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Zhong Lin Wang, Xudong Wang, Jinhui Song, Jin Liu, and Yifan Gao

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A novel approach converts nanoscale mechanical energy into electric energy for self-powering nanodevices.

Zhong Lin Wang, Xudong Wang, Jinhui Song, Jin Liu, and Yifan Gao
Georgia Institute of Technology

Although nanodevices fabricated using nanomaterials such as nanotubes or nanowires offer low power consumption, powering them can still be challenging.[1–3] Adding a battery could sufficiently increase their size to inhibit their application. Developing miniature power packages and self-powering methods will be key to their use in a variety of applications, including those for wireless sensing; in-vivo, real-time, and implantable biological devices; environmental monitoring; and personal electronics. Consequently, researchers are developing innovative nanotechnologies to convert various forms of energy (such as solar energy[4]) into electric energy for low-power nanodevices.

In our own work, we've used piezoelectric zinc-oxide nanowire (ZnO NW) arrays to demonstrate a novel approach for converting nanoscale mechanical energy into electric energy.[5–7] Here, we review the fundamental principle behind the nanogenerator, present an approach for improving its performance, and discuss some of the challenges we face in pushing this technology to reach its potential.

The nanowire nanogenerator

The nanogenerator relies on some external disturbance, such as a vibration or sonic wave, bending aligned NW arrays. In theory, a voltage drop occurs in the NW's cross section when the NW bends laterally, resulting in positive voltage on the tensile side and negative voltage on the compressive side.[5]

Using small-deflection approximation, we applied the perturbation theory to calculate the potential piezoelectricity distribution in a NW when a lateral force pushes its tip.[8]

Calculating piezoelectric potential

Our calculation shows that the NW's piezoelectric potential doesn't depend on the z-coordinate along the NW except when close to the two ends. The magnitude of piezoelectric potential for a NW that's 50 nanometers in diameter and 600 nm long is approximately 0.4 volts under a lateral deflection force of 80 nanonewtons (see figure 1). The maximum potential at the NW's surface is directly proportional to the NW's lateral displacement and inversely proportional to the NW's length-to-diameter aspect ratio. The maximum potential voltage (V) at the NW's surface at the tensile (T) and compressive (C) sides is

$$V_{\max}^{(T,C)} = \pm\frac{1}{\pi}\frac{1}{\kappa_0+\kappa_\perp}\frac{f_y}{E}\left[e_{33}-2(1+\nu)e_{15}-2\nu e_{31}\right]\frac{1}{a} \quad (1)$$

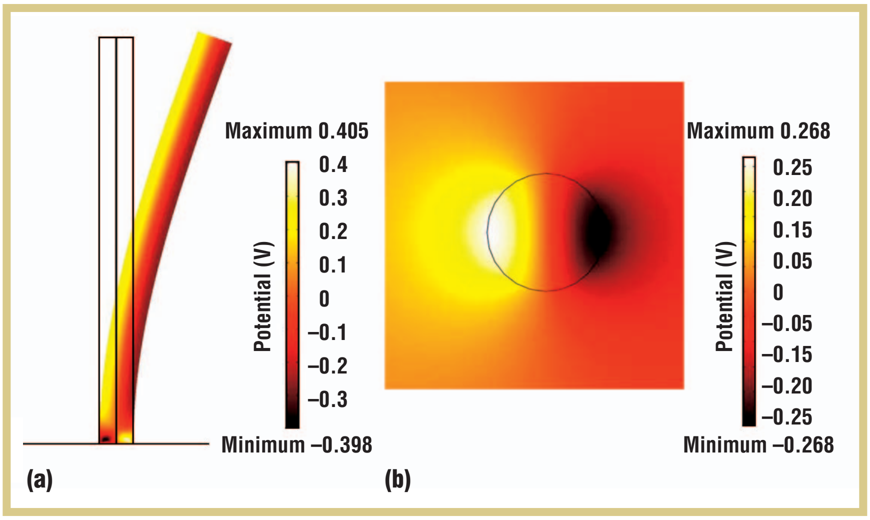


Figure 1. Potential distribution for a zinc-oxide nanowire (ZnO NW) that's 50 nanometers in diameter and 600 nm long at a lateral bending force of 80 nanonewtons: (a) side and (b) top cross-sectional (at z0 = 300 nm) output of the piezoelectric potential in the NW given by finite-element calculation.

where f_y is the transverse force for deflecting the NW; κ_0 is the permittivity in vacuum; $\kappa_{11} = \kappa_{22} = \kappa_\perp$ is the dielectric constant; e_{31}, e_{33}, and e_{15} are the piezoelectric coefficients; ν is the Poisson ratio; and a is the NW's radius.

