Single Micro/Nanowire Pyroelectric Nanogenerators as Self-Powered Temperature Sensors

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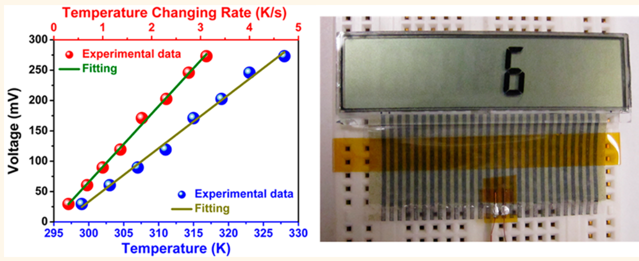
ABSTRACT



We demonstrated the first application of a pyroelectric nanogenerator as a self-powered sensor (or active sensor) for detecting a change in temperature. The device consists of a single lead zirconate titanate (PZT) micro/nanowire that is placed on a thin glass substrate and bonded at its two ends, and it is packaged by polydimethylsiloxane (PDMS). By using the device to touch a heat source, the output voltage linearly increases with an increasing rate of change in temperature. The response time and reset time of the fabricated sensor are about 0.9 and 3 s, respectively. The minimum detecting limit of the change in temperature is about 0.4 K at room temperature. The sensor can be used to detect the temperature of a finger tip. The electricity generated under a large change in temperature can light up a liquid crystal display (LCD).

KEYWORDS: PZT · micro/nanowire · pyroelectric · nanogenerator · temperature sensor

Heat sources are an important source of energy in our daily life, which can be harvested for powering some small electronic devices and systems.[1,2] The conventional thermoelectric generators mainly rely on the Seebeck effect that utilizes a temperature difference across a device to drive the diffusion of charge carriers.[3,4] The existence of a temperature difference is a must for these devices. The thermoelectric generators cannot work when the environment temperature is spatially uniform and under a time-dependent temperature fluctuation. In this case, pyroelectric nanogenerators (PNG) based on ZnO nanowires have been fabricated as a key technology for converting heat energy into electricity.[5] The mechanism of PNG is based on the change of spontaneous polarization in certain anisotropic solids due to the temperature fluctuation.[6] The PZT nanomaterials may be a good choice for the PNG due to a large pyroelectric coefficient.[7]

Micro/nanosensors have attracted much attention due to their potential applications in detecting the micro/nano-objects such as a particle, cell, DNA, and so on.[8−11] Micro/nanomaterials are important for fabricating these small scale sensors. The self-powered nanotechnology is based on driving a nanodevice by harvesting energy from its working environment instead of a conventional battery or any other energy storage/supply system.[12−14] There is an urgent need to develop nanotechnology that harvests energy from the environment to power these sensors.[15−17] It means that we can use the PNG as a self-powered temperature sensor that automatically detects temperature without using a battery as the power source. This approach can greatly enhance the adaptability and mobility of such devices. Although some temperature sensors have been reported,[18−20] there are few studies about using a single PZT micro/nanowire PNG as a self-powered temperature sensor. Here, a single PZT micro/nanowire PNG was fabricated, which was used as a self-powered temperature sensor. The output voltage of the sensor was found to linearly increase with an increasing rate of change in temperature of the detected heat sources. The response time and reset time of the fabricated sensor are about 0.9 and 3 s, respectively. It can be used to detect the minimum temperature change of about 0.4 K at room temperature. We also demonstrated that the temperature sensor can be used to detect the temperature of

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the finger surfaces and light a LCD under a heated temperature of 473 K.

RESULTS AND DISCUSSION

The PZT micro/nanowires were obtained by using a simple mechanical method. The detailed fabrication method is given in the Experimental Section. Figure 1a shows an optical image of the obtained PZT micro/nanowires. The SEM image of a single PZT microwire is shown in Figure 1b. The diameter and length of the microwire are about 2 and 10 μm, respectively. The schematic of the fabricated PNG is shown in Figure 1c. The large size PZT microwires were chosen for easy manipulation under an optical microscope. The same methodology and principle can be applied to the PZT nanowires. A long PZT microwire was placed on a thin glass substrate and the two ends of the microwire were then fixed by silver paste. The external heat can effectively reach the PZT microwire by using the thin glass substrate of about 0.15 mm. A thin PDMS layer was used to package the device, which can avoid the effect of atmosphere and prevent the PZT microwire from contamination or corrosion.

