

Flexible Pyroelectric Nanogenerators using a Composite Structure of Lead-Free KNbO₃ Nanowires

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Energy-harvesting and conversion devices using nanotechnology have received increasing interest recently because they have potential applications in self-powered nanodevices and nanosystems.^[1–3] Piezoelectric nanowires have been extensively investigated for nanogenerators (NGs).^[4–7] The nanowire-based solar cells can only work under light-illumination conditions.^[8–10] Owing to the small sizes, it is difficult for nanowire thermoelectric devices to maintain the temperature difference across a nanoscale distance.^[11] An alternative approach is to use pyroelectric-based energy harvesting, where the temperature dependence of the spontaneous polarization can result in the flow of electrons for electric output.^[12–14] Moreover, it has been reported that a size-driven enhancement of the pyroelectric coupling leads to a giant pyroelectric current and voltage generation by the polarized ferroelectric nanomaterials in response to temperature fluctuations.^[15] It has been reported that the spontaneous polarization and the pyroelectric coefficient of bulk KNbO₃ are about 0.41 C/m² and 5 nC/cm²K at 300 K, respectively.^[16] Although there have been some studies about the piezoelectric property of KNbO₃ materials and its applications,^[17,18] there have been no reports about KNbO₃-nanowire-based pyroelectric NGs. PZT nanomaterials may be a good choice for pyroelectric NGs due to their large pyroelectric coefficient.^[12] However, it is important to explore cost-effective pyroelectric NGs by using easily accessible and non-toxic ferroelectric nanowires.^[19,20]

In this work, we report pyroelectric NGs fabricated using lead-free KNbO₃ nanowires, for the first time. The grown KNbO₃ nanowires have a single-crystalline structure with a growth direction of [011]. By forming a composite of KNbO₃ nanowires with polydimethylsiloxane (PDMS) polymer, flexible NGs were fabricated easily after applying a direction poling

process. The mechanisms of pyroelectric NGs are discussed. The NGs were also used to harvest energy from sunlight illumination and fabricate hybrid NGs with solar cells.

We fabricated a composite of the KNbO₃ nanowires and PDMS polymer in a volume ratio of 3:7 to imbue our NGs with flexibility. The pyroelectric device mainly consists of three layers, as schematically shown in Figure 1a. The Ag and ITO films act as top and bottom electrodes, respectively. As described in the experimental section, the KNbO₃ nanowires were grown by a simple hydrothermal method. Figure 1b shows a transmission electron microscopy (TEM) image of single KNbO₃ nanowires. The corresponding selected area electron diffraction (SAED) pattern confirms that the phase is of the perovskite structure. The high-resolution transmission electron microscopy (HR-TEM) image indicates that the nanowires are single-crystalline and free of defects. Combining the SAED patterns and HR-TEM images, the growth direction of the nanowire is confirmed to be along the [011] direction. Due to the use of PDMS polymer layer in NGs, the devices are flexible and can be bent, as shown in Figure 1c. The SEM image of a single KNbO₃ nanowire in Figure 1d shows that the surface of the nanowire is clean and the diameter is about 150 nm. Figure 1e shows an enlarged cross-sectional SEM image of a KNbO₃ nanowire-PDMS polymer composite. It can be clearly seen that the nanowires were randomly oriented and well-dispersed without aggregations.

After a positive direction poling process, the electric dipoles in KNbO₃ nanowires would tend to align along the electric-field direction from top to bottom, as shown in the inset of Figure 2a. Figure 2 shows the generated open-circuit voltage and short-circuit current under the different changes in temperature. When the temperature increases from room temperature (RT), 295 K, to a higher value, positive current/voltage peaks can be observed. The opposite output is observed when the temperature decreases from RT 295 K to a lower value. Under a change in temperature of about 40 K, the obtained current and voltage peaks were about 120 pA and 10 mV, respectively. The output current/voltage increased with increasing the rate of change in temperature. After a negative direction poling process, the electric dipoles in the KNbO₃ nanowires would tend to align along the electric-field direction from bottom to top, as shown in the inset of Figure 3a. The measured open-circuit voltage and short-circuit current of the NG under the different changes in temperature are shown in Figure 3. Under the same change in temperature, the variation of the voltage/current output for the NGs in Figure 2 and 3 are opposite. The output of the NGs can be increased by increasing the change in temperature. Usually, the output current I of the pyroelectric NGs can be determined by the equation of $I = pA \frac{dT}{dt}$, where p is the pyroelectric

