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RAPID COMMUNICATION

Transparent flexible nanogenerator as self-powered sensor for transportation monitoring

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Abstract
In this paper, we fabricated transparent flexible nanogenerators (NGs) by employing flexible polydimethylsiloxane (PDMS) substrate for the growth of ZnO nanowires. The fully packaged NG showed good transparency with a transmittance of 50–60% in the visible range. The output voltage and current was 8 V and 0.6 μA, respectively, corresponding to an output power density of ~5.3 mW/cm^3. The NG also showed excellent robustness and could stably scavenge energy from the motion of a vehicle. Based on this characteristic, we demonstrated its application as a self-powered sensor for monitoring vehicle speed and detecting vehicle weight.

Introduction

Harvesting energy from our living environment has been a critical issue for sustainable development and has attracted long-lasting interest since the beginning of this century [1]. Mechanical energy is among the most abundant and reliable energy sources in our daily life, which is accompanying us regardless of the weather or temperature conditions as for solar [2] and thermoelectric energy [3]. Recently, piezoelectric nanogenerator (NG) has been developed that converts mechanical energy into electric energy employing the coupled piezoelectric and semiconducting properties of ZnO nanostructures [4–6]. The advancement of NG provides us with an alternate energy resource and pushes forward the investigation on wireless self-powered systems [7–9]. Various types of mechanical energy sources have been scavenged by NG including sonic wave [10], respiration [11], and air/liquid pressure [12]. In our previous work, the application of NG has been demonstrated as a self-powered tire-pressure sensor [13]. However, the setup required that NG should be installed inside the tire of the vehicles, which resulted in relatively high cost and sophisticated manipulation. Therefore, it will be more favorable if NG can be fixed onto the road and be applied as a self-powered sensor for transportation monitoring.

As for practical applications of NGs, both high output and excellent performance in other aspects are required to better

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accommodate the environment and human activity. The integration of transparency and flexibility characteristics is of dramatic importance in the development of NGs, especially for its potential applications in flexible electronics, artificial skins, and touch screens. Several works focusing on this issue have been reported [14–16] by using flexible polymeric substrate and transparent electrode materials like ITO [14], graphene [15], and carbon nanotube [16]. Though good flexible and transparent performance has been achieved, rare attention was paid to the real applications of the transparent flexible NG.

Polydimethylsiloxane (PDMS) is an optically clear, biocompatible, and fully rollable silicon elastomer, which is the core material for soft lithography to fabricate micro-fluidic devices [17]. It has been widely applied in the field of biological sensing [18], flexible solar cell [19], and tissue engineering [20]. We also have previous investigation that utilized PDMS as a template for the growth of ZnO NW array [21]. In this work, we successfully fabricated transparent and flexible NGs using ZnO nanowire (NW) array grown on PDMS substrate by the wet chemical approach. The fully packaged NG showed good transparency, flexibility, and robustness. Furthermore, the NG device had the capability to harvest energy under the rolling vehicle tire with stable output. Based on this character, we demonstrated its unique application as a self-powered dynamic sensor to detect vehicle speed and vehicle weight, which is of significance for practical applications in monitoring transportation flow.

Results and discussions

The structure of the transparent flexible nanogenerator (TFNG) is schematically shown in Figure 1a. First, the PDMS substrate was prepared by the gel-casting technique. A transparent and stretchable substrate with an ideal thickness was obtained. Closely packed ZnO NWs were uniformly grown on the PDMS substrate by the wet chemical approach, as the core component of the TFNG. The scanning electron microscopy (SEM) images of the NWs are shown in Figure 1b (top-view) and c (cross-sectional view). The diameter of the NWs was around 500 nm as indicated by the inset of high magnification image in Figure 1b, and the length of the NWs was around 6 μm. It was observed that the NWs had a hexagonal cross-section, and were grown densely to form a textured film, which was similar with the results in our previous works [7]. Then, polymethyl methacrylate (PMMA) was spin-coated on the NWs as an insulation layer. Finally, transparent ITO electrodes were deposited on the top and bottom surfaces of the composite structure. The effective size of the TFNG was 1.5 cm × 1 cm.

