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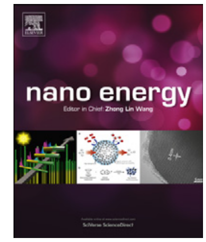

RAPID COMMUNICATION

Single crystalline lead zirconate titanate (PZT) nano/micro-wire based self-powered UV sensor

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Abstract
Ultra-long and flexible single-crystalline lead zirconate titanate $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) nano/micro-wires (N/MWs) were synthesized via a hydrothermal method. Owing to the self-polarization effect of the as-synthesized PZT N/MWs', the N/MWs can be used to directly fabricate a nanogenerator (NG) without being poled under electric field. Using such an NG, we demonstrated a flexible, self-powered system for detecting UV irradiance by utilizing the cycled contraction-expansion of a flexible rubber membrane.

Introduction

Collecting energy using nanomaterial from the environment has attracted extensive attention [1-6]. Compared with solar energy, thermal energy and other energy forms, mechanical energy is more popular in our living environment especially in biological system. NG fabricated using piezoelectric materials can be used to convert tiny mechanical energy in our living environment such as air flowing, heart beating and so on, to electricity. In addition, due to its small size, NG can be effectively integrated with the nano/micro-scale functional devices to form a self-powered nanosystem. NG based self-powered nanosystem has been proven viable by self-powered pH sensor, UV sensor, small liquid crystal display, commercial laser diode, pressure/speed sensor, environmental sensor and so on [7-11]. In order to get considerable output, these NGs are fabricated using NW arrays or NW textured film [9-11].

As a conventional piezoelectric material with the highest piezoelectric coefficient, bulk PZT ceramic has been widely used as transducers, sensors, actuators etc. for its high Curie point, large remnant polarization and stability over a large range of temperature [12,13]. However the conventional bulk piezoelectric transducer is very hard to drive and need to work near its resonant frequency, which greatly reduces their efficiency for harvesting irregular mechanical energy of tiny amplitude and low frequency. Compared with bulk materials, one dimensional nanostructure materials usually possess superior mechanical properties [14]. So using PZT NW's superior mechanical property and high intrinsic piezoelectric coefficient, it should be feasible to effectively

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collect irregular tiny mechanical energy of different amplitudes and frequencies in the environment. Recently, one dimensional single crystalline PZT NWs have been synthesized by the polymer assisted hydrothermal method [15,16]. Compared with PZT thin film and microfiber, the single crystalline PZT NW doesn't need high temperature to increase its crystallinity, which makes it compatible with the general fabrication methods of NG. However, the synthesized PZT NWs are too short to be used for the fabrication.

In this paper, the ultra-long and flexible single crystalline PZT N/MWs with diameters varying from hundreds of nanometers to several micrometers and lengths between 10 μm and 70 μm were synthesized via the polymer assisted hydrothermal method. A single crystalline PZT N/MW based NG was fabricated with open circuit voltage 0.12 V and short circuit current of 1.1 nA. Combining the NG with a nano-scale UV sensor, we demonstrated a flexible self-powered system for detecting UV irradiance utilizing the pulses of a pressure pipe.