We can restate equation 1 in terms of the NW's maximum deflection at the tip as

$$V_{\max}^{(\mathrm{T,C})} = \pm\frac{3}{4(\kappa_0+\kappa_\perp)}\left[e_{33}-2(1+\nu)e_{15}-2\nu e_{31}\right]\frac{a^3}{l^3}\nu_{\max} \qquad (2)$$

where ν_{max} is the NW tip's maximum deflection and l is the NW's length. This means that the electrostatic potential directly relates to the NW's aspect ratio instead of its dimensionality. For a NW with a fixed aspect ratio, the piezoelectric potential is proportional to the maximum deflection at the tip.

Figure 2 presents the mechanism for creating and separating the charges through a NW. For a vertical and straight ZnO NW (figure 2a), the NW's deflection by an atomic force microscope (AFM) tip creates a strain field that stretches the outer surface and compresses the inner surface (figure 2b). As a result, a piezoelectric potential builds across the NW, making the stretched side positive and the compressed side negative (figure 2c) if the electrode at the NW's base is grounded. The relative displacement of the Zn^{2+} cations with respect to the O^{2-} anions—caused by the piezoelectric effect in the wurtzite crystal structure—creates this potential. Consequently, these ionic charges can't freely move or recombine without releasing the strain. The potential difference is maintained as long as the deformation is in place and no foreign free charges (such as from the metal contacts) are injected.

We now consider the charge-accumulation and -releasing processes. The first step is a charge-accumulation process, which occurs when the AFM conductive tip that induces the deformation is in contact with the stretched surface of positive potential V^T (see figure 3a). The platinum metal tip has a potential of nearly zero, $V_m = 0$, so the metal-tip –ZnO interface is negatively biased for $\Delta V = V_m - V^T < 0$. Considering the as-synthesized (that is, synthesized without any modifications) ZnO NWs' n-type (negative charge) semiconductor characteristic, the platinum –ZnO semiconductor interface is, in this case, a reverse-biased Schottky diode (see figure 3a), and little current flows across the interface. (A Schottky diode is like a one-way gate that only allows a current to flow from the metal into the semiconductor.)

The next step is the charge-releasing process. When the AFM tip is in contact with the NW's compressed side (figure 3b), the metal-tip –ZnO interface is positively biased for $\Delta V = V_m - V^C > 0$. In this case, the metal semiconductor interface is a positively biased Schottky diode, and it produces a sudden increase in the output electric current. The current is the result of a potential ΔV-driven flow of electrons from the semiconductor ZnO NW to the metal tip. The flow of the free electrons from the loop through the NW to the tip will neutralize the ionic charges distributed in the volume of the NW, thus reducing the magnitudes of the potential V^C and V^T.

Realizing piezoelectric potential

We designed a set of experiments to prove the proposed mechanism. We used an AFM to mechanically manipulate a single ZnO wire. We selected a long ZnO wire that was large enough to see under an optical microscope, and we used silver paste to affix one end of the ZnO wire to a silicon substrate and left the other end free. The substrate was intrinsic silicon, so its conductivity was rather poor. A small distance between the wire and the substrate (except at the affixed side) eliminated friction (see figure 4).