The fabricated PNG was attached on a heater, where the temperature of the heater can be controlled. Figure 2a shows the cyclic changes in temperature of the PNG and the corresponding differential curve. Under forward connection, a sharp negative voltage/current pulse (about 60 mV/0.6 nA) was observed when the temperature was increased from 296 to 333 K, as shown in Figure 2b. After reversely connecting the PNG to the measurement system (Figure 2c), the obtained opposite voltage/current signals indicate that the measured signals were generated by the fabricated PNG. Usually, the pyroelectric current I can be described as $I = pA(\mathrm{d}T/\mathrm{d}t)$, where p is the pyroelectric coefficient, A is the electrode area, $(\mathrm{d}T/\mathrm{d}t)$ is the rate at which the temperature is changed.[21] To confirm that the output signals in Figure 2 panels b and c were generated by the pyroelectric effect, we set the different rates of change in temperature, as shown in Figure 2d. It can be clearly seen that the output current of PNG linearly increases with an increasing rate of change in temperature. The corresponding output voltage of PNG also was found to have a linear relationship with the rate of change in temperature, as shown in Supporting Information, Figure S1. A control experiment was carried out using the devices without the PZT microwire. No appreciable voltage pulse signals can be observed for this case under the similar temperature fluctuations (Supporting Information, Figure S2). These results indicate that the obtained signals in Figure 2 are due to the pyroelectric effect of a PZT microwire.

Before the fabricated PNG can be used as a self-powered temperature sensor, we need to obtain the relationship between the output voltage of the sensor and temperature. In the sensor measurement process, the PNG was attached on the surface of a metallic body (Figure 3a), which is beneficial for good heat dissipation. When the sensor is off contact with the heat source, there is no observable output voltage. When the sensor is in contact with the heat source (the temperature of 303 K), a negative voltage pulse (−60 mV) can be observed, as shown in Figure 3b. When the heat source is moved out of in-contacting with the sensor, a positive voltage pulse can be observed, which is consistent with the results in Figure 2. Moreover, under the reversed connection condition, the reversed output voltage signals can be observed. Figure 3c shows the enlarged negative pulse signal, where the maximum width of the pulse is about 30 s. The response time is about 0.9 s, where a negative noise signal can be observed (the dark arrow). The response time of 0.9 s was confirmed further by using the positive pulse signal (Supporting Information, Figure S3). In Figure 3c, the observed noise signal before the voltage peak is associated with the movement of the sensor in measurement process. When the heat source was moved out of contact, the positive output voltage signal returned to 0. By fitting the $V-T$ curve in Figure 3d, the decay time of temperature response follows an exponential decay function, where the time constant is 3 s. The decay mechanism is related to the heat dissipation

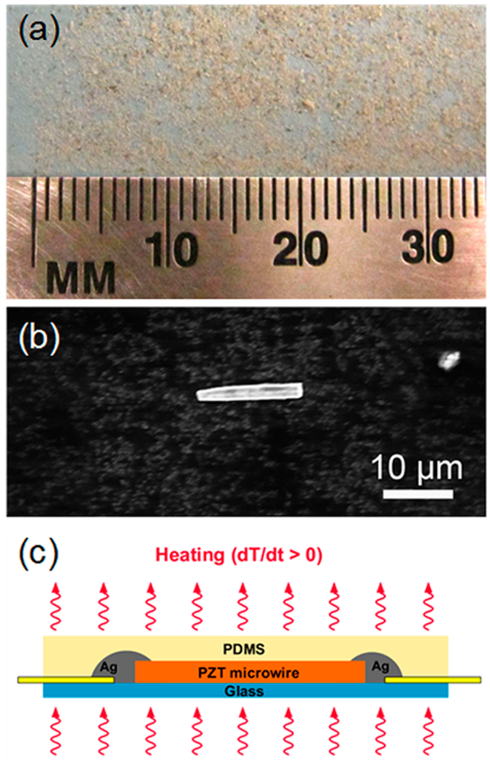

Figure 1. (a) Photograph of the obtained PZT micro/nanowires. (b) SEM image of a single PZT microwire. (c) Schematic diagram showing the structure of a single PZT microwire pyroelectric nanogenerator.

