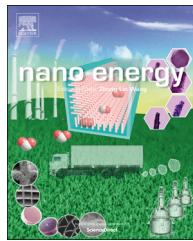


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RAPID COMMUNICATION

Triboelectric nanogenerator built inside clothes for self-powered glucose biosensors

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Received 21 March 2013; accepted 28 March 2013

Available online 6 April 2013

KEYWORDS

Triboelectric nanogenerator;
Self-powering;
Glucose biosensor

Abstract

A triboelectric nanogenerator (TENG) based on the contact-separation mode between a patterned polydimethylsiloxane (PDMS) film and an Al foil was fabricated between clothes for harvesting body motion energy. Under the generally walking, the maximum output of voltage and current density are up to 17 V and 0.02 μ A/cm², respectively. The TENG with a single layer size of 2 cm \times 7 cm \times 0.08 cm sticking on the clothes was demonstrated as a sustainable power source that not only can directly light up 30 light-emitting diodes (LEDs), but also can charge a lithium ion battery by persistently clapping clothes. The electric energy stored in the lithium ion battery was used to power a biosensor for detecting glucose. The detection of bioactive chemicals in our body using the energy harvested from body motion is demonstrated. Moreover, due to the sensitivity and desirable stability to periodic vibration, the TENG was used to measure stride frequency as well.

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Introduction

In the recent years, attention has been paid to technologies of how to convert ambient energy, such as light [1], heat [2],

wind [3] and vibration [4], into electric energy to meet the needs of independent and maintenance-free power sources widely applied in personal electronics, implantable sensors, environmental monitoring, etc. It is known that mechanical motion/vibration is everywhere and at all time in our life. Several approaches aiming at harvesting mechanical energy in our living environment have been demonstrated [5–7]. At the earliest, piezoelectric nanogenerator was invented by Wang's group using ZnO nanowire arrays in 2006. Subsequently, many nanogenerators based on the piezoelectric effect are fabricated using various piezoelectric

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materials [7-14]. Recently, triboelectric nanogenerator (TENG) is another type of mechanical energy harvester invented by Wang's group [15]. It can convert mechanical energy into electricity based on triboelectric effect, and the output power is sufficient to drive some conventional portable/mobile electronics [13,16].

Due to the advantages of high performance, easy fabrication, cost effective and green process, research on TENG is attracting a lot of attention, and many significant achievements are reported [17-20]. In this paper, we demonstrate the first application of TENG for harvesting body vibration/movement energy by integrating TENG on layered clothes. The electricity generated by clapping clothes can directly light up commercial white LEDs or can be stored in a lithium ion battery to subsequently power a biosensor [21], demonstrating a self-powered glucose sensor for biomedical diagnosis. Furthermore, TENG is also used as an active sensor for detecting the stride frequency of a person.

Experimental section

A. Fabricating TENG in layered clothes

The TENG consists of a Cu film, a Polydimethylsiloxane (PDMS) film and an Al foil, where the Cu film served as the electrode layer of the PDMS film. In a typical process, the elastomer and the cross-linker (Sylgard 184, Dow Corning) were mixed in a rate of 10:1 (w/w) and then coated on a homemade anodic aluminum oxide (AAO) substrate. After vacuum process for 30 min, the unformed PDMS is transferred into a furnace at 85 °C for 1 h to get cured. After cooled down, the cured PDMS was peeled off from the AAO substrate. The surface without patterns was closely pasted on the copper film. The Al foil was pasted on the outside surface of the inner shirt, while the unit of PDMS and copper film was stuck onto the inside surface of the external clothes with the patterned PDMS surface outward to the Al foil.

B. The measurement of the TENG

Before and after the TENG stuck onto the clothes, the output performance of the TENG was measured using Stanford Research Systems. SR560 and SR570 low noise current amplifiers were used to record voltage/current, respectively.