We recorded both the topography (the scanner's feedback signal) and corresponding output-voltage images across a load simultaneously with the AFM tip's movement across the wire. The topography image reflects the change in normal force perpendicular to the substrate, which shows a bump only when the tip scans over the wire. We continuously monitored the out-

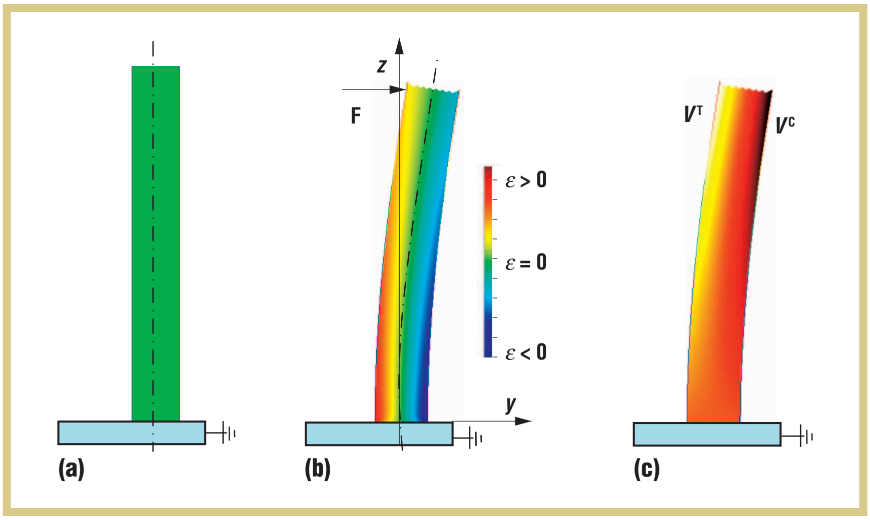


Figure 2. Creating and separating charges through a NW: (a) A schematic depiction of a wire; (b) longitudinal strain εz distribution in the wire after being deflected by an atomic force microscope (ATM) tip from the side; and (c) potential distribution in the wire as a result of piezoelectric effect.

put voltage between the conductive tip and the ground as the tip scanned over the wire. We didn't apply any external voltage during the experiment. We captured the entire experimental process and output images on video, so we could visualize how this process generates electricity.

We captured the topography image regardless of whether the tip passed over the wire, because it was a representation of the normal force that the cantilever received. When the tip pushed the wire but didn't go over and across it (see the flat output signal in the topography image in figure 5a), no voltage output was produced. This indicates that the stretched side didn't produce a piezoelectric discharge event. Once the tip went over the wire and touched the compressed side, as indicated by a peak in the topography image, we observed a sharp voltage output peak (figure 5b).

By analyzing the positions of the peaks observed in the topography image and the output voltage image, we noticed that the discharge occurred after the tip nearly finished crossing the wire. This clearly indicates that the compressed side produced the negative piezoelectric discharge voltage.

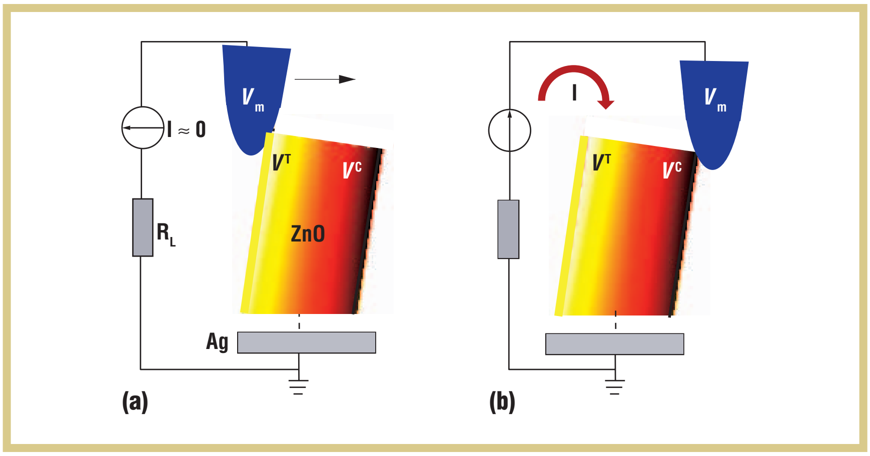


Figure 3. Accumulating and outputting charges through a NW. Metal and semiconductor contacts between the AFM tip and the semiconductor ZnO wire at two reversed local contact potentials (positive and negative), showing (a) reverse and (b) forward-biased Schottky rectifying behavior.

An innovative design

Although the AFM-based approach has been useful in exploring the principle of the nanogenerator and its potential for technological applications, we needed an innovative design to drastically improve the nanogenerator's performance.

