blood. Many organic compounds and inorganic ions presented in human blood could affect the specific activity of the enzymes, such as white and red blood cells, urea, HCO_3^- , Mg^{2+} , and Ca^{2+} .^[17]

Harvesting energy from the environment and driving electric devices is a beautiful dream for human beings. Additional studies showed that the NBFC works even using watermelon juice as the biofuel (see Figure S7, Section VI in the SI), with

Table 1. Comparison of our NBFC and one-compartment biofuel cells.

Reference	BFC	Anode/cathode	Description	Proton conductor type	Open circuit voltage [V]	Power output [$\mu\text{W cm}^{-2}$]
I [18]	Glucose– O_2	GOx–bilirubin oxidase (BOD)	Consists of two 7 μm diameter, 2 cm long, 0.44 mm^2 , electrocatalyst-coated carbon fibers	Solution	0.52	4.3
II [19]	Glucose– O_2	GOx–laccase	The same as Case I; one of the smallest biofuel cell reported	Solution	0.4	137
III [20]	Glucose– O_2	Cellobiose dehydrogenase–laccase	Membrane-, mediator- and cofactor-less biofuel cell	Solution	0.73	>5
IV [17]	Glucose– O_2	Cellobiose dehydrogenase–BOD	Membrane-, mediator- and cofactor-less biofuel cell, operating in human serum	Solution	0.62	3
V ^[a]	Glucose– O_2	GOx–laccase	Consists of two 3 mm \times 3 mm, 500 μm separated, electrocatalyst-coated electrodes, a Nafion NW as proton conductor	Nafion NW	0.23	~30 (in 1 wt.-% glucose/PBS solution)
					0.12	~5.6 (in blood)

^[a] This work.

