

1.6 V Nanogenerator for Mechanical Energy Harvesting Using PZT Nanofibers

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ABSTRACT Energy harvesting technologies that are engineered to miniature sizes, while still increasing the power delivered to wireless electronics,^{1,2} portable devices, stretchable electronics,³ and implantable biosensors,^{4,5} are strongly desired. Piezoelectric nanowire- and nanofiber-based generators have potential uses for powering such devices through a conversion of mechanical energy into electrical energy.⁶ However, the piezoelectric voltage constant of the semiconductor piezoelectric nanowires in the recently reported piezoelectric nanogenerators^{7–12} is lower than that of lead zirconate titanate (PZT) nanomaterials. Here we report a piezoelectric nanogenerator based on PZT nanofibers. The PZT nanofibers, with a diameter and length of approximately 60 nm and 500 μm , were aligned on interdigitated electrodes of platinum fine wires and packaged using a soft polymer on a silicon substrate. The measured output voltage and power under periodic stress application to the soft polymer was 1.63 V and 0.03 μW , respectively.

KEYWORDS Lead zirconate titanate (PZT), piezoelectric nanogenerator, nanofiber, electrospinning, mechanical energy, bio-MEMS.

Recently, the piezoelectric properties of several nanowires, nanofibers, and nanorods from zinc oxide,⁹ lead zirconate titanate (PZT),¹³ cadmium sulfide,¹⁴ barium titanate,¹⁵ and gallium nitride¹⁶ have been successfully demonstrated. These one-dimensional piezoelectric nanostructures convert mechanical energy into electrical energy. As examples, various nanogenerators based on ZnO nanowires^{9–12} and fine fibers^{7,8} proposed by Wang et al. have been successfully demonstrated for potential applications in converting low-frequency vibration and biomechanical energy into electrical energy. However, the piezoelectric voltage constant of the piezoelectric nanomaterials and output voltage and power of the nanogenerators still needs further improving for practical applications. Furthermore, the fabrication method of the semiconductor piezoelectric nanomaterials could pose some drawbacks that might affect the performance of the nanogenerator. It is difficult to grow single crystal nanowires longer than 50 μm with diameters less than 100 nm. The nanogenerator fabrication method and the output voltage of the nanogenerator could be significantly restricted by the short length of nanowires.

In order to overcome some of the drawbacks of the existing devices and to demonstrate the possibility of energy harvesting using PZT nanomaterials, a highly efficient nanogenerator based on laterally aligned PZT nanofibers on interdigitated electrodes was created and reported herein. PZT is a widely used piezoelectric ceramic material with high piezoelectric voltage and dielectric constants, which are ideal

properties of active materials for mechanical to electrical energy conversion. For a given volume under the same energy input, PZT can generate much higher voltage and power outputs than other semiconductor types of piezoelectric materials. As a ceramic material, bulk and thin film PZT structures are extremely fragile, especially when subjected to alternating loads. Matters are made worse since thin film and microfiber¹⁷ structures are typically sensitive to high-frequency vibration. However, unlike bulk, thin films or microfibers, PZT nanofibers prepared by an electrospinning process exhibit an extremely high piezoelectric voltage constant (g_{33} , 0.079 Vm/N), high bending flexibility, and high mechanical strength, which have been demonstrated in ref 13. Therefore, utilizing PZT nanofibers in energy harvesting technology could provide a new way to make a portable, flexible, highly efficient device with a low-frequency vibration nature, since the nanofibers could be woven into fabrics and made into composites.

The nanogenerator device fabrication began by electrospinning¹⁸ PZT nanofibers and depositing them on the preprepared interdigitated electrodes of platinum fine wire (diameter of 50 μm) arrays, which were assembled on a silicon substrate (Figure 1a). The diameters of PZT nanofibers were controlled to be around 60 nm (Figure 1b) by varying the concentration of poly vinyl pyrrolidone (PVP) in the modified sol–gel solution. The PZT nanofibers obtained were continuous, while the distance between two adjacent electrodes was 500 μm as designed. A pure perovskite phase was obtained by annealing at 650 $^{\circ}\text{C}$ for about 25 min. Subsequently, a soft and polymer (polydimethylsiloxane, PDMS) was applied on top of the PZT nanofibers (Figure 1c). The interdigitated electrodes of fine platinum wires were