First, we had to stop using the AFM

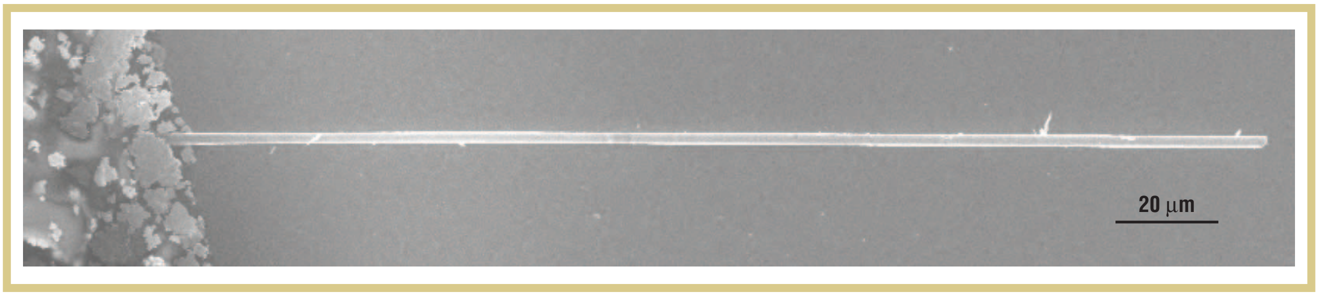


Figure 4. Scanning Electron Microscopy images of a ZnO wire with one end affixed by silver paste onto a silicon substrate and the other end free.