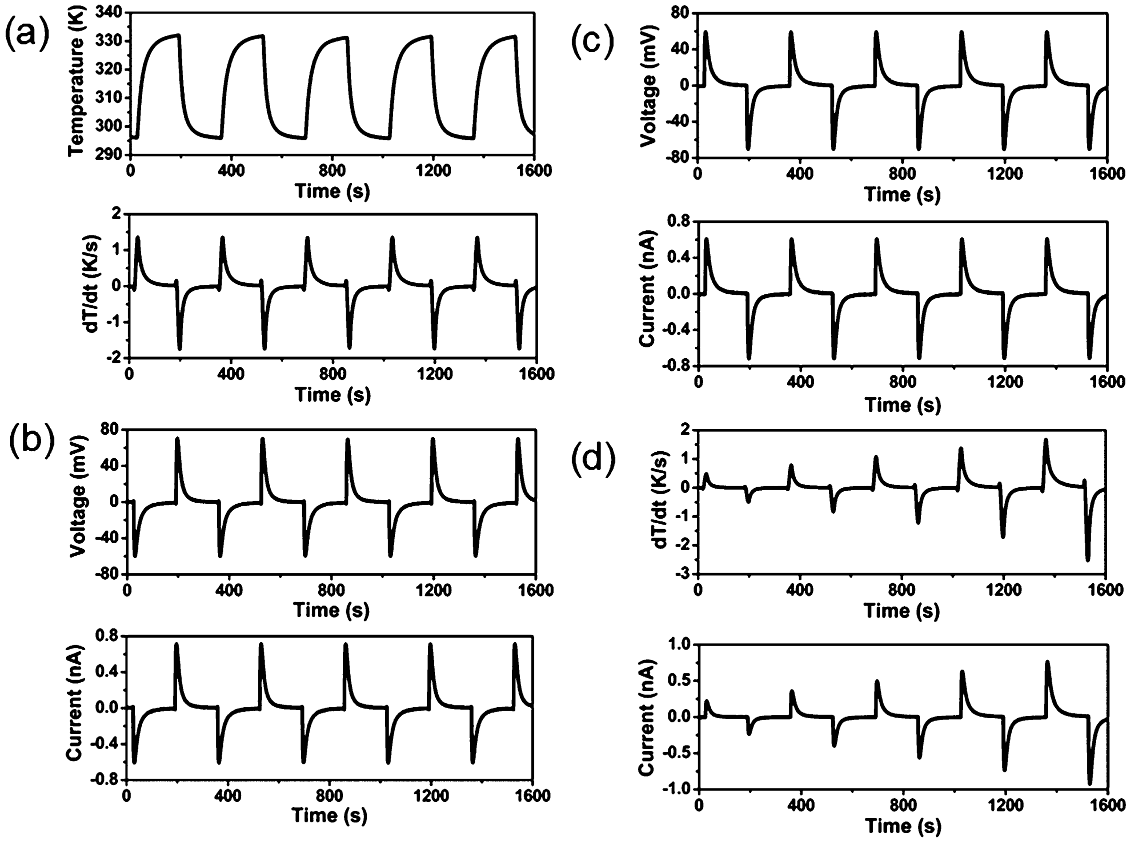

Figure 2. (a) The cyclic changes in temperature of a single PZT microwire pyroelectric nanogenerator and the corresponding differential curve. (b, c) The measured output voltage and current of the device under the forward (b) and reversed (c) connection conditions when it was subject to the cyclic temperature change in panel a. (d) The measured output current of the device under the different rates of change in temperature.

of the sensor in contact with the metallic body. The reset time of the temperature sensor is about 3 s, where it is defined as the time need to recover to 1/e (37%).[20] The response time and reset time of the PNG temperature sensor are much shorter than those of the thermoelectric temperature sensor.[20]

Figure 4a shows the output voltages of the fabricated sensor when it was used to touch the heat sources with the different temperatures. It can be seen that the output voltage increases with an increasing temperature of the heat source. The corresponding temperature changing rates were shown in Supporting Information, Figures S4 and S5, indicating that the rate of change in temperature linearly increases with an increasing temperature of the heat source. The output voltage linearly increases with an increasing rate of change in temperature (Figure 4b), which is consistent with the results in Figure 2d and Supporting Information, Figure S1. Due to the linear relationship between the rate of change in temperature and the temperature of heat source (Figure S5), the output voltage also was found to have a linear relationship with the temperature of heat source, as shown in Figure 4b. The linear relationships indicate that the fabricated sensor has a good performance for detecting not only the temperature of heat sources but also the rate of change in temperature. Figure 4c shows that the minimum detection limit of the sensor is 0.4 K at room temperature, resulting in an output voltage of about 6 mV. If the change in temperature is smaller than it is in Figure 4d, the output voltage of the sensor will be smaller than that of the noise signal.