The working mechanism of the NG is based on the piezoelectric property of the ZnO textured film, according to our previous model [7]. When the flexible NG device is deformed by an external force, a piezoelectric potential (piezopotential) will be introduced in the ZnO textured film. As a result, a potential difference will be generated across the top and bottom electrodes due to induced charges, and it will drive the electrons flowing in the external load until equilibrium. When the external force is released and the NG recovers to its original shape, the piezopotential vanishes and the accumulated electrons will flow back in the opposite direction. Thus, an alternating current output signal is expected from the electrical measurement [22]. Here, we used numerical calculation to theoretically estimate the generated piezopotential with an applied stress,

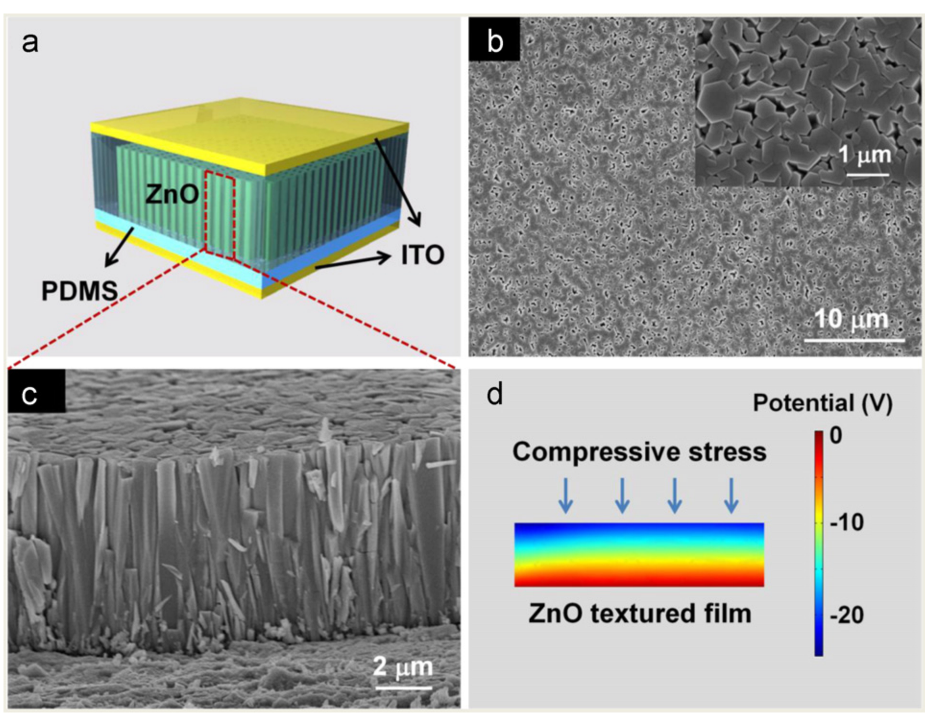

Figure 1 Structure and working principle of the transparent flexible nanogenerator (TFNG): (a) A schematic illustration of the typical composite structure of the TFNG. (b) The top-view SEM image of the as-grown ZnO NW arrays. The inset is a high magnification of the image. (c) The cross-sectional SEM image of the as-grown ZnO NW arrays. (d) Demonstration of the working principle of the TFNG from numerical calculation of the piezopotential in the ZnO textured film.

as illustrated in Figure 1d. For simplicity purpose, it was assumed that the textured film only experienced normal compressive stress during the deformation process. It was calculated that the piezopotential was 25 V with a compressive stress of 40 MPa.

The as-fabricated TFNG showed good transparency and flexibility characteristics, which was revealed by the photograph of the TFNG in Figure 2a. The enclosed rectangular region indicated effective area of the TFNG, which was deposited with ITO electrode. The inset indicated that the stretchable PDMS substrate could even be folded by the tweezers, without any obvious impairment to the structure of the device. Figure 2b shows the measured transmittance of the PDMS substrate and TFNG device using an ultraviolet-visible (UV-vis) spectrophotometer. It was observed that the transmittance of the PDMS film was over 80%, and that of the fully packaged device was around 50–60% in the visible range. The major limit of the transmittance was the scattering effect of the coated ITO electrode. The transmittance of the final device could be significantly enhanced if we used commercialized ITO electrode with better quality and higher transmittance.