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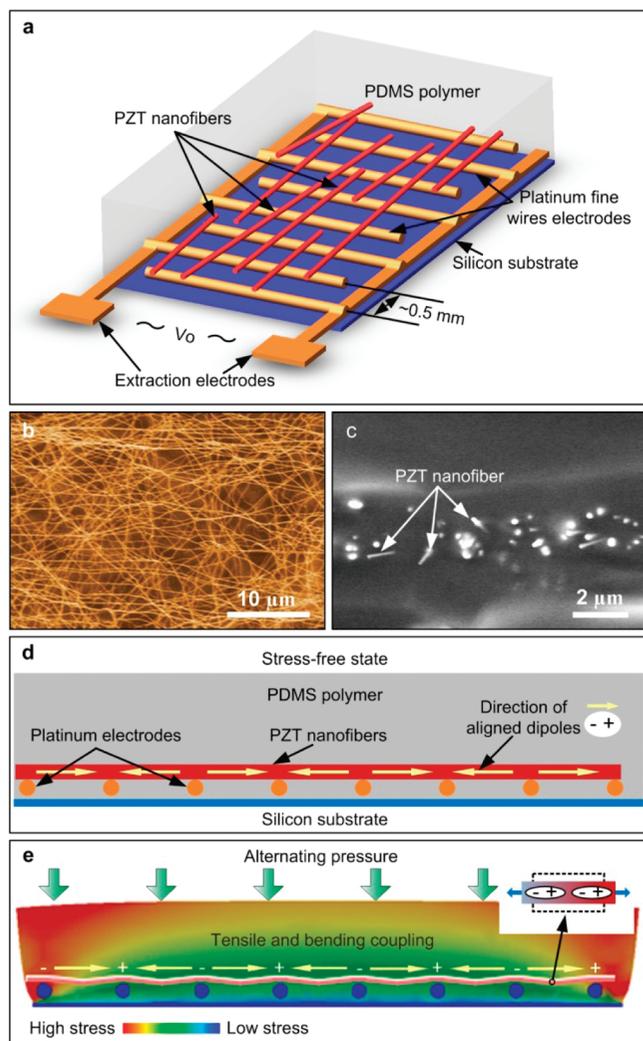


FIGURE 1. Concept and power generation mechanism of the PZT nanofiber generator. (a) Schematic view of the PZT nanofiber generator. (b) Scanning electron microscopy (SEM) image of the PZT nanofiber mat across the interdigitated electrodes. (c) Cross-sectional SEM image of the PZT nanofibers in the PDMS matrix. (d) Cross-sectional view of the polled PZT nanofiber in the generator. (e) Schematic view explaining the power output mechanism of the PZT nanofibers working in the longitudinal mode. The color presents the stress level in PDMS due to the application of pressure on the top surface.

connected by extraction electrodes to transport harvested electrons to an external circuit (see Supporting Information, Figure S1). Finally, the PZT nanofibers were polled by applying an electric field of $4 \text{ V}/\mu\text{m}$ across the electrodes (Figure 1d) at a temperature of above $140 \text{ }^\circ\text{C}$ for about 24 h. The nanogenerator can be released from the silicon substrate or prepared on flexible substrates, depending on the requirements of the applications for energy harvesting.

The nanogenerator device and power generation mechanism are illustrated in Figure 1d–e in which PZT nanofibers were working in the longitudinal mode with an alternating pressure applied on the top surface of the nanogenerator. The applied pressure was transferred to the PZT nanofibers