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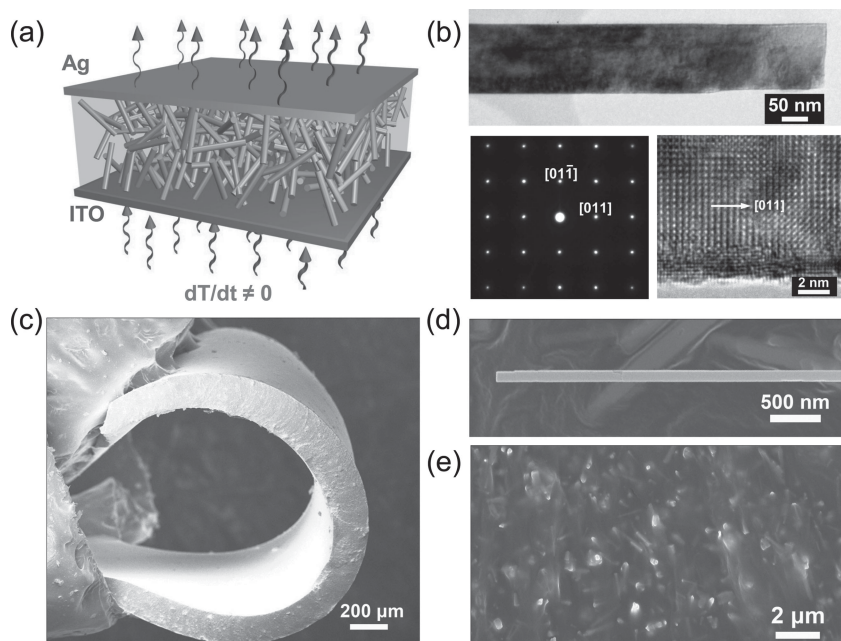


Figure 1. a) Schematic diagram showing the structure of the pyroelectric nanogenerator. b) TEM image of a single KNbO₃ nanowire, the corresponding SAED pattern of the nanowire, and the corresponding HR-TEM image of the nanowire. c) SEM image of a bent KNbO₃-PDMS composite film. d) SEM image of a single KNbO₃ nanowire. e) SEM image of the enlarged cross-section of the KNbO₃-PDMS composite film in (c).

coefficient, A is the effective area of the NG, dT/dt is the rate of change in temperature.^[21] The rates of change in temperature are shown in Figure 2a and 3a. It can be clearly seen that the output current of the NGs in Figure 2 and 3 can increase with increasing the rate of change in temperature, which is consistent with the equation of output current.

To confirm that the obtained signals were due to the KNbO₃ nanowires, we performed three control experiments. Firstly, we tested the output voltage from only PDMS polymer without KNbO₃ nanowires after the same positive direction poling process. These were not observed under the different changes in temperature (Supporting Information, Figure S1). Secondly, under the different changes of temperature, we tested the output voltage of the NG fabricated from the KNbO₃ nanowire-PDMS polymer composite before (Figure S2a,b) and after (Figure S2c,d) a positive direction poling process, respectively. Before the poling process, there was no observed output signal. After the poling process, voltage peaks can be clearly seen in Figure S2c,d. Thirdly, the linear superposition test in Figure S3 shows that the output current of NG could be