C. The fabrication of glucose sensor

Nanoscaled CuO was prepared by the composite molten salt method [23]. In a typical reaction, 6 g of mixed (LiNO₃/KNO₃=1/2) was put in a 25 mL Teflon-lined autoclave, and 1 mmol CuSO₄·5H₂O and 2 mmol KOH were added into the mixed nitrates. The vessel was sealed and then kept at 200 °C for 24 h, and then let cool down naturally. The final products were washed with deionized water and absolute ethanol. Subsequently, the nanostructures were characterized by XRD (Paralytical XRD-660) and SEM (SEM, LEO 1550) and EDS, which is shown in Figure S4.

The graphite electrode was polished and cleaned with deionized water. After dried, the graphite electrode was coated by 50 µL dispersed CuO ethanol solution, and dried under an infrared lamp. Then, 10 µL of 0.5 wt% Nafion was dropped on the surface of the electrode in order to immobilize the CuO nanocrystals on the graphite electrode and to improve the anti-interferent ability. Finally, the CuO catalyst modified electrode was obtained after covering the electrode with epoxy resin leaving an open area of 5 mm × 4 mm. For comparison, a pure graphite electrode covered with 10 µL of 0.5 wt% Nafion on its surface was fabricated.

Results and discussion

The TENG is based on the contact electrification between a patterned PDMS film as the top plate and an Al foil as the bottom plate. The schematic diagram of the TENG is shown in Figure 1a. A Cu film, as the electrode layer, is closely pasted on the smooth surface of the PDMS film, with the patterned surface outward. The friction is induced between the patterned surface of PDMS and the Al foil. The patterned surface of PDMS film (Figure 1b) was made to enhance the triboelectric charging and characterized using scanning electron microscopy (SEM). The uniform arrays are made of the patterned surface of PDMS film.

To explore the performance of the TENG, a home-made motor system was employed to apply periodical compressive force onto the TENG. As triggered by a force with controlled frequency and amplitude, an open-circuit voltage and a short-circuit current density were generated, as shown in Figure 1c and d under the forward connection to the measurement system, respectively. The output voltage is up to 83 V and the corresponding output current density can research 0.32 µA/cm². Figure 1e and f reveal the output signal of the TENG under the reversed connection. Moreover, the alternating electric output signal can be rectified by a full-wave bridge circuit for the further usage, as shown in Figure S1. The mechanism of the polymer-metal TENG is based on that the electrons flow through an external load as driven by the potential difference between the two electrodes induced by triboelectric effect [19].

To harvest the mechanical energy from a human walking, the TENG was stuck onto the clothes. Specifically, the PDMS film pasted on the Cu electrode layer was stuck on the inside surface of the outer clothes with the Al foil on the outside surface of the shirt. Then the outer clothes was buttoned, the photograph is present in Figure 2a with the details of the TENG revealed in the bottom half. The output voltage and current density produced during a general walking can easily reach 10 V and 0.01 µA/cm², respectively. Meanwhile, the output signal under reversed connection is shown in Figure S2b and c. When walking, a positive output signal with a subsequent negative output signal are generated alternatively. Specifically for a human walking, when one leg stepped forward, a positive signal was generated; then, a negative signal was received with the other leg followed up with the previous one. In this process, the vibration/swing of the cloth generated from walking can drive the two plates of the TENG to switch from contact to separation periodically. Video 1 (see the supporting