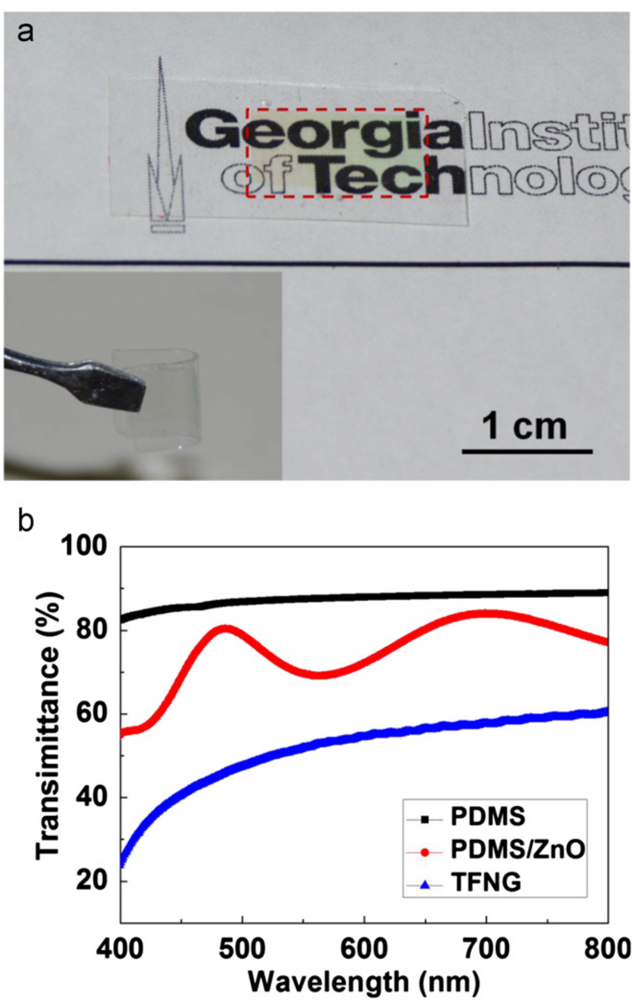

Figure 2 Optical property of the TFNG device: (a) Photographs of the TFNG device illustrating its transparency and flexibility. (b) The transmittances of the PDMS substrate, PDMS coated with ZnO seed layer and the final TFNG device.

To test the electrical output performance of the NG, we used a linear motor to apply a bending force to the NG. Since the thickness of the PDMS substrate (~200 μm) was much larger than the length of the NWs (~6 μm), it could be estimated that the NWs only experienced compressive stress in the bending process, which is consistent with the condition in the numerical calculation. Figure 3a and b shows the measured output performance of the NG device. With the strain of 0.12% at a strain rate of 3.56% s^{-1}, the open-circuit voltage and short-circuit current were measured to be 8 V and 0.6 μA, respectively, corresponding to a power density of ~5.3 mW/cm^3. This output is high enough for powering up small electronic devices, and it is also comparable to our previous results [7]. Since the NG was extraordinarily flexible owing to the unique characteristic of the PDMS substrate, the whole device could serve as an energy harvesting component in various working conditions, such as driven by wind blowing or body movement. Figure S1 shows the output voltage of the NG driven by blowing of light wind with various speeds. The output voltage could reach up to 1 V at a low speed of 2.4 m/s. Figure S2 and Video S1 show that the TFNG device could harvest energy from finger tapping and the harvested energy was able to directly power up a small liquid crystal display (LCD). These experimental results validate the advantage of the flexible NG over relative rigid NG based on silicon wafer or polystyrene (PS) substrate. The TFNG in this work could harvest energy under extended environmental conditions, especially with small perturbations, and shows better environmental compatibility.

On the other side, the NG device is robust enough and has the capability of scavenging energy under the rolling of the vehicle tires on the road, as shown in Figure 3c. The inset shows an enlarged shape of the output voltage versus time curve with respect to the rolling and releasing process. The output voltage was around 10 V. The whole process was recorded in Video S2 (output voltage) and Video S3 (output current). The high output performance of the NG device under the rolling of the wheel was quite stable, as revealed by the stability test in Figure 3d. It should be noted that the output voltage of the TFNG did not show significant decay even after continuous rolling for 1 h (~500 cycles). This experiment demonstrates the robustness of the NG device. It also supports our idea that this NG device could serve as a reliable energy harvester on the road, to scavenge the mechanical energy from the moving vehicle and power up some small electronic equipment beside the road.