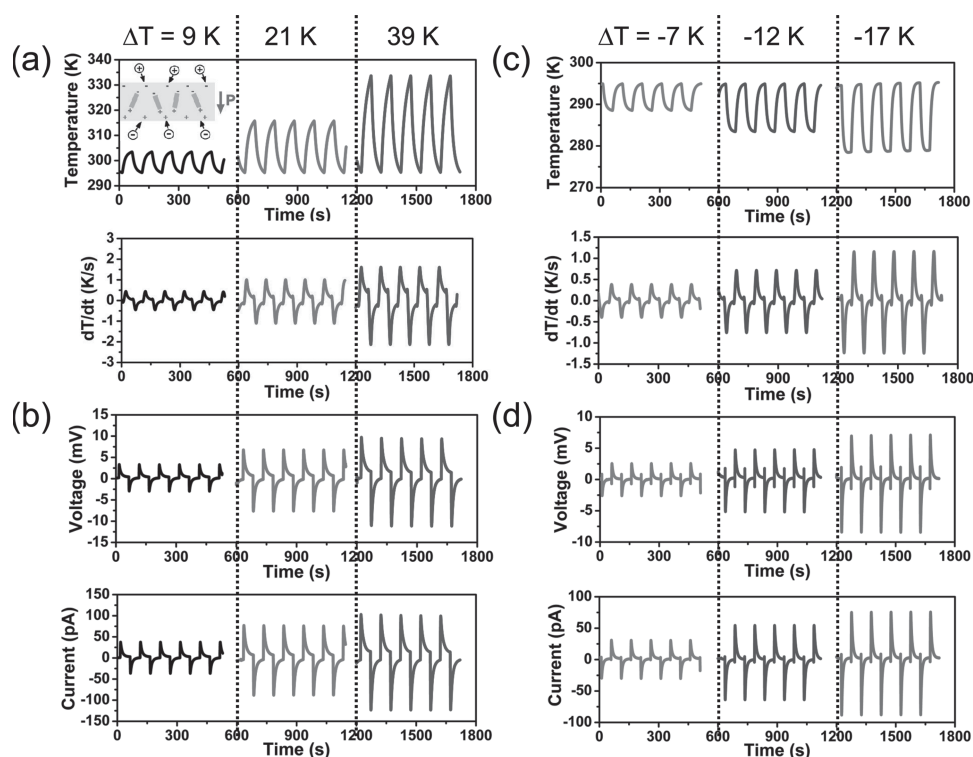


Figure 2. a) The cyclic change in the different heated temperatures in the nanogenerator and the corresponding differential curves. The inset shows a schematic of the negative electric dipoles in the nanogenerators. b) Measured open-circuit voltage and short-circuit current of the nanogenerator under the conditions in (a). c) The cyclic change in the different cooled temperatures in the nanogenerator and the corresponding differential curves. d) The open-circuit voltage and short-circuit current of the nanogenerator under the conditions in (c).

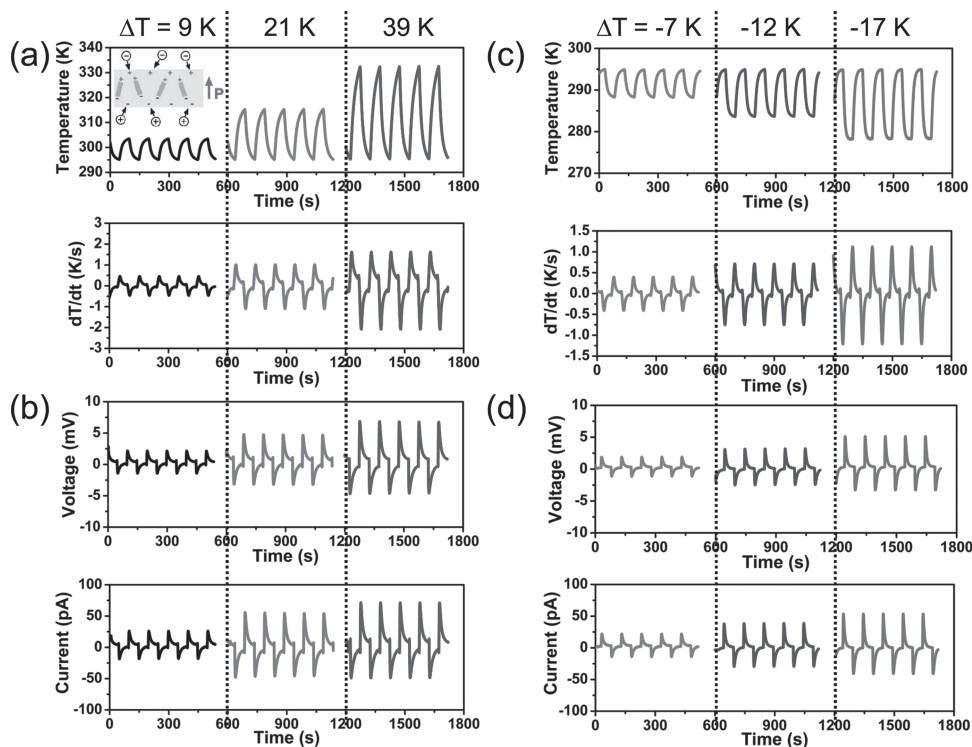


Figure 3. a) The cyclic change in the different heated temperatures in the nanogenerator and the corresponding differential curves. The inset shows a schematic of the positive electric dipoles in the nanogenerators. b) The open-circuit voltage and short-circuit current of the nanogenerator under the conditions in a. c) The cyclic change in the different cooled temperatures in the nanogenerator and the corresponding differential curves. d) The open-circuit voltage and short-circuit current of the nanogenerator under the conditions in (c).

enhanced or weakened when the two NGs were connected in parallel with the same polarities or opposite polarities, respectively. There results confirm that the observed output voltage/current was indeed generated by the KNbO_3 nanowires.