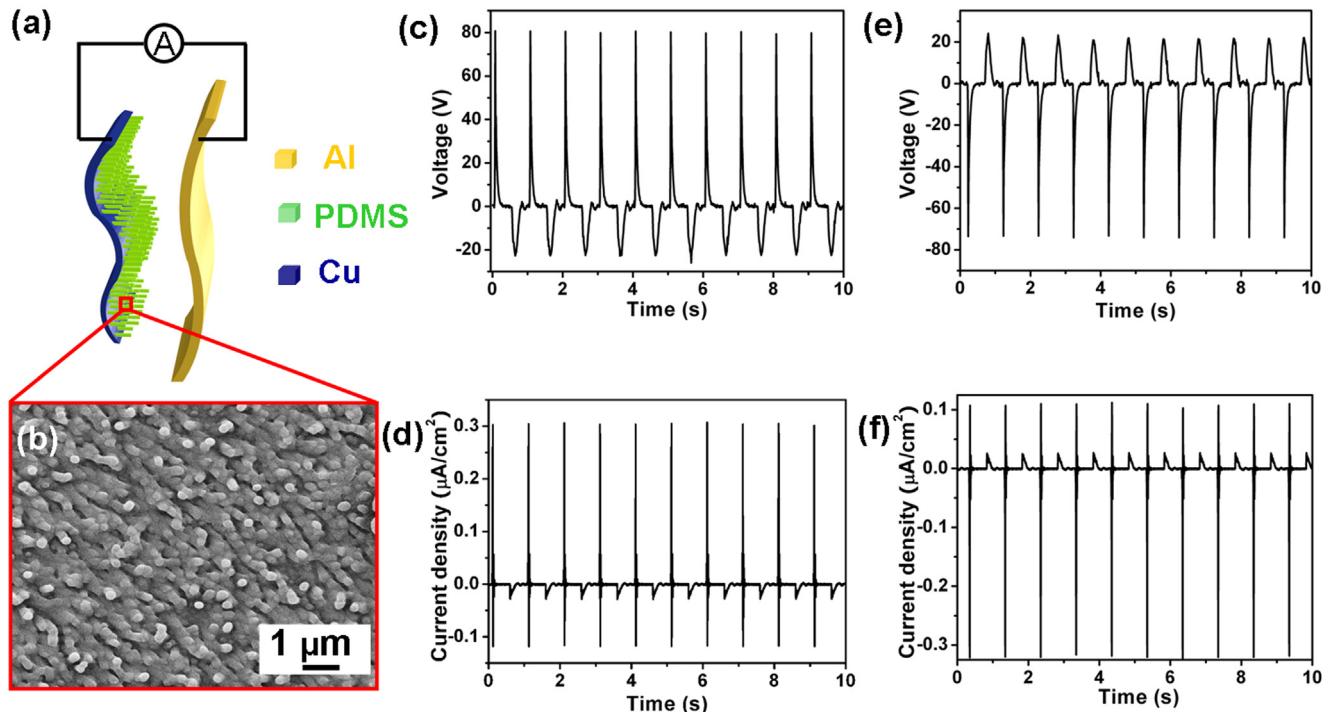


Figure 1 (a) Schematic diagram of the fabricated TENG. (b) SEM image of the PDMS nanostructure array. The output voltage and current density of the TENG under the forward connection (c,d) and the reversed connection (e,f) to the measurement.