Results and discussion

Synthesis and characterization of the ultra-long single crystalline PZT N/MWs

The ultra-long and flexible single crystalline PZT N/MWs were synthesized via a polymer assisted hydrothermal method [15]. And their structure had been studied by electron microscopy and X-ray diffraction (XRD). The synthesized single crystalline PZT N/MWs have diameters varying from hundreds of nanometers to several micrometers and lengths between 10 μm and 70 μm (Figure 1a, inset). They possess good mechanical properties, and can even be bent to a curvature of 0.09 1/μm without destroying their structure, as shown in Figure 1a. XRD pattern of PZT N/MWs is shown in Figure 1b. It demonstrates that the final products were well crystallized and all diffraction peaks can be indexed with the tetragonal structure of PZT (Joint Committee on Powder Diffraction Standards [JCPDS] Card no. 33-0784); no additional diffraction peaks from the impurities were detected. Figure 1c shows the transmission electron microscopy (TEM) image of a representative single PZT N/MWs with diameter about 250 nm and length up to tens of micrometers. The dot-like selected area electron diffraction (SAED) pattern (Figure 1c, inset) can be indexed as the (001), (110) and (111) diffractions of the tetragonal PZT, illustrating that the N/MW was a single crystal. High-resolution TEM (HRTEM) was utilized to investigate the microstructure. Regular fringes with a spacing of 0.415 nm corresponding with the (001) lattice plane of tetragonal PZT are shown in Figure 1d. Such phenomenon confirms the axis orientation of the PZT submicron wire is along the [001] direction.

Fabrication and characterization of the single crystalline PZT N/MW based NG

The NG's design is shown in Figure 2a, where a single crystalline PZT N/MW without being poled is placed on a

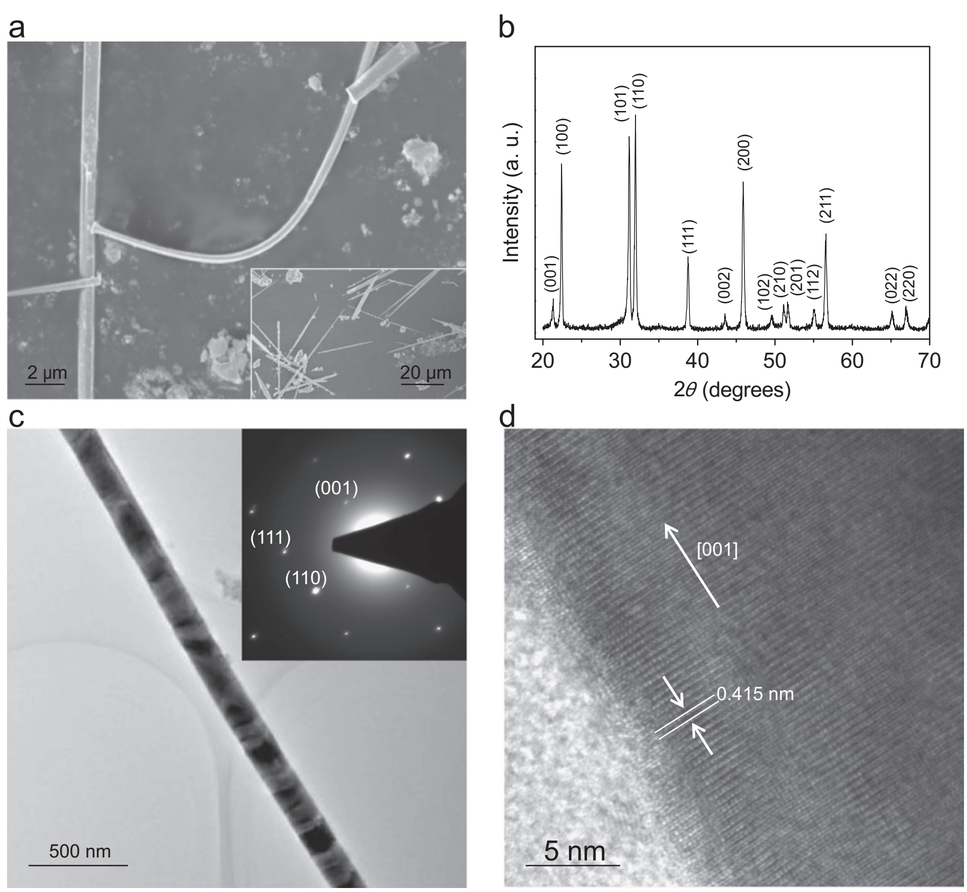

Figure 1 (a) SEM image of a bended single PZT N/MW. The inset shows an overall image of PZT N/MWs, (b) XRD pattern of the sample, (c) TEM image of a typical PZT NW. The inset shows the SAED pattern of that NW and (d) HRTEM image of PZT NW.