In order to understand the experimental results in Figure 2 and 3, we propose a mechanism for the pyroelectric NG with consideration of the minimization of the polarization energy and thermodynamics, as shown in Figure 4. Traditionally, since the internal electric dipoles of a ferroelectric material are coupled to the material lattices, anything that changes the material lattices will change the strength of the electric dipoles (the spontaneous polarization). It has been reported that the electric dipoles can rotate in ferroelectric $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ materials, because the material is made of multidomains.^[22] According to the principle of thermodynamics,^[23] the amplitude of the lattice thermal vibrations increases with temperature, resulting in enlarged vibrations of the internal electric dipoles of ferroelectric materials. The average axial vibrations of the electric dipoles have no contribution to the change in the spontaneous polarization. However, transverse wobbling of the electric dipoles around their equilibrium axis is possible, resulting in a change in the magnitude of the effective spontaneous polarization. The wobbling amplitude corresponds to the amplitude of lattice thermal vibrations.

The mechanism is based on the thermally induced random wobbling of the electric dipole around its equilibrium axis, the magnitude of which increases with increasing temperature. The spontaneous electric dipoles in KNbO_3 nanowires,

originating from Nb^{5+} ion movement in NbO_6 octahedra, can have six possible orientations along the $\langle 001 \rangle$ directions. In our fabricated NGs, the nanowires were randomly oriented inside the PDMS polymer. When a high positive electric field is applied to pole the structure, the electric dipoles in KNbO_3 nanowires tend to align along the electric-field direction from top (Ag) to bottom (ITO). Although some domains may still tilt from the electric-field direction, all of the domains should have electric dipole components along the electric-field direction. Due to thermal fluctuations under room temperature, the electric dipoles will randomly oscillate within a degree from their respective aligning axes (Figure 4a). The total average strength of the spontaneous polarization from the electric dipoles is a constant at a fixed temperature; thus, there is no output current of the NG (Figure 4a). If we apply a change in temperature in the NG from room temperature to a higher temperature, the increase in temperature will result in that the electric dipoles oscillate within a larger degree of spread around their respective aligning axes (Figure 4b); consequently, the total average spontaneous polarization is decreased due to the spread of the oscillation angles.^[12] The quantity of induced charges in the electrodes are thus reduced, resulting in a flow of electrons from the ITO to the Ag electrode, as shown in Figure 4b. If the NG is cooled instead of heated, the spontaneous polarization will be enhanced since the electric dipoles oscillate within a smaller degree of spread angles due to lower thermal activity (Figure 4c); thus, the total magnitude of the polarization is increased. Thus, the amount of induced charges in the