through the PDMS matrix and resulted in charge generation due to the combined tensile and bending stresses in the PZT nanofibers. A voltage difference between the two adjacent electrodes was thereby induced due to this separation of charge. The interdigitated electrodes could enhance the power output of the nanogenerator. The piezoelectric nanofibers between each pair of adjacent electrodes served as unit cells, and each cell was connected in parallel. By controlling the electric field distribution during the electrospinning process (see Supporting Information, Figure S2), PZT nanofibers were laterally aligned on the interdigitated electrodes. The distance between the anodes and the cathodes was about 0.5 mm, as shown in Figure 1a. Electrons generated in the PZT nanofibers could transfer through the electrodes when the PZT nanofibers were subjected to external stresses. Compliant PDMS was able to cover the entire PZT nanofiber/electrode structure due to the placement of the PZT nanofibers in a levitated position above the silicon substrate. The stress in the longitudinal direction, caused by the Poisson's ratio of the composites, could be directly transferred to the PZT nanofibers when there was a stress applied on the polymer matrix in the vertical direction. To avoid excessive stresses on the PZT nanofibers and to minimize the risk of damaging the electrical connection of the electrodes, the silicon substrate was packaged along with the nanogenerator as a rigid mechanical backing. This support could potentially be replaced by a flexible plastic backing for different applications. The final cured thickness of the PDMS polymer matrix was about 2 mm.

The potential generated from the PZT nanofibers between the interdigitated electrodes is given by¹³

$$\Delta V = \int_0^l g_{33} \sigma(l) dl \quad (1)$$

where l is the length of the nanofibers across two adjacent electrodes, $\sigma(l)$ is the stress function along the axial direction of the nanofiber, and g_{33} is the piezoelectric voltage constant. By considering only the stress in the longitudinal direction:

$$\sigma(l) = E_p \left(\frac{\sigma_{xx}}{E_{11}} - \frac{\sigma_{yy}}{E_{11}} \cdot \nu - \frac{\sigma_{zz}}{E_{11}} \cdot \nu \right) \quad (2)$$

(see Supporting Information), where E_p is the modulus of PZT nanofiber, E_{11} is the longitudinal modulus of the composites, ν is the Poisson's ratio of the matrix, and σ_{xx} , σ_{yy} , and σ_{zz} are the stresses along the three directions. Thus, the output voltage can be written as

$$\Delta V = \int_0^l g_{33} \cdot E_p \left(\frac{\sigma_{xx}}{E_{11}} - \frac{\sigma_{yy}}{E_{11}} \cdot \nu - \frac{\sigma_{zz}}{E_{11}} \cdot \nu \right) dl \quad (3)$$

For a given applied load or impact energy, the maximum output voltage is primarily determined by the piezoelectric voltage constant. From our previous study,¹³ the piezoelectric voltage constant of PZT nanofiber is roughly $0.079 \text{ Vm}/\text{N}$, which is much higher than that of the PZT bulk ($0.025 \text{ Vm}/\text{N}$) or the PZT microfiber composite value ($0.059 \text{ Vm}/\text{N}$).¹⁹ By inspection, the significantly larger g_{33} and l/A ratio