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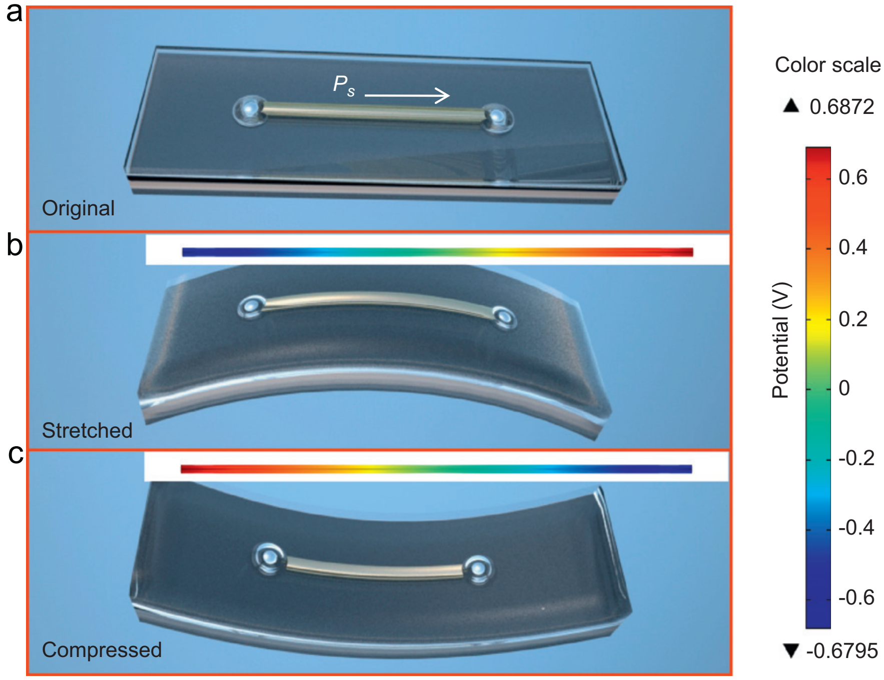

Figure 2 Design and simulation of single N/MW NG on a flexible substrate. (a) A single crystalline PZT N/MW is placed on a PET substrate, with its both ends bonded to the substrate by silver paste. Finally the entire system is packaged with PDMS. *Ps* indicates the polarization direction of the PZT N/MW. (b and c) Situations when the substrate is bended up and down, respectively. The insets in (b and c) show the calculated piezoelectric potential distribution in the stretched and compressed NG. The dimension of the simulated N/MW has a radius $a=250$ nm, length $l=30$ μm. The maximum strain magnitude of the N/MW is 2×10^{-5}.

flexible polyester (PET) substrate with its two ends bonded to the substrate by silver paste, and the entire structure is packaged using the polydimethylsiloxane (PDMS) to improve its stability. The details of the experimental setup and the measurement are much the same as the first lateral packaged piezoelectric fine wires NG. [17] When the substrate was bent, a tensile or compressive strain of magnitude about 2×10^{-5} was induced in the wire (see Supplementary Information). This strain can cause a potential drop along the wire, and forcing the electron to move in the external circuit, thus forming a current. We did a finite element simulation to get a clear picture about the piezoelectric potential distribution in the NG using COMSOL software, which is shown in Figure 2b and c. For simplicity, we consider the N/MW as a cylinder in the calculation. The color scale distribution reveals the piezopotential distribution. The parameters used in the COMSOL software are as follows: radius $a=250$ nm, length $l=30$ μm, strain amplitude 2×10^{-5}, material PZT-5H. From our calculation, a 1.37 V voltage formed between the two ends of PZT N/MW.