Besides the energy harvesting function, we also performed further investigation on the applications of the NG device as a self-powered sensor for transportation monitoring on the road. Herein, the NG device was employed to detect the vehicle speed and vehicle weight instantly. Figure 4a illustrates the basic principle of vehicle speed monitoring using NG. Generally, two NG devices with similar size were placed consequently along the rolling path of a moving vehicle. The distance between the two NG devices was fixed as Δs=0.6 m. As the front tire of the vehicle rolled on the two NGs subsequently, two successive voltage peaks could be recorded by the measurement system, with a measurable time interval of Δt. Assuming that the vehicle speed was constant during this quick process, we were able to calculate the instant vehicle speed simply by $v=\Delta s/\Delta t$. Figure 4b–e lists the measured voltage peaks under the rolling tire of the

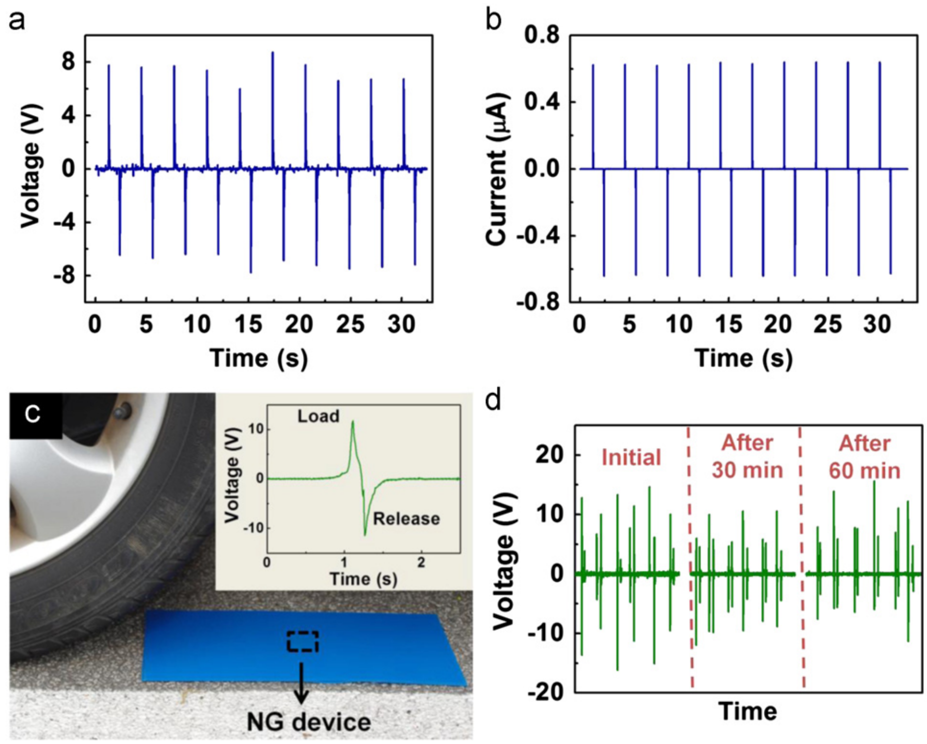

Figure 3 Output performance of the TFNG and the demonstration of energy harvesting by tire rolling: (a) Output voltage and (b) output current of the TFNG, induced by the bending force of a linear motor. The device was strained to 0.12% at a strain rate of 3.56% s^{-1}. (c) The photograph showing the experimental setup for harvesting energy under the rolling of the vehicle tire. The NG device was fixed on the road by inserting it between two polystyrene (PS) plates. The inset shows a typical output voltage peak induced by the loading and unloading of the vehicle tire. (d) The measurement of the stability of the TFNG driven by vehicle tire.