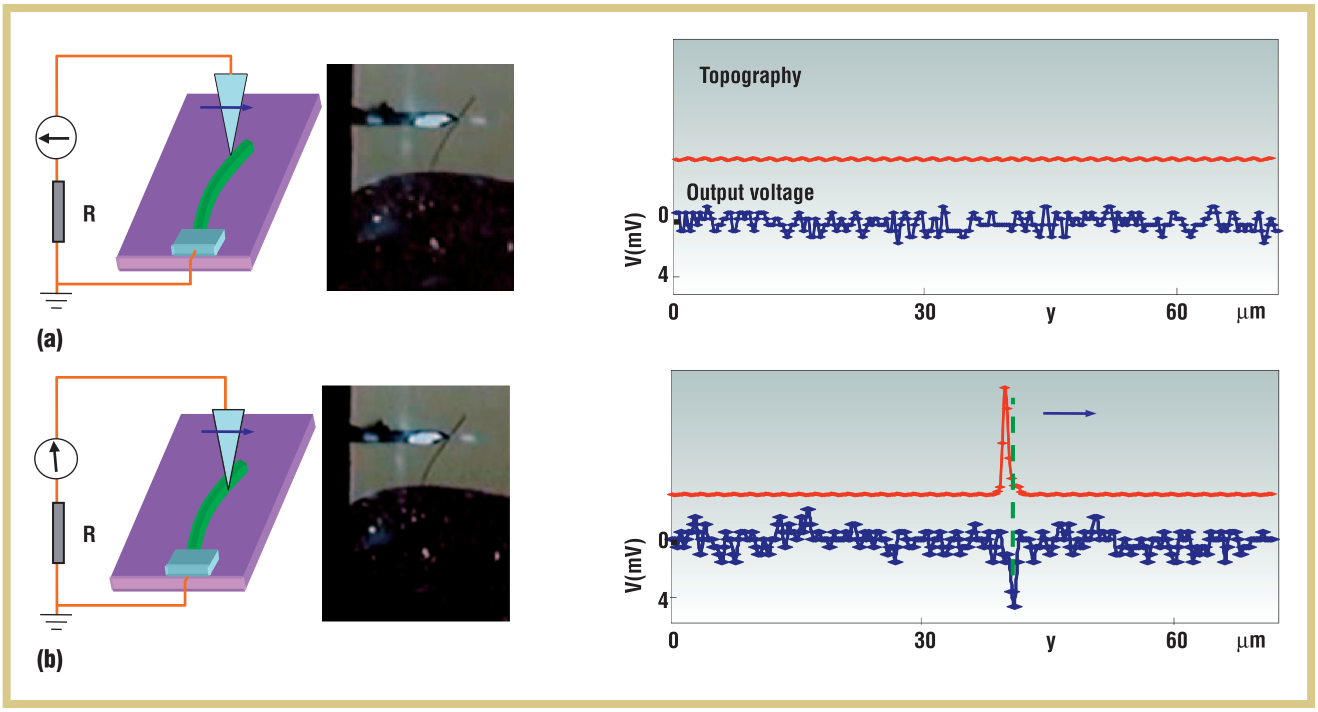


Figure 5. In-situ observation of converting mechanical energy into electric energy by a piezoelectric ZnO wire, shown via two characteristic snapshots and the corresponding topography and output voltage images. (a) The AFM tip pushes the wire toward the right side but doesn't go above and across its width, which the topography image indicates. We didn't detect any output voltage. (b) The AFM tip pushes the wire toward the right side and goes above and across its width, as the peak in the topography image indicates. The output voltage image showed a sharp negative peak. There is a delay in the output voltage peak in reference to the normal force image (the peak in the topography image). "Y" represents the relative position of the scanning tip perpendicular to the wire.

to mechanically deform the NWs, so we could generate power using an adaptable, mobile, and cost-effective approach. Second, we needed all the NWs to generate electricity simultaneously and continuously, so we could effectively collect and output all of the electricity. Finally, the energy to be converted into electricity had to be provided in the form of waves or vibrations from the environment, so the nanogenerator could operate independently and wirelessly.

A wave- or vibration-driven nanogenerator

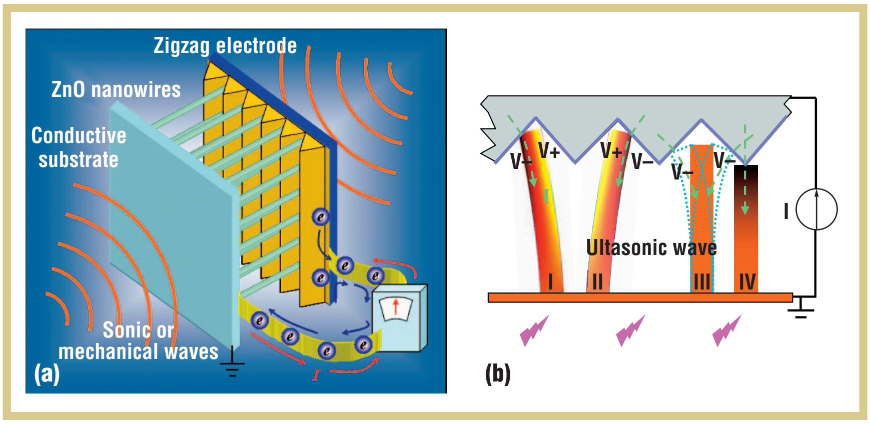
Figure 6a schematically shows our experimental setup,[9] in which a zigzag silicon electrode coated with platinum covers an array of aligned ZnO NWs. The platinum coating isn't only for enhancing the electrode's conductivity but also for creating a Schottky diode at the interface with ZnO. Then, we placed the electrode above the NW arrays, manipulated it from a controlled distance, and carefully packaged it to separate the electrode from the NWs.

The design relies on a unique coupling between the aligned ZnO NWs' piezoelectric and semiconducting properties. The asymmetric piezoelectric potential across the width of a ZnO NW and the Schottky contact between the metal electrode and the NW are the two key processes for creating, separating, preserving and accumulating, and outputting the charges.

We designed a top electrode to achieve the coupling process and play the AFM tip's role, and its zigzag trenches act as an array of aligned AFM tips. When subjected to the excitation of an ultrasonic wave, the zigzag electrode can move down and push the NW. This leads to a lateral bending, which creates a strain field across the NW's width, so the NW's outer surface is in tensile strain and its inner surface in compressive strain. When the electrode contacts the NW's stretched surface, which has a positive piezoelectric potential, the platinum metal –ZnO semiconductor interface is a reversely biased Schottky diode, resulting in little current flowing across the interface (see figure 6b). This process creates, separates, and preserves and accumulates charges.