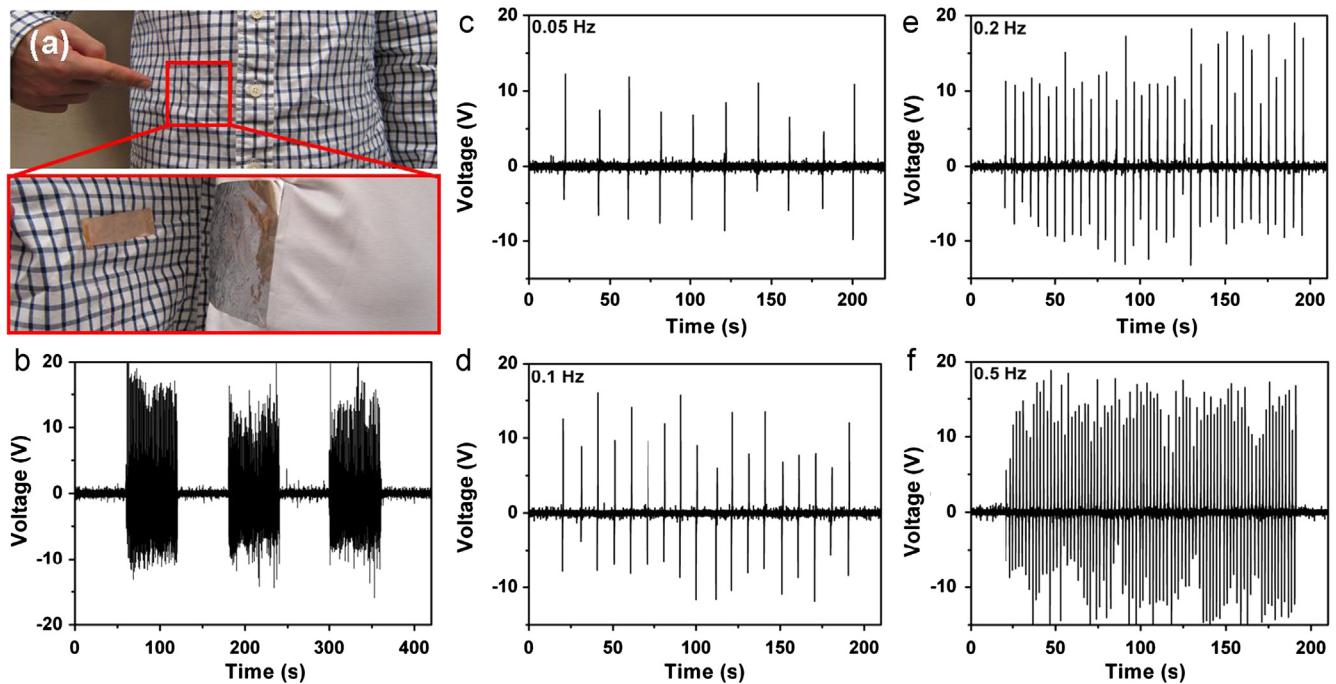


Figure 2 (a) Photograph of a working TENG (2 cm × 7 cm × 0.08 cm in size) stuck onto the clothes with the shirt buttoned. (b) The output voltage of the TENG when walking. (c,d,e,f) The output voltage signals at different stride frequency, 0.05 Hz (c), 0.1 Hz (d), 0.2 Hz (e) and 0.5 Hz (f).

information) recorded that the output signals were generated by human walking in a real-time manner.

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.nanoen.2013.03.024>.

Owing to the sensitivity and stability of output voltage of the TENG on clothes to body movement, the TENG was employed to measure the walking frequency. The output voltage signals with different frequencies are represented