The practical measurement shows the open circuit voltage and short circuit current are 0.12 V and 1.1 nA, respectively, as is shown in Figure 3a and b. In order to verify this is the true signal generated by the NG, the switching-polarity measurement [18,19] was carried out, as shown in Figure 3a and b, the voltage and current signal could flip signs as the connect direction was alternated. And the output signals fit with the characters of ferroelectric NG (see Supplementary Information). Our NG can work in a large wide range of strains and frequencies, as shown in Figure 3c and d, maintain its stability over a long time (Figure 4), these features are critical for collecting irregular mechanical energy in the environment (Figure 5). Q3

Toward a self-powered nanosystem

The ultra-small size of a single PZT N/MW NG makes it an ideal power source for implantable nanodevices. It can be fixed on blood vessels to harvest the pulse energy to power a nanodevice. Figure 4a shows the schematics of the entire system imitating blood pulse driven self-powered nanosystem. Experimentally, we used two pressure pipes (inner diameter 7 mm, outer diameter 10 mm) with the interface connected with a flexible rubber membrane to simulate pulse movement in the blood vessel. Filling the pipes with water, when one flexible rubber membrane being pressed by a finger (the squeezing pressure is 4571 Pa–13714 Pa), the other flexible rubber membrane will show a small expansion pulse. Attach one NG on one of the rubber membrane, then squeeze the other rubber membrane periodically, the produced pulse movement could drive the NG to work. The single crystalline PZT N/MW based NG and a ZnO NW based UV sensor were connected in series. A voltmeter was connected in parallel with the ZnO UV sensor to detect voltage drop of the sensor. When using the UV light illuminate the sensor, the induced electrons and holes could decrease the ZnO's resistivity, thus an obvious reduced voltage drop could be detected by the voltmeter, so the decreased voltage could be used to indicate the existence of UV irradiance. The experimental results as shown in Figure 4b reveals that our NG based self-powered nanosystem