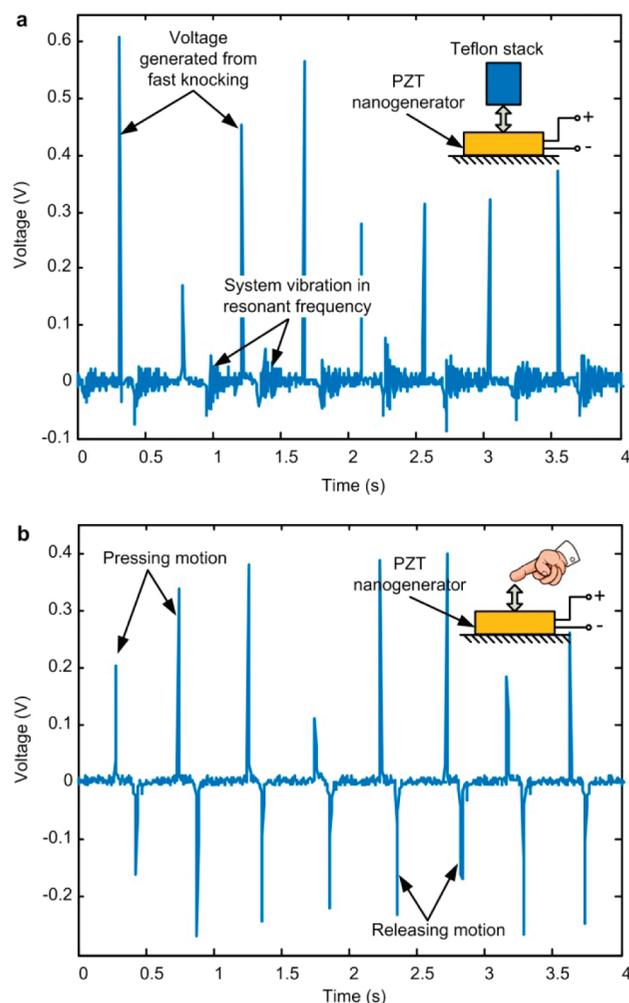


FIGURE 2. Measurements of output voltage from PZT nanofiber generator. (a) Voltage output measured when a small Teflon stack was used to impart an impulsive load on the top of the PZT nanofiber generator. The inset in (a) shows the schematic of a Teflon stack tapping on the nanogenerator. (b) Voltage output measured when using a finger to apply a dynamic load on the top of the generator. The inset in (b) shows the schematic of a finger applying the dynamic load.

of the nanofiber generator should result in a much higher voltage output compared to that of the PZT microfibers¹⁷ under the same loading condition. For the same reason, PZT nanofibers could also be used as an ultrahigh sensitivity force/vibration sensor.

Two applications of this nanogenerator have been demonstrated. In the first application, output voltage from the PZT nanofiber generator was measured when it underwent an impulsive loading, applied by tapping the top of the generator with a small Teflon stack. As shown in Figure 2a, the generated voltage, which was induced by piezopotential driven transient flow of electrons under the external load,²⁰ reached 600 mV when a larger impact was applied on the nanogenerator by the periodic knocking. The higher the impact energy applied on the surface, the higher the output voltage generated by the device. The damping effect of the

soft polymer matrix on the resonant frequency was also observed during the energy harvesting process. In the second application, fingers were used to apply a periodic dynamic load on the top of the nanogenerator during which the positive and negative voltage outputs were observed, see Figure 2b. The negative voltage distribution was generated due to the reverse-flowing carriers when the external load was removed and the piezopotential vanished. The highest output voltage recorded during the test was 1.63 V (see Supporting Information, Figure S4). The amplitudes of the voltage outputs depended on how much pressure was applied on the nanogenerator surface.

The characteristics of the nanogenerator as a potential power supply were further investigated by measuring generated voltage versus strain in the polymer matrix under varying dynamic load frequencies and power output versus load resistance, both using a dynamic mechanical analyzer (DMA). (The experimental setup is shown in Supporting Information, Figure S5) The voltage generated by applying a harmonic force at the frequency of 250 rad/s (~ 39.8 Hz) and a specified maximum strain of 12% applied on the polymer matrix is shown in Figure 3a. The positive and negative voltages were generated due to the sinusoidal load oscillations applied by the DMA (Figure 3a). The peak to peak open circuit voltage V_{p-p} increased as the maximum strain applied increased. The maximum V_{p-p} was 1420 mV under a maximum applied strain along the PZT nanofibers of $\sim 7.5 \times 10^{-5}$ % (established from mathematical and finite element method models, see Supporting Information) at 250 rad/s as shown in Figure 3b. The V_{p-p} versus various excitation frequencies under a maximum applied strain on the PDMS surface of 2.25% is illustrated in Figure 3c. The highest output voltage of 62 mV occurred at a frequency of 220 rad/s (~ 35 Hz), corresponding to the lowest resonant frequency of the entire architecture. Voltage outputs were also recorded when varying the load resistances from 0.1 to 10 M Ω under a maximum specified strain of 10% applied on PDMS surface and a harmonic load frequency of 250 rad/s, see Figure 3d. The power delivered to the load could be estimated from

$$P_L = \frac{1}{T} \int \frac{V_o(t)^2}{R_L} dt \quad (4)$$

where $V_o(t)$ is the real-time voltage, R_L is the load resistance, and T is the period of load application. The maximum measured output power reached 0.03 μ W with a load resistance of 6 M Ω , as shown in Figure 3d.