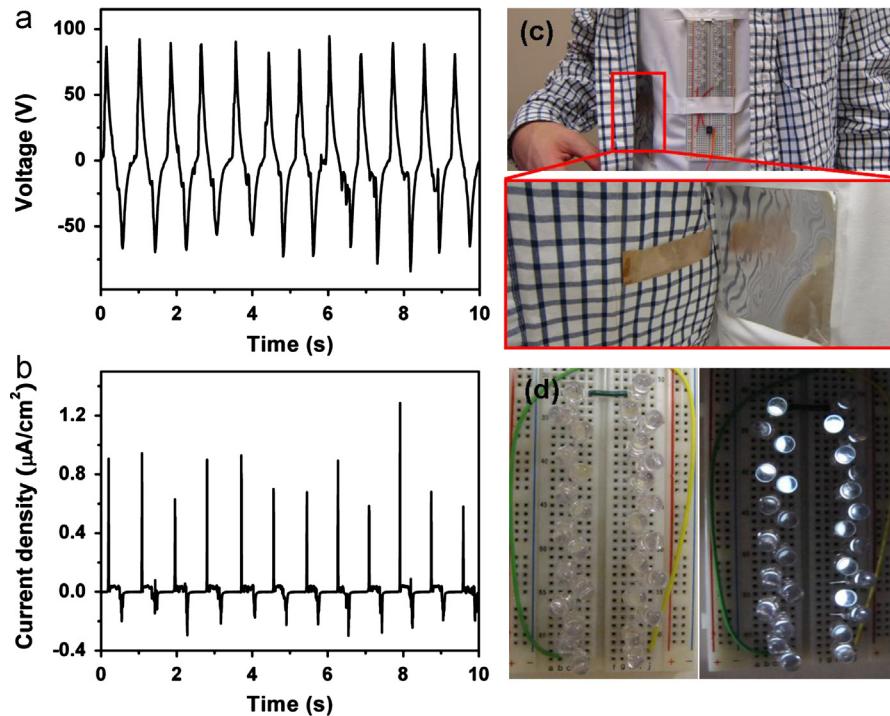


Figure 3 (a,b) Output voltage (a) and current density (b) of the TENG stuck onto clothes when clapping. (c) Photograph of the working TENG stuck onto the clothes with the shirt unbuttoned. (d) Snapshots of several white LEDs connected in series before (left) and while (right) clapping the clothes.

in Figure 2c, d, e and f, which is corresponding to different walking frequencies (0.05, 0.1, 0.2, and 0.5 Hz).

To improve the output performance of the TENG, a larger force was applying on the TENG by clapping it with hands. Figure 3a illustrates the output voltage and current density, as shown in Figure 3b, indicating that the largest output voltage and current density can be up to 100 V and $1.35 \mu\text{A}/\text{cm}^2$, respectively. The output signal under reversed connection is given in Figure S3, showing the TENG together with several LEDs attached on the body. A close-up photo illuminates the structure of the TENG before buttoned, as shown in the bottom half of Figure 3c. As expected, 30 LEDs were lighted up when clapping the corresponding part of the clothes, which is represented in Figure 3d. It can be also seen in the movie 2 in the supporting materials.

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Usually, the alternating current pulse generated by the TENG can not directly drive biosensors due to the requirement for a stable direct current or higher power consumption. It is necessary to store the energy in a lithium ion battery so that the power to the biosensor can be regulated. A glucose sensor was fabricated as follows. A graphite electrode modified by CuO nanostructures and a pure graphite electrode were prepared. To confirm the stability of the sensor, we first used a DC voltage power source to drive its operation for detecting glucose. Figure 4a shows the current response of the two electrodes to successive additions of 0.1 mM glucose to 0.1 M NaOH at an applied potential of 0.8 V, indicating that the electrode modified by CuO nanostructure shows a highly enhanced response to the change of glucose concentration, which is in contrast to the

low response of the pure graphite electrode. The corresponding calibrated sensitivity plot of CuO modified electrode is illustrated in Figure 4b, showing a good linear range from 0.1 mM to 1 mM. The improved performance is associated with the larger surface area, higher surface energy and enhanced electron transfer ability of the CuO nanostructures [22].

To fabricate a self-powered detecting system, a lithium ion battery was charged by the TENG continuously driven by clapping the clothes for many times. The schematic diagram of self-powered glucose biosensing system is shown in Fig. S5a. Figure 4c shows the charging and the subsequent constant-current discharging curves of the lithium ion battery. After more than 2 h of clapping at a frequency of about 2 Hz, the battery was charged from 440 to 800 mV. By repeating the same procedures, the battery was recharged and used to power the glucose biosensor based on the CuO nanostructure modified graphite electrode. The response curve is presented in Figure 4d, indicating that the biosensor can be powered by using the electricity supplied by the charged battery. As a result, the detection of the bioactive chemical in our body can be carried out using the energy from the movement of our body although further improvement is clearly necessary for biological detection based on the TENG.