An important application of the fabricated sensor is that it can be used to detect the temperature changing rate and the temperature when a finger tip touched the sensor. Figure 5a shows that the sensor was fixed on a soft foam plastic substrate, which can avoid the fracture of the sensor when the finger was used to touch it. When the finger touched the sensor, there was a negative output voltage peak of about −60 mV, as shown in Figure 5b. When the finger was moved out, a positive output voltage peak can be observed. However, the peak value is much smaller than 60 mV, which is related to the slow heat dissipation of the sensor on the foam plastic substrate. Figure 5c shows the output voltages of the fabricated sensor under the reversed connection condition. The reversed output voltage signals indicate that the data were generated by the sensor. By combining the data in Figure 4b and the obtained output voltage of 60 mV, the values of temperature changing rate and the temperature of finger surfaces were confirmed to be about 0.68 K/s and 303 K

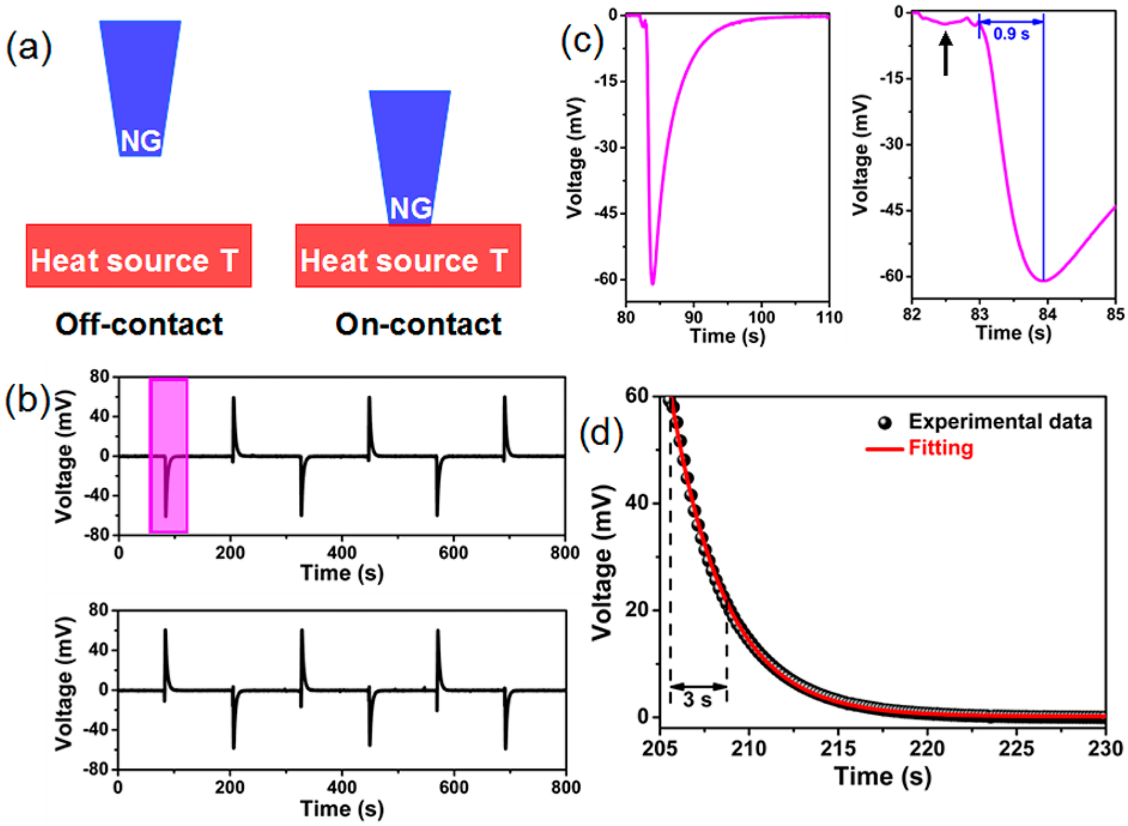

Figure 3. (a) Schematic diagram of the measurement process of the temperature sensor. (b) The output voltages of the sensor under the forward and reversed connection conditions when the temperature of heat source is 303 K. (c) The enlarged negative output voltage pulse in panel b. (d) The enlarged $V-T$ curve of the positive output voltage pulse in panel b when the heat source was moved out.

by averaging the measured values from four repetitions, respectively.