In order to eliminate the influence of the bioelectric field of the human body and the electromagnetic interference from the testing equipment, a free vibration test using the PZT nanogenerator as a damper was conducted (Figure 4a). The output voltage from the nanogenerator was measured when a Teflon cantilever, placed on top of the nanogenerator, was subjected to free vibration, as shown in Figure 4b. The damping ratio ζ and the natural frequency of this system

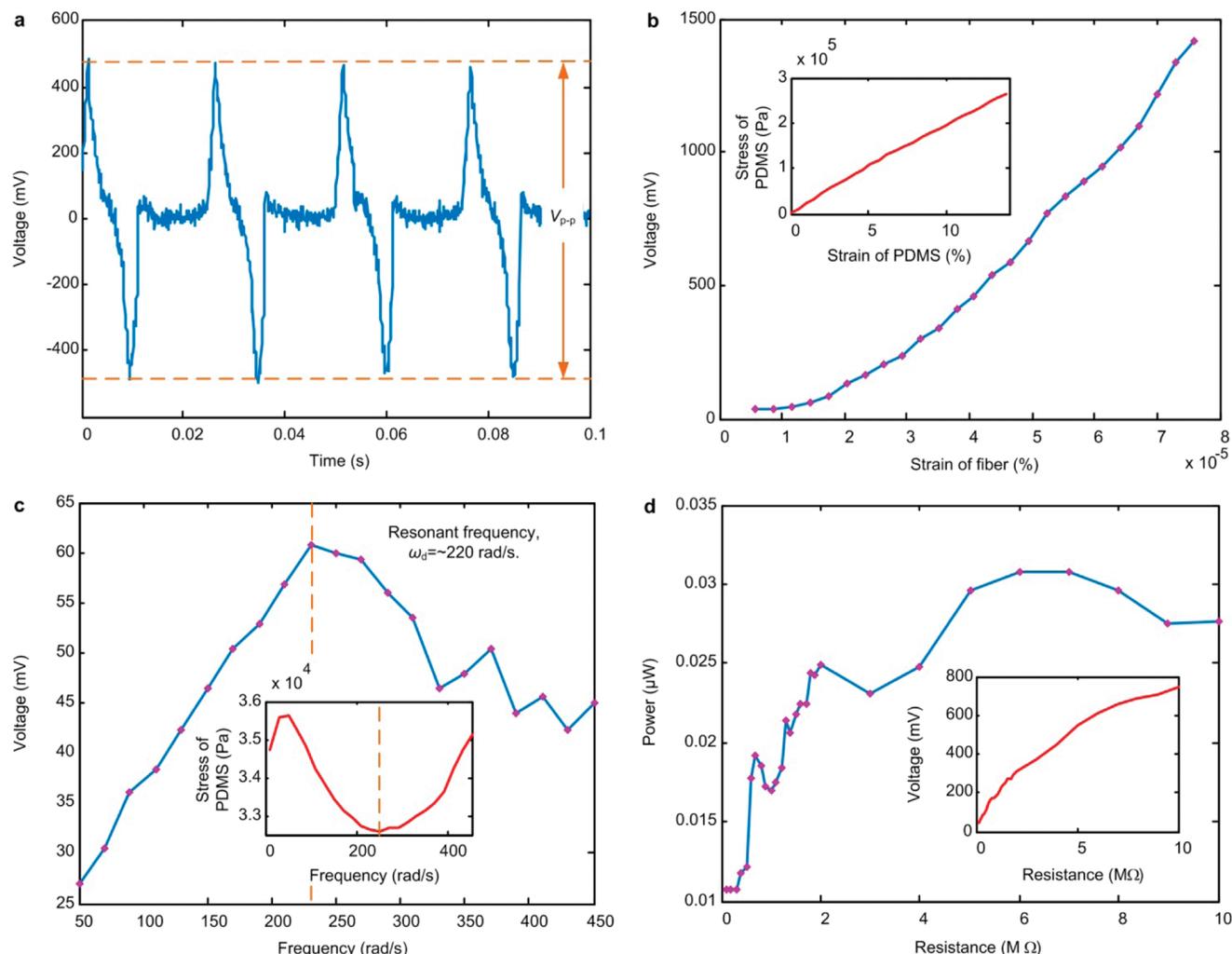


FIGURE 3. Voltage generation properties of PZT nanofiber generator tested via DMA. (a) Voltage output when a harmonic force at the frequency of 250 rad/s (~ 39.8 Hz) and a maximum strain of 12% were applied on the PDMS surface. (b) The open circuit peak to peak voltage output versus strain of PZT nanofiber at the frequency of 250 rad/s (~ 39.8 Hz). The inset in (b) shows the stress of composites versus strain applied between the top and the bottom PDMS surface. (c) The open circuit peak to peak voltage output versus frequencies of the harmonic forces at the maximum strain of 2.25% applied on PDMS. The inset in (c) shows the stress of composites versus frequency applied on the nanogenerator. (d) The power delivered to the load resistors versus the load resistance. The inset in (d) shows the voltage output versus the load resistance.

were determined to be 0.064 and the 49.9 rad/s (~ 7.9 Hz), respectively. The output voltage from a dummy block without PZT nanofibers or any active materials in it was also measured using the same setup. The measured result revealed that the amplitude of noise signal is only at about 10 mV level. This confirmed that the power output from the PZT nanogenerator was in fact the energy harvested from mechanical vibration.