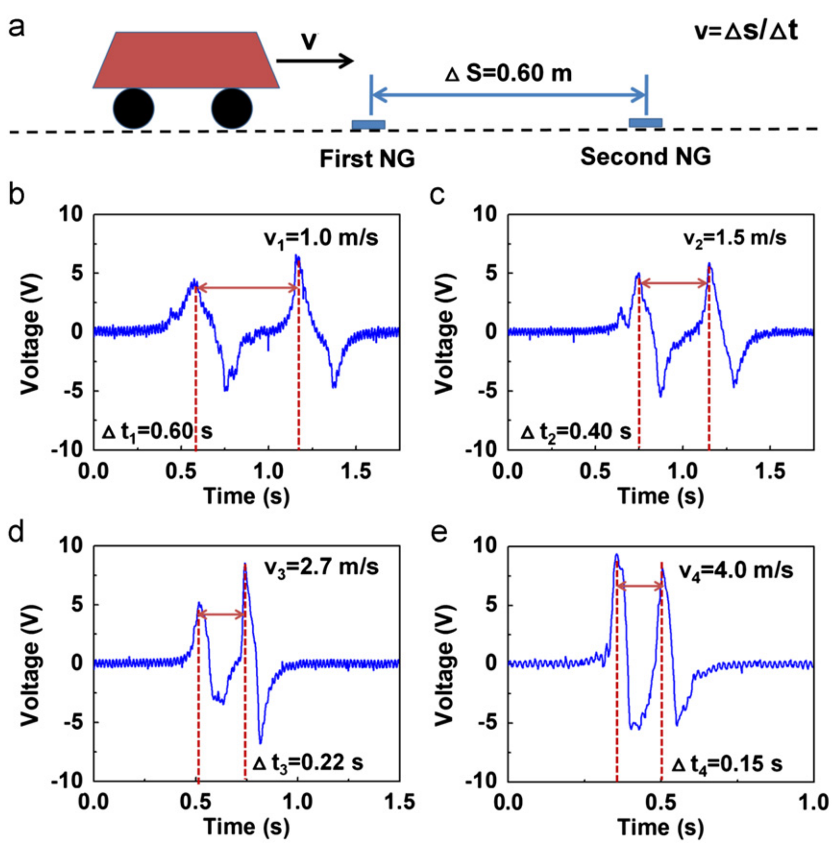

Figure 4 Application of the TFNG for self-powered transportation monitoring by detecting vehicle speed: (a) A schematic illustration showing the principle for measuring the vehicle speed on the road by the NG device. (b-e) The measured voltage-time relationship induced by vehicle tire with various speeds. The vehicle speed is calculated to be 1.0, 1.5, 2.7, and 4.0 m/s, respectively.

vehicle at various speeds, from 1.0 m/s to 4.0 m/s. The high end detection limit was mainly determined by the sampling rate of the measurement system and the distance between the two NG devices (Δs). At current conditions (the sampling rate is 500 s^{-1} and the NGs' distance is 0.6 m), the detection limit was ~300 m/s and it was high enough for vehicle speed detection even in an express way.

Theoretically, the output voltage of piezoelectric NG increases with the applied strain (or stress) on the structure. This is the principle for the vehicle weight monitoring using NG. Figure 5a shows the output voltage of NG driven by different vehicles with various curb weights, but at a constant and relatively low speed. It could be found that the output voltage increased with the vehicle weight. Figure 5b shows that the averaged output voltages had shown a linear relationship as a function of the curb weight of the vehicles. This result demonstrates the possibility of using NG as a self-powered sensor for monitoring the weight of vehicles on the road. Compared to traditional techniques for transportation monitoring, like speed camera and electronic balance, the NG-based speed and weight monitor has the following advantages: (1) it is a self-powered sensor and does not require external power source or specific maintenance and (2) it is transparent and flexible, which means it can be easily attached onto the road with any sort of environmental conditions, without interrupting the traffic.

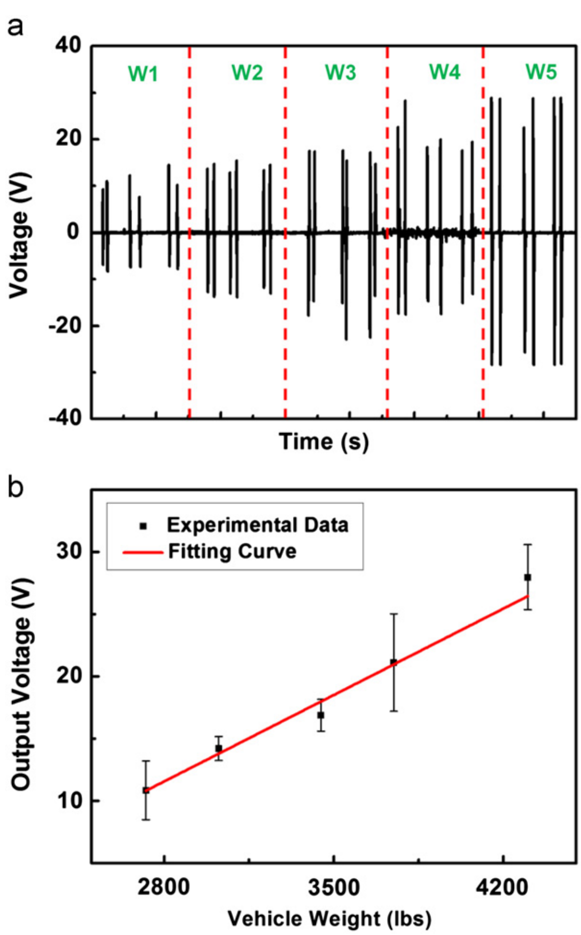

Figure 5 Application of the TFNG as self-powered pressure sensor for monitoring the vehicle weight: (a) Measured output voltages of NG device from tire rolling with various vehicle weights. It was observed that the output voltage increased with increasing vehicle weight. (b) Linear fitting of the average output voltage as a function of the vehicle weight.