Conclusions

In summary, a simple TENG based on the contact electrification has been fabricated based on clothes to harvest body motion energy. The TENG is demonstrated as a power source that not only can directly light up 30 LEDs connected in series, but also can charge a lithium ion battery by clapping

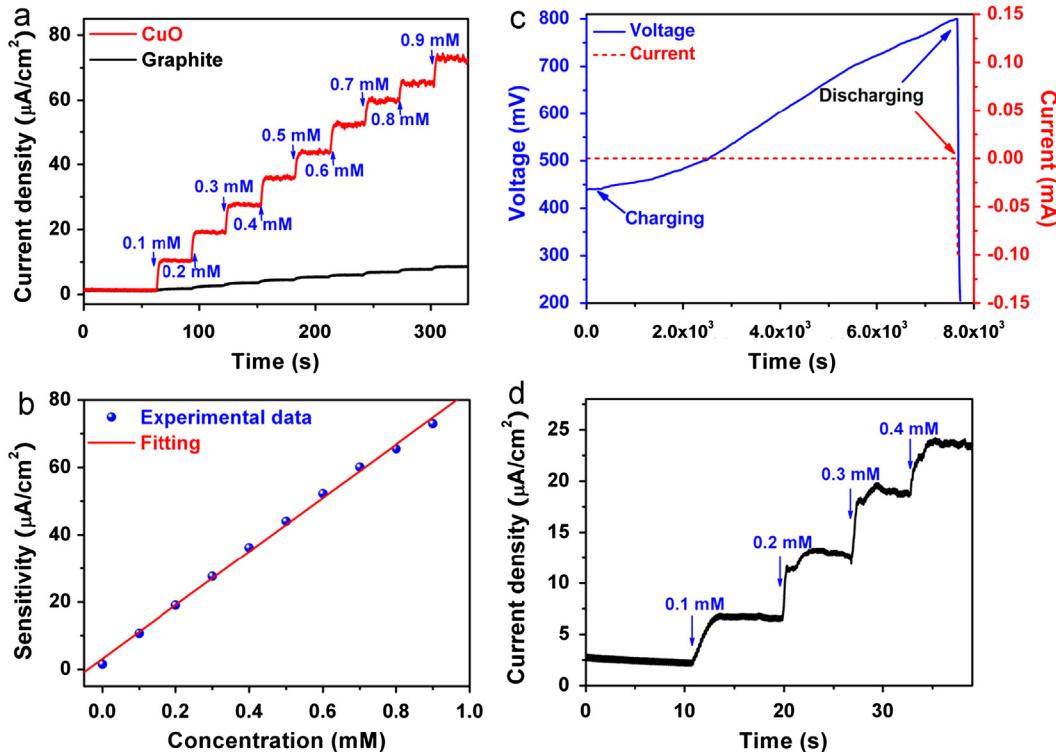


Figure 4 (a) The amperometric response of the CuO modified electrode and a pure graphite electrode to successive additions of 0.1 mM glucose to 0.1 M NaOH solution as it is driven by a standard DC power of 0.8 V. (b) The corresponding calibrated sensitivity plot of CuO modified electrode. (c) The charging and the subsequent constant-current discharging curves of the lithium ion battery. (d) The response curve of the CuO modified electrode powered by the TENG charged battery.

the clothes, which later is used to power a biosensor for detecting glucose. The fabricated TENG has the potential applications in harvesting the wasted biomechanical energy from our bodies for self-powered biosensors.

Acknowledgments

This work was supported by US Airforce, MURI, U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-07ER46394), NSF, and the Knowledge Innovation Program of the Chinese Academy of Sciences (KJCX2-YW-M13). H.L. Zhang and C.G. Hu acknowledge the support of NSFCQ (cstc2012jjB0006), SRFDP (20110191110034), Project (WLYJ SBJRCTD201101) of the Innovative Talent Funds for 985 Project of Chongqing University. H.L. Zhang also would like to acknowledge the fellowship from the China Scholarship Council (CSC).

Appendix A. Supplementary Information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.nanoen.2013.03.024>.