In summary, we have demonstrated a new piezoelectric nanogenerator based on lead zirconate titanate (PZT) nanofibers with a diameter and length of approximately 60 nm and 500 μm , respectively. This nanogenerator presents several advantages over other nanogenerators reported recently.^{7–12} The peak output voltage from this nanogenerator was 1.63 V, and the output power was 0.03 μW with a load resistance of 6 $\text{M}\Omega$. The piezoelectric voltage constant

and dielectric constant of PZT nanofibers were much higher than those of the semiconductor type of piezoelectric nanowires and nanofibers, making this material ideal for nanogenerator or nanobattery applications. The flexible PZT nanofibers were embedded in soft polydimethylsiloxane (PDMS) polymer matrix, which helped prevent the PZT nanofibers from being damaged, thereby extending the life cycle of the nanogenerator. The simple fabrication and assembly process would allow for the facile mass production of this type of nanogenerator.

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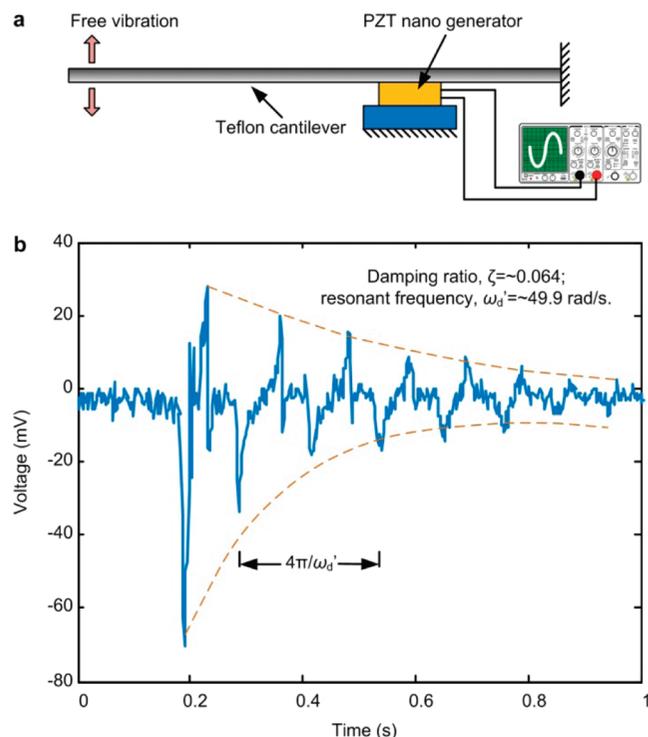


FIGURE 4. Energy harvested from the free vibration of a Teflon cantilever. (a) Schematic of the experimental setup. (b) The open circuit voltage output when the cantilever was under free vibration.

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Supporting Information Available. The fabrication process figure, nanofiber alignment by controlling the electric field during the electrospinning figure, optical microscope

image of PZT nanofibers aligned on the platinum electrode and output voltage during tests figures. Details about the establishment of the strain along the PZT nanofibers using mathematical and finite element method. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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