The fabricated self-powered temperature sensor can be also used in high temperature early warning systems. The data in Figure 4b indicates that the output voltage of the sensor can increase with an increasing temperature of the heat sources. If the temperature of a heat source is high enough, the output voltage of the sensor can be larger than 3 V, which can be used to drive a LCD. Figure 6a shows a PNG sensor, which is attached on a metallic body and connected with a LCD screen (Figure 6b). When there is no change of temperature in the sensor, no number was shown on the LCD screen. When the sensor is in contact with the heat source with the temperature of 473 K (Figure 6c), the number "6" was clearly lighted on the LCD screen.

CONCLUSION

In summary, we have demonstrated the application of a single PZT micro/nanowire PNG as a self-powered sensor for detecting the temperature of heat sources. The output voltage of the sensor linearly increases with an increasing rate of change in temperature. The response time and reset time of the sensor are about 0.9 and 3 s, respectively. The minimum detection limit of the sensor is 0.4 K at room temperature. The temperature of finger surfaces was detected to be about 303 K, where the peak rate of change in temperature is about 0.68 K/s. The sensor can light a LCD when the temperature of the heat source is up to 473 K, which can be used in high temperature early warning systems. The self-powered temperature sensors developed here have potential applications in temperature measurements in environmental sciences, safety monitoring, medical diagnostics, and more.

EXPERIMENTAL SECTION

Fabrication of Single PZT Micro/Nanowire PNG. A bulk PZT was pressed into many PZT micro/nanowires by using large loading forces. A thin glass substrate was washed with ethanol and deionized water under sonication. Under an optical microscope, a single PZT microwire was placed on the glass substrate and the two ends of the microwire were fixed by the silver paste. The entire device was then packaged by PDMS to avoid the effect of atmosphere. By using a high voltage power supply (Bertan, Series 230), we applied a large voltage of 3.5 kV on the single PZT microwire for electric poling at room temperature. The device was attached on a heater, where the temperature was