If we further push the electrode, the bent NW will reach the other side of the zigzag electrode's adjacent tooth. In such a case, the electrode is also in contact with the NW's compressed side, where the metal-semiconductor interface is a forward-biased Schottky barrier, resulting in a sudden increase in the output electric current flowing from the

Figure 6. (a) Schematic diagram showing the direct current nanogenerator built using aligned ZnO NW arrays with a zigzag top electrode. An ultrasonic wave or mechanical vibration drives the nanogenerator, and the output current is continuous. (b) A schematic illustration of the zigzag electrode and its contact with the various NWs configurations and the resulting current.



top electrode into the NW. This is the discharge process. This design works as long as there's a relative displacement between the electrode and the NWs, either vertically or laterally.

We expect the electricity produced by the relative deflection and displacement between the NWs and the electrode—resulting from either bending or vibration—to be output simultaneously and continuously. We can package such nanogenerators to prevent the invasion of liquid, so we can directly place them inside biofluid or any other liquid.[10]

For technological applications, increasing the output power requires increasing the nanogenerator's voltage and current output. The most straightforward way to increase the current and voltage is to stack them in parallel/serial.

Experimenting with 3D integration

We tested three nanogenerators (NG I, II, and III) under the same experimental conditions (see figure 7a–c). NG I exhibited an average short-circuit current of approximately 0.7 nA, and NG II showed a lower noisy signal of 1 nA. We then connected these two nanogenerators in parallel (inset of figure 7d) and tested them under the same condition again. The resultant output current reached an average of approximately 1.8 nA. For NG III, which output approximately 4 nA, the parallel connection of the three nanogenerators gives 5.9 nA output (see figure 7e).

These experiments demonstrate the possibility of raising the power output using 3D integration. The peaks in the output current correspond to turning the ultrasonic wave on and off. We estimated that approximately 500–1,000 NWs were active for producing and outputting electricity. The output current is a sum of the current that all the active NWs generated, while the output voltage is what a single NW produced. If every NW were involved in generating electricity, the output power could reach 10 μW/cm^2, which 3D integration could further improve. Most recently, by optimizing the design and assembling technique, the output has improved to approximately 0.6 μA, corresponding to an output current density of approximately 20 μA/cm^2 of the substrate area.

Advantages and potential applications

The piezoelectric nanogenerator could potentially convert the following into electric energy for self-powering nanodevices and nanosystems:

- mechanical-movement energy, such as body or muscle movement or blood pressure;
- vibration energy, from acoustic or ultrasonic waves; and
- hydraulic energy, such as from the flow of body fluids or blood, the contraction of blood vessels, or dynamic fluid in nature.

The microelectromechanical systems microgenerator, which is mostly built on a piezoelectric thin-film cantilever,[11] can also convert such energy into electric energy. However, the ZnO NW-based nanogenerators offer the following advantages:

- Because NWs can grow on any substrate at a low temperature, you can integrate NW-based nanogenerators with inorganic and organic materials for flexible electronics.
- NW-based nanogenerators work in a wide frequency range, from a few hertz to multiple megahertz. Also, the NW's mechanical resonance isn't required to generate electricity.
- ZnO is biocompatible and environmentally friendly.
- NWs have superelasticity and are very resistive to fatigue, owing to their small diameter, so we expect the nanogenerators to be long-lasting.
- With a large surface area, NW functionality might provide additional advantages, such as surface modification.

Consequently, the NW-based nanogenerator could support important applications in a variety of fields.

For example, it could help wireless self-powered nanodevices harvest energy from the environment. It could also provide a method for indirectly charging a battery. For biomedical sciences, self-powered nanodevices could offer real-time monitoring of blood pressure and blood-sugar levels. They might also perform in-vivo detection of cancer cells or wirelessly measure fluid pressure in the brain. For environmental science, the nanogenerator could remotely sense