Conclusions

In summary, we have successfully fabricated transparent flexible nanogenerators based on close-packed ZnO NWs on flexible PDMS substrate. The NWs show uniform length and diameter, as well as textured-film morphology, which are favorable for the performance of the NG device. The fully packaged TFNG device has shown good flexibility and high transmittance. The output voltage and output current are 8 V and 0.6 μA, respectively, corresponding to a power density of ~5.3 mW/cm^3. It has been demonstrated that the NG device is able to harvest energy under the rolling tire of a moving vehicle, owing from its robust nature. Based on this character of NG, we have demonstrated the self-powered sensors for measuring the vehicle speed and detecting vehicle weight, which has great significance in the applications for transportation monitoring.

Experimental section

Fabrication of the TFNG devices

Transparent PDMS substrate was prepared by the gel-casting technique. The base monomer and curing agent (Sylgard 184, Dow Corning) were mixed with a 10:1 mass ratio and stirred for 10 min. The mixture was then evacuated at room temperature for 20 min to remove the gas bubbles. After that, it was casted onto a relatively rigid, pre-cleaned polyethylene terephthalate (PET) plate and was kept in the oven at 85 °C for 1 h to get cured. The top surface of the PDMS film was treated with oxygen plasma (PC-150, South Bay Technology Inc.) for 30 min to generate more tangled O-H bonds on its surface, which would be favorable for the adhesion between the polymer surface and the ZnO seed layer, which was then deposited by magnetron sputtering. Closely-packed ZnO NW array was grown on the substrate by the hydrothermal approach. The nutrient aqueous solution was composed of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine (HMTA) (Sigma-Aldrich) at equal concentrations of 0.2 mol L^{-1}. The reaction temperature was kept at 95 °C in the convection oven (DKN 400, Yamato). The as-synthesized ZnO NWs were rinsed with distilled water and baked in the oven to remove extra water. Polymethyl methacrylate (PMMA) was spin-coated on the NWs and it served as an insulation layer in the NG. The whole composite structure was peeled off from the PET plate and deposited with transparent indium tin oxide (ITO) electrodes on its top and bottom surfaces, respectively. Silver paste was applied to connect the electrodes with conducting copper wires, which were used to connect to the measurement system.

Optical and electrical measurement of the TFNG

The transmittance of the TFNG device and the PDMS substrates was measured by a Beckman DU® 640 spectrophotometer. The ambient atmosphere was taken as the reference state. The open-circuit voltage and short-circuit current of the TFNG were measured by a Keithley 6514 System Electrometer and an SR570 low noise current amplifier (Stanford Research Systems), respectively. A mechanical linear motor (Labworks Inc., ET-132-203) was utilized to apply a bending force to the TFNG.

Numerical calculation of the piezopotential of the NG

The numerical calculation of the piezopotential was conducted by Comsol 3.5a. Since the ZnO NWs were densely grown on the substrate, we assumed that the NWs formed a textured film. According to the growth mechanism [23], the *c*-axis of the film was chosen to point toward the top electrode. For simplicity purpose, it was also assumed that the textured film only experienced normal compressive stress which was anti-parallel to the direction of the *c*-axis. The size of the unit cell for calculation was $20\ \mu m \times 20\ \mu m \times 6\ \mu m$. The calculated piezopotential was expressed as the rainbow color range in the diagram.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://10.1016/j.nanoen.2012.07.019.

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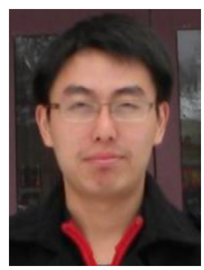

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Yan Zhang received his degree (1995) and Ph.D. degree in Theoretical Physics (2004) from Lanzhou University. Then, he worked as a lecturer and an associate professor (2007) of Institute of Theoretical Physics in Lanzhou University. In 2009 he worked as a research scientist in the group of Professor Zhong Lin Wang at Georgia Institute of Technology. His main research interest and activities are dynamics of time-delay systems, complex networks, self-powered nano/micro-system and theoretical calculation of piezotronic.