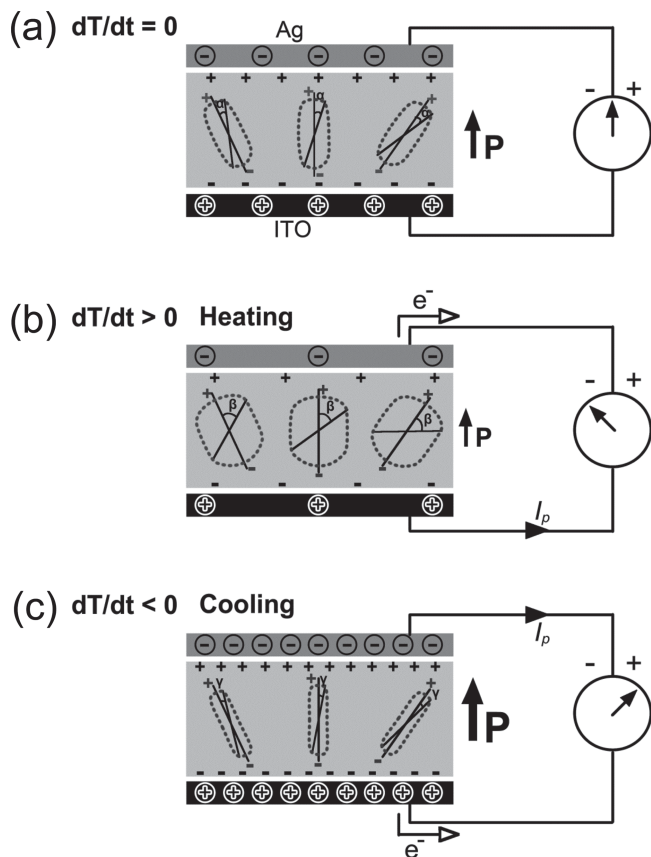


Figure 4. Proposed mechanism of the pyroelectric nanogenerator based on a composite structure of pyroelectric nanowires. a–c) Schematic diagrams of the pyroelectric nanogenerator with negative electric dipoles under room temperature (a), heated (b) and cooled (c) conditions. The angles marked in the diagrams represent the degrees to which the dipole would oscillate as driven by statistical thermal fluctuations. The larger the wobbling angle is, the smaller is the polarization.

electrodes are increased. In such a case, electrons will flow from the Ag to the ITO electrode, as shown in Figure 4c.

Alternatively, when a negative electric field is applied for the poling, the electric dipoles tend to align along the electric field direction from the bottom (ITO) to the top (Ag). For this case, due to the opposite direction of electric dipoles as compared with that in Figure 4a, the output signals will reverse in comparison to the above case, according to the explanation in Figure 4. The mechanism in Figure 4 is consistent with the experimental results in Figure 2 and 3.

The pyroelectric coefficient of the fabricated composite structure (the KNbO_3 nanowires and PDMS polymer in a volume ratio of 3:7) is about $0.8 \text{ nC/cm}^2\text{K}$, which is smaller than that of bulk KNbO_3 ($5 \text{ nC/cm}^2\text{K}$ at 300 K).^[16] This is due to the PDMS polymer in the NGs, since it has no pyroelectric effect. Although the addition of PDMS polymer in the NGs will decrease the total output, it can increase the flexibility of the NGs, which is important for developing flexible energy-harvesting devices.

We have also demonstrated the application of our NGs under sunlight illumination conditions, as shown in Figure 5. In Figure 5a, the temperature induced by sunlight illumination periodically changes from 295 to 298 K , resulting in that the output voltage and current peaks are about 2.5 mV and 25 pA (Figure 5b and 5c), respectively. Figure 5d shows the output current of a hybrid device based on a pyroelectric NG and a ZnO nanowire solar cell,^[10] where the pyroelectric NG is AC power and the solar cell is DC power. The structure of the hybrid device is such that the solar cell is on the top for sunlight illumination and the pyroelectric NG is at the bottom for heating/cooling. To avoid a heating effect from the sunlight on the pyroelectric NG, a thick Al_2O_3 substrate was placed between the solar cell and the pyroelectric NG. Both the cooled (the first one in Figure 5d) and heated (the second one in Figure 5d) NGs can work with the solar cell in separated and parallel modes. Our results demonstrate that the pyroelectric nanogenerators have potential as one of the important nanoenergies, that can be used in self-powered nanodevices and nanosystems.

Although the pyroelectric coefficient of bulk KNbO_3 ($>5 \text{ nC/cm}^2\text{K}$) is larger than that of poly(vinylidene fluoride) (PVDF) ($2.7 \text{ nC/cm}^2\text{K}$),^[16,24] the obtained pyroelectric coefficient of the KNbO_3 -PDMS composite structure ($0.8 \text{ nC/cm}^2\text{K}$) is smaller than that of PVDF. However, we can increase the concentration of the KNbO_3 nanowires in the composite structure to enhance the output of the NG, which could lead to a better performance than that of PVDF. A simple use of KNbO_3 nanowires can lead to a similar pyroelectric effect as for PVDF. Moreover, a high field (greater than 1200 kV/cm) is required to pole the PVDF materials,^[25] which is much larger than that required for KNbO_3 (150 kV/cm).^[26] There are several other merits for the KNbO_3 -nanowire/PDMS-composite-based NG. Firstly, the KNbO_3 nanowires do not contain any toxic elements, suggesting safe applications, like a lead-free self-powered nanosensor. Moreover, a massive production of KNbO_3 nanowires can be obtained by using a simple hydrothermal method, which can enable the fabrication of pyroelectric NGs at a large scale. Secondly, due to the ferroelectricity of KNbO_3 nanowires, the electric field can effectively pole random ferroelectric domains to one direction, which is important for the large-scale production of NGs in the future. Thirdly, the PDMS polymer may play the role of preventing the breakdown of the NGs in the poling process. The fabricated NGs are flexible, which is advantageous for more applications.