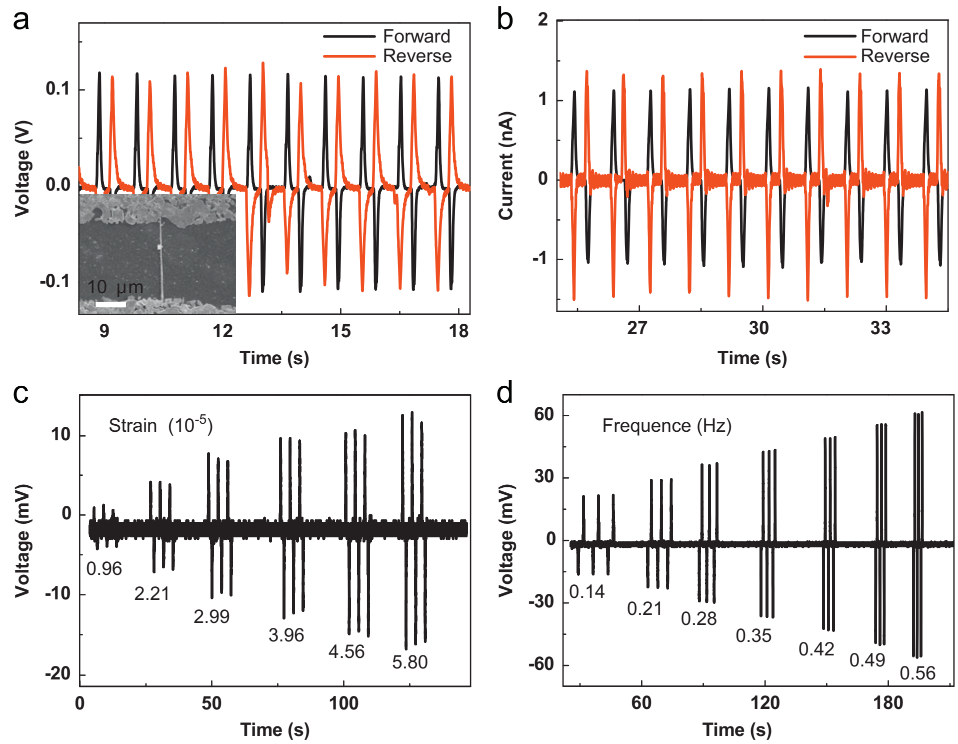

Figure 3 Performance of single PZT single crystalline N/MW NG. (a) Open circuit voltage of the NG when forward-connected and reverse-connected to the measurement system, respectively. The inset is the true-device SEM image, (b) Short circuit current of the NG when forward-connected and reverse-connected to the measurement system, respectively, (c) Open circuit voltage under different strains, and (d) Open circuit voltage under different driving frequencies.

can potentially collect energy from biological system and use that energy to detect the UV irradiance.

Conclusions

Based on a single crystalline PZT N/MW NG, we fabricated a flexible self-powered system for detecting UV irradiance driven by pulse movement. The same system has the potential to be integrated on the blood vessel and utilizing the vessel's pulse movement to work. This result showed our synthesized PZT N/MW is potentially suitable for fabricating a self-powered nanosystem for in-vivo application.

Experimental section

Synthesis and characterization of PZT N/MWs

Zirconium dichloride oxide hexahydrate ($ZrOCl_2\cdot 6H_2O$, 99.0%), tetra-n-butyl titanate ($[C_4H_9O]_4Ti$, 98.0%), lead nitrate ($Pb[NO_3]_2$, 99.0%), potassium hydroxide (KOH, 82.0%), and polyvinyl alcohol (PVA, 99.0%, molecular weight $=1750\pm50$) were used for the synthesis of PZT ($Pb(Zr_{0.52}Ti_{0.48})O_3$) N/MW. All these chemical reagents were purchased without further purification. First, 16.5 ml 0.08 mol L^{-1} deionized solution of $ZrOCl_2$, 12.0 ml 0.10 mol L^{-1} alcoholic solution of $(C_4H_9O)_4Ti$ and 25.0 ml 1.50 mol L^{-1} ammonia were mixed together. Under stirring for 30 min, co-precipitated hydroxide $Zr_{0.52}Ti_{0.48}O(OH)_2$ was formed. Then, the precipitant was filtered and washed with deionized water for several times, was re-dispersed by 20 ml deionized water in a 200 ml beaker. After that, 0.92 g $Pb(NO)_3$, 5.47 g KOH and 20.0 ml 0.01 g mL^{-1} PVA were added into the solution, successively. Under magnetic stirring for 0.5 h, the as-prepared sol was transferred into a 25 ml autoclave. Finally, the autoclave was put into an oven for 12 h at 200 °C. After filtering, washing and desiccating at 60 °C for 24 hours, yellow powders with PZT N/MWs were obtained.

The crystal structure of the PZT powders was characterized by X-ray diffraction (XRD) on a Rigaku D/max-2400 diffractometer with Cu K_α radiation. Field emission scanning electron microscope (SEM) observations were carried on a Hitachi S-4800 with an acceleration voltage of 5 kV. Transmission electron microscope (TEM) and high-resolution (HRTEM) observations were performed using a JEM 2010 working with an acceleration voltage of 200 kV.

Fabrication of the NG and UV sensor

Single crystalline PZT N/MW with diameter ~500 nm and length ~70 μm was chosen for fabricating NG. First, a piece of PET film with thickness of 0.3 mm was washed with acetone, ethanol and deionized water using ultrasonic cleaner, in sequence. Then, the N/MW was bonded on PET film with silver paste, and both of its ends were connected with Al (Si 1%) alloy wire whose diameter was 25.4 μm. Finally, PDMS was used to package the entire system to make the NG robust. Single crystalline ZnO NW synthesized by the chemical vapor deposition (CVD) method was chosen for fabricating UV sensor, and it had a diameter about hundreds of nanometer and length about hundreds of micrometer. The