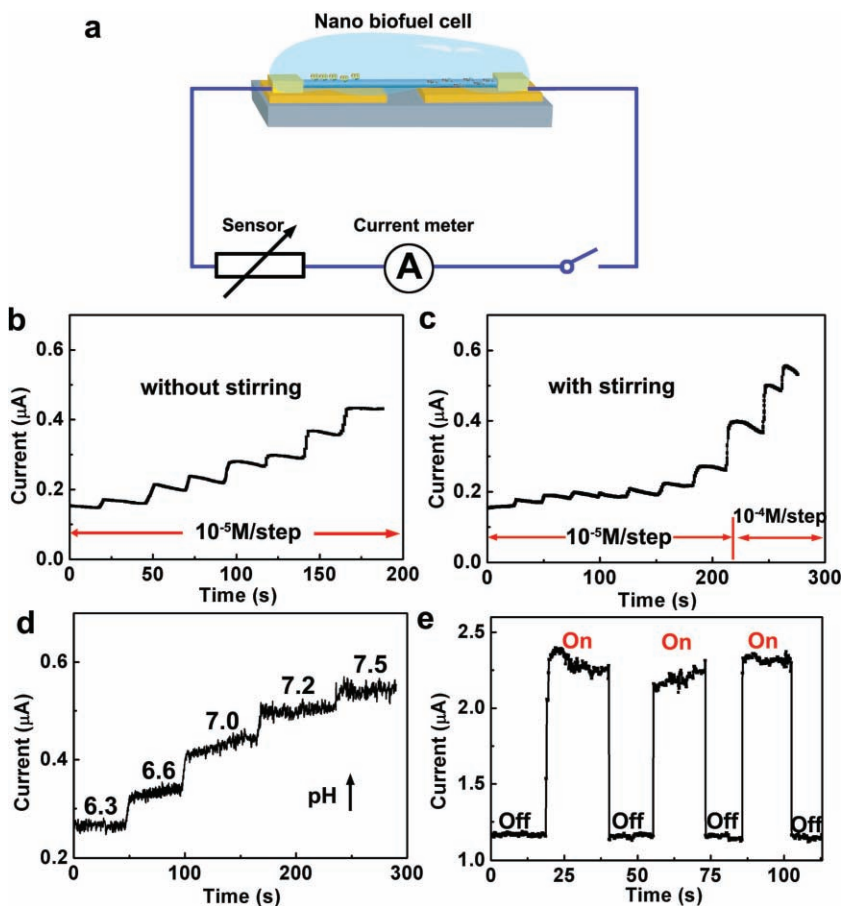


Figure 4. Self-powered nanodevices driven by our NBFC. a) As shown in this schematic, an NBFC, a nanosensor and a current meter were connected in series, and the only power source for driving the nanodevice was the NBFC. b,c) Current response of a glucose nanosensor driven by the NBFC. An obvious amperometric response can be seen when the glucose solution is added into the PBS solution drop by drop as a function of time. The difference between them is that the solution in case (b) is without stirring, while that in case (c) is stirring. Thus, the current response curve decreases quickly in case (c), while the current response curve keeps relatively stable in case (b). d) Current response of a pH nanosensor driven by the NBFC. NaOH and HNO₃ are used to modify the pH. The current increases when the pH increases, and decreases with the decreasing of pH (not shown here), as indicated by the flat steps. e) A CNT-based visible light sensitive photon nanosensor driven by a NBFC in responding to the on and off of visible light.

the output of the NBFC being similar to those obtained using glucose solution and human blood as biofuels.

The NBFC can be directly integrated with a single NW-based nanosensor for building a self-powered chemical- or bio-sensor, which typically requires an operation power as low as a few nanowatts if one excludes the RF unit.^[21,22] By integrating an NBFC with a single NW-based pH sensor or glucose sensor fabricated using ZnO nanowire, a self-powered nanosensor is formed (Figure 4a).^[23] The NW glucose and pH sensors were fabricated according to the literature^[24–28] (see Section VIII in the SI). For the glucose sensor, a rapid and obvious amperometric response was exhibited on the successive addition of glucose solution, and the current remained constant when no glucose solution was added (Figure 4b). To confirm that the amperometric response was truly induced by the sensor, a stirring was introduced in our test to vary the glucose concentration,

as shown in Figure 4c. The obvious amperometric response was still exhibited on the successive addition of glucose solution. However, it can be seen that the current decreased when no glucose was added into the solution. This can be attributed to the quick decreasing of local concentration of glucose near the sensor as a result of stirring.

The current responses of the pH sensor driven by the NBFC are shown in Figure 4d. NaOH solution was used to modify the pH of the solution, and the pH of the solution was monitored in real time by a pH meter. The current increased when the pH was increased step by step because the conductance of the pH sensor varied in different pH solutions. Figure 4e shows a CNT-based visible photon sensor driven by the NBFC. An obvious amperometric response was presented when the light was turned on and off. These studies show that the NBFC can truly serve as a power source not only for driving in vivo nanosensors, but also for other devices.

The NBFC has a significantly high power output in comparison to the nanogenerators fabricated based on other approaches. The single NW nanosolar cell produced an output of 50–200 pW by converting strongly focused solar energy into electricity.^[2] Although it has been demonstrated for powering a nanodevice, it may not be suitable for in vivo biosensing possibly due to the undetectable light intensity. The single wire nanogenerator for harvesting mechanical energy usually has a much lower output power.^[4] Our NBFC of a single NW can produce an output of 0.5–3 μW, which is strong enough to serve as a power source for in vivo self-powered nanodevices. Such performance can be largely enhanced and scaled up with the integration of multiple nanowires.

In summary, we have demonstrated an innovative single nanowire biofuel cell for harvesting chemical/biochemical energy for