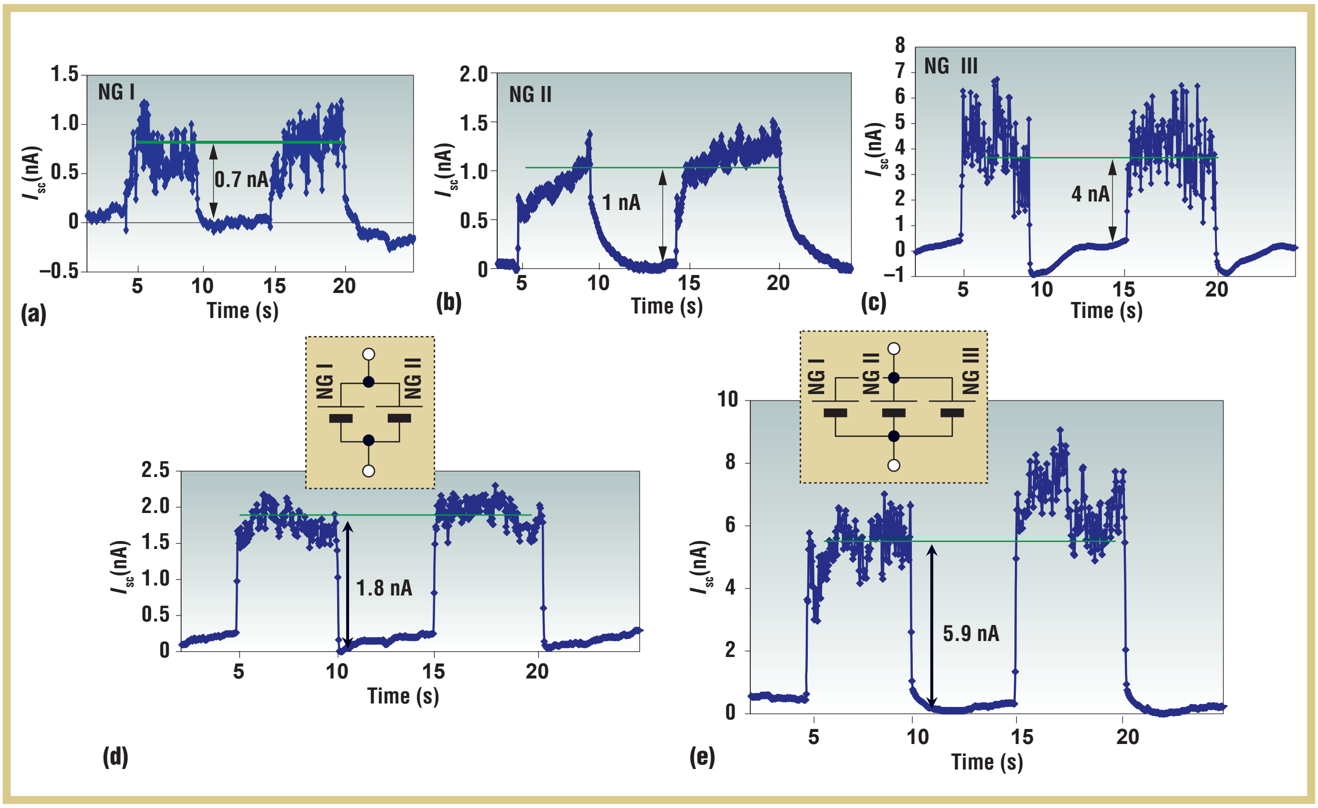


Figure 7. A short-circuit current (ISC) measured from an integrated nanogenerators system. We measured the current signal from three individual nanogenerators: (a) NG I, (b) NG II, and (c) NG III. (d) The current signal we measured from connecting NG I and II in parallel. (e) The current signal we measured from connecting NG I, II, and III in parallel. (Insets show the connection configuration.)

gas and chemical species and track animal-migration activities.

For personal electronics, it offers the possibility of charging a battery using energy harvested from a human walking, swinging his or her arms, or stretching his or her legs. It might also harvest energy from sound and ultrasound waves, wind and air flow, mechanical vibration, or even thermal noises. The nanogenerator could also help harvest and recycle wasted energy, such as energy created by a tire's pressure change, a moving car's mechanical vibration, or a tent surface's vibration.

To meet these goals, however, we'll need to overcome quite a few challenges.

First, we need to raise the nanogenerator's output voltage. This will require producing highly uniform and patterned NW arrays, so most of the NWs will be active for outputting electricity. This will also require optimizing the electrode's design to reduce system capacitance.