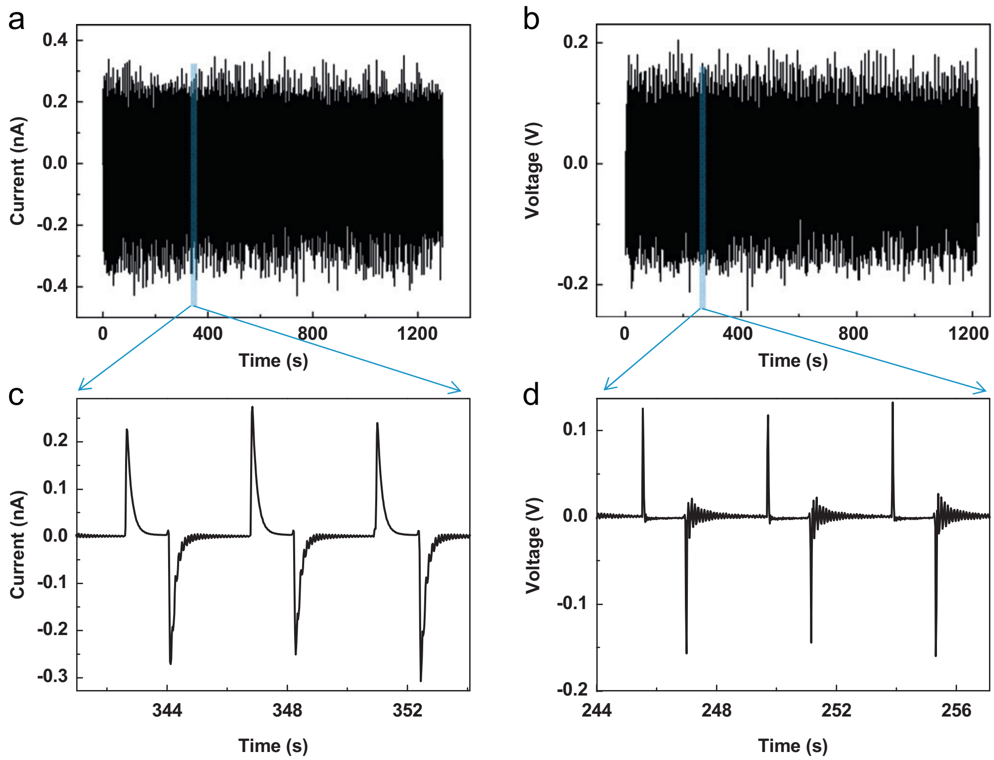

Figure 4 Short-circuit current (a) and open-circuit voltage (b) of a PZT NG after long time running. (c and d) are the enlarged figures from (a and b), respectively.