powering in vivo nanodevices. The output of the NBFC reaches 0.5–3 μW, which is sufficient to drive pH, glucose or photon sensors. The high output power, low cost and easy fabrication process, large-scale manufacturability, high 'on-chip' integrability and stability demonstrates its great potential for in vivo biosensing. The NBFC provides a new approach for self-powered nanotechnology that harvests electricity from the environment for applications such as implantable biomedical devices, wireless sensors, and even portable electronics that are important for biological sciences, environmental monitoring, defense technology and even personal electronics.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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- [1] Z. L. Wang, *Sci. Am.* **2008**, 298, 82.
- [2] B. Z. Tian, X. L. Zheng, T. J. Kempa, Y. Fang, N. F. Yu, G. H. Yu, J. L. Huang, C. M. Lieber, *Nature* **2007**, 449, 885.
- [3] A totally self-powered nanosystem should include the nanodevices, power harvesting unit, electrical measurement system, data processing logic system and, possibly, wireless communication unit (RF technology).
- [4] Z. L. Wang, J. H. Song, *Science* **2006**, 312, 242.
- [5] X. D. Wang, J. H. Song, J. Liu, Z. L. Wang, *Science* **2007**, 316, 102.
- [6] Y. Qin, X. D. Wang, Z. L. Wang, *Nature* **2008**, 451, 809.
- [7] A. Guiseppi-Elie, C. H. Lei, R. H. Baughman, *Nanotechnology* **2002**, 13, 559.
- [8] C. X. Cai, J. Chen, *Anal. Biochem.* **2004**, 33275.
- [9] D. Li, Y. N. Xia, *Adv. Mater.* **2004**, 16, 1151.
- [10] C. F. Pan, H. Wu, C. Wang, B. Wang, L. Zhang, Z. D. Cheng, P. Hu, W. Pan, Z. Y. Zhou, X. Yang, J. Zhu, *Adv. Mater.* **2008**, 20, 1644.
- [11] A. Huggett, D. Nixon, *Lancet* **1957**, 2, 368.
- [12] T. de Lumley-Woodyear, P. Rocca, J. Lindsay, Y. Dror, A. Freeman, A. Heller, *Anal. Chem.* **1995**, 67, 1332.
- [13] S. Calabrese Barton, H.-H. Kim, G. Binyamin, A. Heller, *J. Am. Chem. Soc.* **2001**, 123, 5802.
- [14] F. Trudeau, F. Daigle, D. Leech, *Anal. Chem.* **1997**, 69, 882.
- [15] R. S. Yang, Y. Qin, L. M. Dai, Z. L. Wang, *Nat. Nanotechnol.* **2009**, 4, 34.
- [16] R. S. Yang, Y. Qin, C. Li, L. M. Dai, Z. L. Wang, *Appl. Phys. Lett.* **2009**, 94, 022905.
- [17] V. Coman, R. Ludwig, W. Harreither, D. Haltrich, L. Gorton, T. Ruzgas, S. Shleev, *Fuel Cells* **2010**, 10, 9.
- [18] N. Mano, F. Mao, A. Heller, *J. Am. Chem. Soc.* **2002**, 124, 12962.
- [19] T. Chen, S. C. Barton, G. Binyamin, Z. Q. Gao, Y. C. Zhang, H. H. Kim, A. Heller, *J. Am. Chem. Soc.* **2001**, 123, 8630.
- [20] V. Coman, C. Vaz-Dominguez, R. Ludwig, W. Herreither, D. Haltrich, A. L. De Lacey, T. Ruzgas, L. Gorton, S. Shleev, *Phys. Chem. Chem. Phys.* **2008**, 10, 6093.
- [21] Y. Cui, Q. Q. Wei, H. K. Park, C. M. Lieber, *Science* **2001**, 293, 1289.
- [22] Y. Huang, X. Duan, Y. Cui, L. Lauhon, K. Kim, C. M. Lieber, *Science* **2001**, 294, 1313.
- [23] J. Zhou, N. S. Xu, Z. L. Wang, *Adv. Mater.* **2006**, 18, 2432. ZnO is a material that can be slowly dissolved by biofluids, but it takes more than 10 h to dissolve a nanowire. As for our experiments were done within 30 min, the surface dissolution, if any, would have been minimal and should not have affected the sensor measurements.
- [24] M. Ahmad, C. F. Pan, J. Iqbal, J. Zhu, *Chem. Phys. Lett.* **2009**, 480, 105–109.
- [25] M. Ahmad, C. F. Pan, Z. X. Luo, J. Zhu, *J. Phys. Chem. C* **2010**, 114, 9309.
- [26] J. F. Zhang, C. M. Li, X. Q. Cui, J. X. Wang, X. W. Sun, H. Dong, C. Q. Sun, *Electroanalysis* **2007**, 19, 1008.
- [27] B. S. Kang, F. Ren, Y. W. Heo, L. C. Tien, D. P. Norton, S. J. Pearton, *Appl. Phys. Lett.* **2005**, 86, 112105.
- [28] Y. Cui, Q. Q. Wei, H. K. Park, C. M. Lieber, *Science* **2001**, 293, 1289.
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