References

- [1] B. Tian, X. Zheng, T.J. Kempa, Y. Fang, N. Yu, G. Yu, J. Huang, C.M. Lieber, *Nature* 449 (2007) 885-890.
- [2] Y. Yang, W. Guo, K.C. Pradel, G. Zhu, Y. Zhou, Y. Zhang, Y. Hu, L. Lin, Z.L. Wang, *Nano Letters* 12 (2012) 2833-2838.
- [3] R. Zhang, L. Lin, Q.S. Jing, W.Z. Wu, Y. Zhang, Z.X. Jiao, L. Yan, R.P.S. Han, Z.L. Wang, *Energy and Environmental Science* 5 (2012) 8528.
- [4] G. Zhu, A.C. Wang, Y. Liu, Y. Zhou, Z.L. Wang, *Nano Letters* 12 (2012) 3086-3090.
- [5] S.P. Beeby, R.N. Torah, M.J. Tudor, P. Glynne-Jones, T. O'Donnell, C.R. Saha, S.J. Roy, *Journal of Micromechanics and Microengineering* 17 (2007) 1257-1265.
- [6] P.D. Mitcheson, P. Miao, B.H. Stark, E.M. Yeatman, A.S. Holmes, T.C. Green, *Sensors and Actuators A: Physical* 115 (2004) 523-529.
- [7] Z.L. Wang, J.H. Song, *Science* 312 (2006) 242-246.
- [8] X.D. Wang, J.H. Song, J. Liu, Z.L. Wang, *Science* 316 (2007) 102-105.
- [9] Y. Qin, X.D. Wang, Z.L. Wang, *Nature* 451 (2008) 809-813.
- [10] R. Yang, Y. Qin, L. Dai, Z.L. Wang, *Nature Nanotechnology* 4 (2009) 34-39.
- [11] X.D. Wang, *Nano Energy* 1 (2012) 13-24.
- [12] R. Zhang, L. Lin, Q. Jing, W.Z. Wu, Y. Zhang, Z. Jiao, L. Yan, R.P.S. Han, Z.L. Wang, *Energy and Environmental Science* 5 (2012) 8528-8533.
- [13] X.H. Yang, G. Zhu, S. Wang, R. Zhang, L. Lin, W. Wu, Z.L. Wang, *Energy and Environmental Science* 5 (2012) 9462-9466.
- [14] T.C. Hou, Y. Yang, Z.H. Lin, Y. Ding, C. Park, K.C. Pradel, L.J. Chen, Z.L. Wang, *Nano Energy*, in press.
- [15] F.R. Fan, Z.Q. Tian, Z.L. Wang, *Nano Energy* 1 (2012) 328-334.
- [16] G. Zhu, Z.H. Lin, Q.S. Jing, P. Bai, C.F. Pan, Y. Yang, Y.S. Zhou, Z.L. Wang, *Nano Letters* 13 (2013) 847-853.
- [17] F.R. Fan, L. Lin, G. Zhu, W. Wu, R. Zhang, Z.L. Wang, *Nano Letters* 12 (2012) 3109-3114.

- [18] G. Zhu, C.F. Pan, W.X. Guo, C.Y. Chen, Y.S. Zhou, R.M. Yu, Z.L. Wang, *Nano Letters* 12 (2012) 4960-4965.
- [19] S.H. Wang, L. Long, Z.L. Wang, *Nano Letters* 12 (2012) 6339-6346.
- [20] J.W. Zhong, Q.Z. Zhong, F.R. Fan, Y. Zhang, S.H. Wang, B. Hu, Z.L. Wang, J. Zhou, *Nano Energy*, in press.
- [21] D. Clark, L. Sokoloff, 1999, *Basic Neurochemistry: Molecular, Cellular and Medical Aspects*, Lippincott, pp. 637-670.
- [22] E. Reitz, W.Z. Jia, M. Gentile, Y. Wang, Y. Lei, *Electroanalysis* 20 (2008) 482-486.
- [23] X. Wang, C.G. Hu, H. Liu, G.J. Du, X.S. He, Y. Xi, *Sensors and Actuators B: Chemical* 144 (2010) 220-225.



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