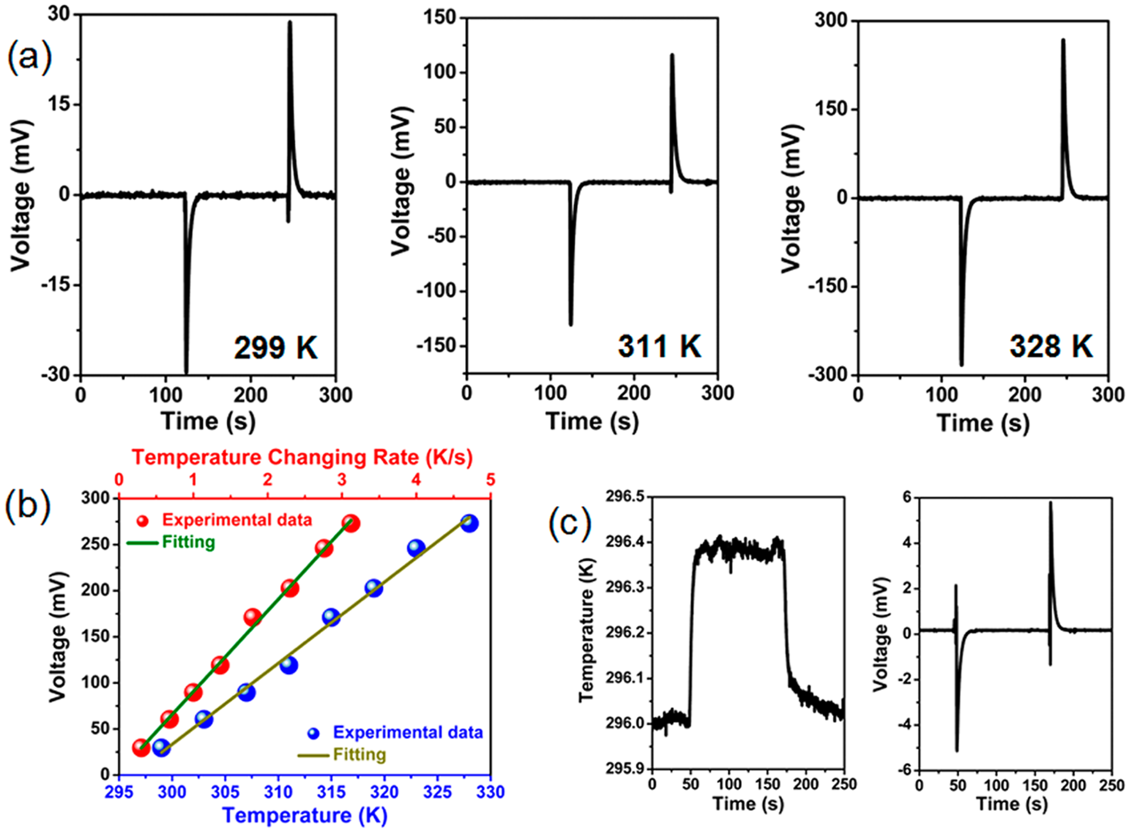

Figure 4. (a) The measured output voltages of the sensor under the different temperatures of the heat source. (b) Dependence of the output voltage on the temperature changing rate and the temperature of the heat source. (c) The minimum change in temperature of the sensor and the corresponding output voltage.

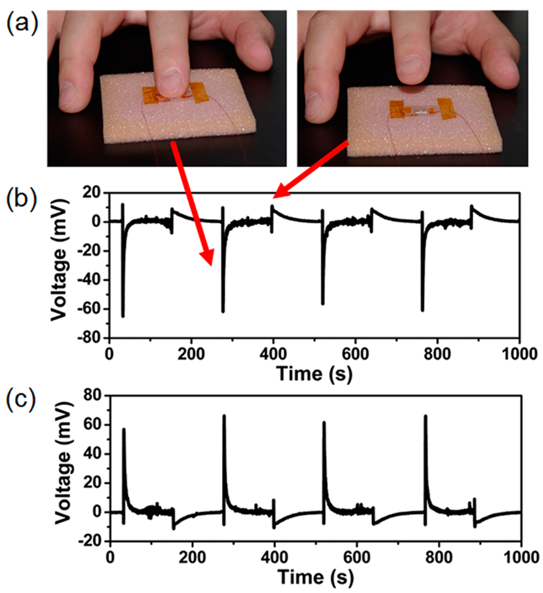

Figure 5. (a) The optical images when a finger touched the fabricated sensor and was then moved out. (b) The $V-T$ curve when the finger touched the sensor in four times under the forward connection condition. (c) The corresponding $V-T$ curve under the reversed connection condition.

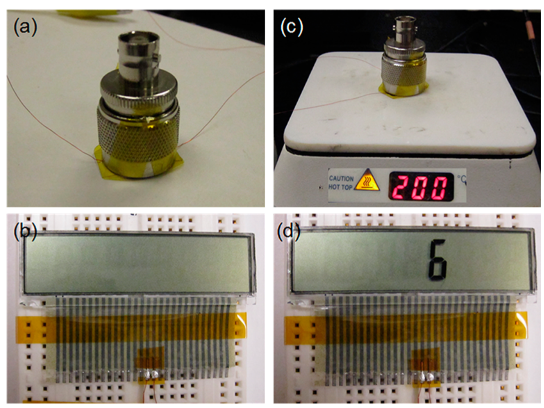

Figure 6. (a) The optical image when a self-powered sensor was attached on a metallic body. (b) The optical image of a LCD screen, which is connected to the sensor in panel a. (c) The optical image when the sensor is in contact with a hot-plate with the temperature of 473 K. (d) The optical image of the lighted LCD screen, which is connected to the pyroelectric generator in panel c.

controlled by the applied voltages and measured by using a temperature sensor.

Measurements of Self-Powered Temperature Sensors. The single PZT microwire PNG was attached on a metallic body, which was used as self-powered temperature sensors. In all the experiments, the room temperature was confirmed to be 296 K. A heater was used as the detected heat sources. When the sensor was not in contact with the heat sources, it was placed on a metallic plate to maintain room temperature. When the sensor was used to detect the temperature of finger surfaces, the sensor was attached on a soft foam plastic substrate, where the thin glass substrate is on the top. When the sensor was used to drive a LCD, a hot-plate with a highest temperature of 773 K was used as the heat sources. The output signals of the fabricated devices were measured by using a low-noise voltage preamplifier (Stanford Research System Model SR560) and a low-noise current preamplifier (Stanford Research System Model SR570).

Conflict of Interest: Conflict of InterestThe authors declare no competing financial interest.

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Supporting Information Available: (1) The measured output voltage of the device under the different rates of change in temperature in Figure 2d; (2) control experiment, no observed output voltage of the device without PZT micro/nanowires under the cyclic heating process; (3) enlarged output voltage pulse signal when the heat source was moved out; (4) rates of change in temperature of the sensor under the different temperatures of heat sources; (5) plot showing the linear relationship between the temperature of heat sources and the temperature changing rate. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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