In summary, we report pyroelectric nanogenerators fabricated using a lead-free KNbO_3 -nanowire/PDMS-polymer composite for the first time. The output voltage/current of the fabricated nanogenerators can be modulated in a controlled manner due to the change of ferroelectric domains tuned by electric fields. The voltage/current outputs of the nanogenerators under heating and cooling conditions show an opposite change and can be enhanced by increasing the change in temperature. By using the nanogenerators, energy harvesting from sunlight induced heat, and hybrid nanogenerators with a solar cell were demonstrated, indicating that the pyroelectric nanogenerators may have extensive applications in self-powered nanodevices and nanosystems.

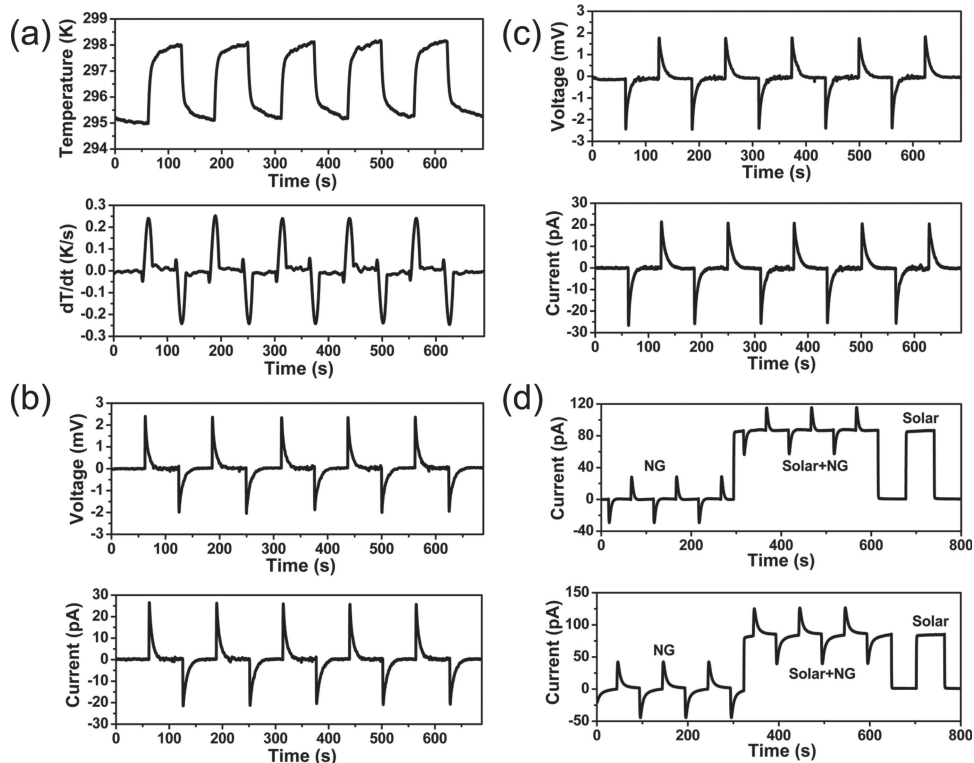


Figure 5. a) The cyclic change in the different heated temperatures in the nanogenerator from sunlight illumination and the corresponding differential curves. b,c) Measured open-circuit voltage and short-circuit current of the pyroelectric nanogenerator at forward connection (b) and reversed connection (c) to the measurement system, when it was subject to the repeated temperature change in (a). d) The output current of the hybrid nanogenerator based on the parallel P3HT/ZnO nanowire solar cell and pyroelectric nanogenerator under the repeated cooling (top) and heating (bottom) conditions.

Experimental Section

Fabrication of the Pyroelectric Nanogenerators: The KNbO_3 nanowires were synthesized by the hydrothermal method. 0.63 mol of KOH (35.3 g, 90%) was dissolved in the 50 mL of distilled water and then 1.24 mmol of Nb_2O_5 (0.33 g, 99.99%) was added into the KOH solution. Thoroughly stirred solutions were transferred to a stainless-steel autoclave with a 100 mL Teflon lining to undergo a hydrothermal reaction at 150 °C for 6 d. The obtained white powders were further annealed at 400 °C for 12 h. The annealed KNbO_3 nanowires were thoroughly mixed with polydimethylsiloxane (PDMS) with the volume ratio of 3:7. A KNbO_3 -PDMS composite film of about 200 μm was fabricated by a spin-coating technique. Ag and ITO served as the top and bottom electrodes, respectively. Note that the electric polarization of KNbO_3 film is almost saturated above 150 kV/cm.^[26] We applied an electric field of about 160 kV/cm for electric poling at room temperature.