Second, we need to broaden the driving frequency span, particularly in the low-frequency range, which covers most vibrations ubiquitously existing in ambient environments and biological systems. Considering the power-generation principle, the electricity output will more likely be separated pulses under low-frequency excitation. Therefore, we might need a capacitor to store the electricity before applying it.

Third, we need 3D integration to raise the nanogenerators' voltage and current, which could raise the entire package's output power.

Fourth, we need to optimize the packaging technology, studying its fatigue behavior and energy-dissipation process to prolong its life.

Fifth, we need to explore energy-storage technology. Under most conditions, we can't expect to obtain much power. When the harvested energy is insufficient to maintain continuous device operation, applications can be limited to small-duty cycles that allow for self-sustainable operations. For example, they could transmit or collect data for one second out of every minute while harnessing energy the rest of the time.

Finally, we expect additional challenges will arise from the new field of nanopiezotronics that has developed out of using coupled piezoelectric-semiconducting properties as proposed for the nanogenerator.[12,13] Using nanopiezotronics, we've fabricated piezoelectric-field effect transistors;[14] a piezoelectric diode;[15] and piezoelectric force, humidity, and chemical sensors.[16]

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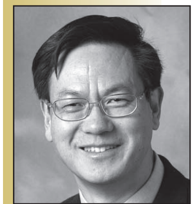
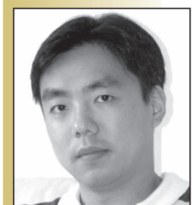
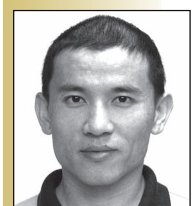


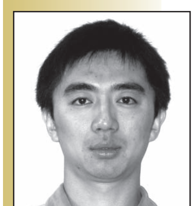
Zhong Lin Wang is a Regents' Professor and College of Engineering Distinguished Professor at Georgia Institute of Technology. His research interests include the science and application of nanoparticles, nanowires and nanobelts; functional oxide and smart materials for sensing and actuating; and nanomaterials for biomedical applications and nanodevices. He received his PhD in physics from Arizona State University. He's a fellow of the American Physical Society and the American Association for the Advancement of Science. Contact him at the School of Materials Science and Eng., 771 Ferst Dr. NW, Georgia Inst. of Technology, Atlanta, GA 30332-0245; zhong.wang@mse.gatech.edu; www.nanoscience.gatech.edu/zlwang.



Xudong Wang is a research scientist in the school of Materials Science and Engineering at Georgia Institute of Technology. His research includes designing, assembling, and testing piezoelectric-nanowire-based devices. He received his PhD in materials science engineering from Georgia Institute of Technology. Contact him at the School of Materials Science and Eng., 771 Ferst Dr. NW, Georgia Inst. of Technology, Atlanta, GA 30332; xdwang@gatech.edu; www.nanoscience.gatech.edu/zlwang/group/xw.htm.



Jinhui Song is a PhD candidate in the school of Material Science and Engineering, Georgia Institute of Technology. His research interests include synthesizing and characterizing large-scale 1D aligned nanowires, investigating nanostructure properties using AFM, and fabricating nano devices based on nanowires. He received his MS in physics from Georgia Institute of Technology. Contact him at the School of Materials Science and Eng., 771 Ferst Dr. NW, Georgia Inst. of Technology, Atlanta, GA 30332; gtg518i@mail.gatech.edu.



Jin Liu is a PhD candidate in the School of Electric and Computer Engineering at Georgia Institute of Technology. His research mainly focuses on fabricating piezoelectric nanowire-based devices and developing novel processes for the integration of top-down and bottom-up approaches in nanoscale devices. He received his MS in electric and computer engineering from Georgia Institute of Technology. Contact him at the School of Materials Science and Eng., 771 Ferst Dr. NW, Georgia Inst. of Technology, Atlanta, GA 30332; gt1687c@mail.gatech.edu

Yifan Gao is a graduate research assistant at Georgia Institute of Technology. His research interests include packaging of nanogenerators and theoretical calculations of piezoelectric nanosystems. He received his BS in physics from Peking University of China. Contact him at 771 Ferst Drive, J. Erskine Love Bldg., Atlanta, Georgia 30332-0245; yifan@gatech.edu.