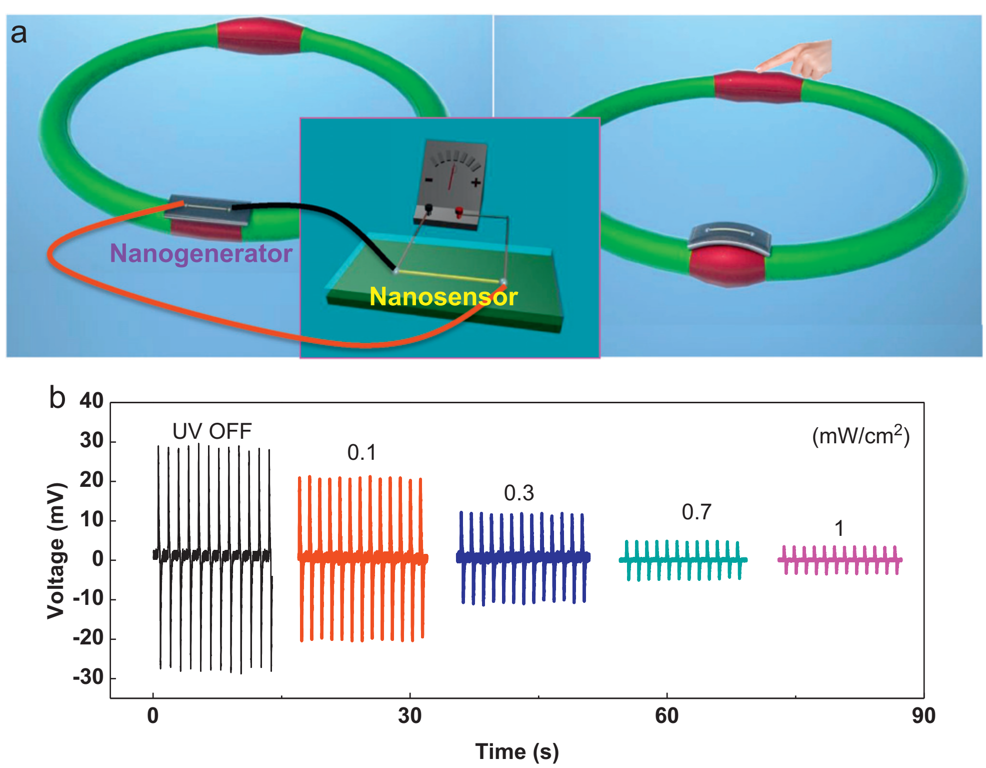

Figure 5 (a) A schematic of using an NG to harvest energy of the pulse movement of the pressure pipe to power for a nano-scaled UV sensor, and (b) UV response under different intensities of UV irradiance.

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same method was used for fabricating UV sensor, except for the packaging procedure.

Test method

Preamplifiers (*SR*570, *SR*560) were used to test the voltage and current signal of NG. *LinMot* linear motor (*E*1100) was used to drive the NG. One end of NG was fixed on a testing stage, leaving the other end free. The free end was tied to the linear motor via a cotton wire. The PET film was bent and released periodically through the linear motor's back and forth movement. By changing the orientation between the PET film and linear motor, strain mode and compress mode were acquired, respectively. If the PET's side with the NG was faced right to the linear motor the compressed mode was achieved, else the stretched mode was gotten. Through exchanging positive and negative connector, forward connection and reversed (defined arbitrarily) connection were acquired, respectively. In the polarization study, *Keithley* high voltage supply (248) was used. And 10 V/μm electric field was applied to pole the PZT N/MW; meanwhile, the device was heated up to about 120 °C during the poling process.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2012.09.001.

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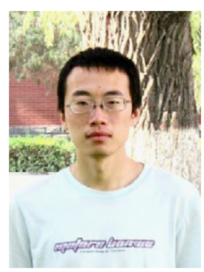

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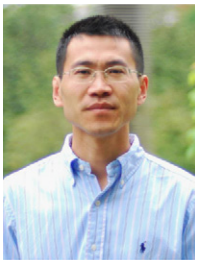

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Zhong Lin Wang received his Ph.D. from Arizona State University in physics. He now is the Hightower Chair in Materials Science and Engineering, Regents' Professor, Engineering Distinguished Professor and Director, Center for Nanostructure Characterization, at Georgia Tech. Dr. Wang has made original and innovative contributions to the synthesis, discovery, characterization and understanding of fundamental physical properties of oxide nanobelts and nanowires, as well as applications of nanowires in energy sciences, electronics, optoelectronics and biological science. His discovery and breakthroughs in developing nanogenerators established the principle and technological road map for harvesting mechanical energy from environment and biological systems for powering a personal electronics. His research on self-powered nanosystems has inspired the worldwide effort in academia and industry for studying energy for micro-nano-systems, which is now a distinct disciplinary in energy researchand future sensor networks. He coined and pioneered the field of piezotronics and piezo-phototronicsby introducing piezoelectric potential gated charge transport process infabricating new electronic and optoelectronic devices. Details can be found at http://www.nanoscience.gatech.edu.

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