Electrical Measurements: All of the electrical characterization measurements of the NGs were conducted after connecting the Ag and ITO layers as electrodes. A thermoelectric-based heater and cooler served to apply a periodic change in temperature to the NGs. A temperature sensor was used to detect the change in temperature in the NGs. The open-circuit voltage and the short-circuit current were measured via voltage and current preamplifiers (Stanford Research SR570 and SR560), respectively.

Supporting Information

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

Acknowledgements

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- [1] J. A. Paradiso, T. Starner, *IEEE Pervasive Computing* **2005**, *4*, 18.
- [2] S. Xu, Y. Qin, C. Xu, Y. G. Wei, R. Yang, Z. L. Wang, *Nat. Nanotechnol.* **2010**, *5*, 367.
- [3] Y. F. Hu, Y. Zhang, C. Xu, L. Lin, R. L. Snyder, Z. L. Wang, *Nano Lett.* **2011**, *11*, 2572.
- [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] R. S. Yang, Y. Qin, L. M. Dai, Z. L. Wang, *Nat. Nanotechnol.* **2009**, *4*, 34.
- [8] B. Tian, X. Zheng, T. J. Kempa, Y. Fang, N. Yu, G. Yu, J. Huang, C. M. Lieber, *Nature* **2007**, *449*, 885.
- [9] Y. Dong, B. Tian, T. Kempa, C. M. Lieber, *Nano Lett.* **2009**, *9*, 2183.
- [10] Y. Yang, W. Guo, Y. Zhang, Y. Ding, X. Wang, Z. L. Wang, *Nano Lett.* **2011**, *11*, 4812.

- [11] G. Sebald, D. Guyomar, A. Agbossou, *Smart Mater. Struct.* **2009**, *18*, 125006.
- [12] S. B. Lang, *Phys. Today* **2005**, *58*, 31.
- [13] J. D. Zook, S. T. Liu, *J. Appl. Phys.* **1978**, *49*, 4604.
- [14] C. Ye, T. Tamagawa, D. L. Polla, *J. Appl. Phys.* **1991**, *70*, 5538.
- [15] A. N. Morozovska, E. A. Eliseev, G. S. Svechnikov, S. V. Kalinin, *J. Appl. Phys.* **2010**, *108*, 042009.
- [16] P. Günter, *J. Appl. Phys.* **1977**, *48*, 3475.
- [17] L. Liang, Y. L. Li, S. Y. Hu, L. Chen, G. Lu, *J. Appl. Phys.* **2010**, *108*, 094111.
- [18] K. Yamanouchi, H. Odagawa, T. Kojima, A. Onoe, A. Yoshida, K. Chikuma, *Electron. Lett.* **1998**, *34*, 702.
- [19] L. E. Cross, *Nature* **2004**, *432*, 24.
- [20] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, *Nature* **2004**, *432*, 84.
- [21] S. B. Lang, S. A. M. Tofail, A. A. Gandhi, M. Gregor, C. Wolf-Brandstetter, J. Kost, S. Bauer, M. Krause, *Appl. Phys. Lett.* **2011**, *98*, 123703.
- [22] C.-L. Jia, K. W. Urban, M. Alexe, D. Hesse, I. Vrejoiu, *Science* **2011**, *331*, 1420.
- [23] J. A. Beattie, I. Oppenheim, *Principles of Thermodynamics*, Elsevier Scientific Publishing Company, Amsterdam **1979**.
- [24] R. W. Whatmore, *Rep. Prog. Phys.* **1986**, *49*, 1335.
- [25] T. Furukawa, M. Date, E. Fukada, *J. Appl. Phys.* **1980**, *51*, 1135.
- [26] T. Shiraishi, H. Einishi, S. Yasui, M. Ishikawa, T. Hasegawa, M. Kurosawa, H. Uchida, Y. Sakashita, H. Funakubo, *Jpn. J. Appl. Phys.* **2011**, *50*, 09ND11.