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Air/Liquid-Pressure and Heartbeat-Driven Flexible Fiber Nanogenerators as Micro/Nano-Power Source or Diagnostic Sensors

By *Zetang Li* and *Zhong Lin Wang**

We present a new approach for fabricating flexible fiber nanogenerators (FNGs) that can be used for smart shirts, flexible electronics, and medical applications. These FNGs are based on carbon fibers that are covered cylindrically by textured zinc oxide (ZnO) thin films. Once subjected to uni-compression by applying a pressure, the cylindrical ZnO thin film is under a compressive strain, resulting in a macroscopic piezopotential across its inner and exterior surfaces owing to the textured structure of the film, which is the driving force for generating an electric current in the external load. Using such a structure, an output peak voltage of 3.2 V and average current density of 0.15 μA cm^{-2} are demonstrated. The FNGs rely on air pressure, so that it can work in a non-contact mode in cases of rotating tires, flowing air/liquid, and even in blood vessels. Pressure-driven FNGs added to a syringe show potential to harvest energy in blood vessels, gas pipes, and oil pipes, as long as there is a fluctuation in pressure (or turbulence). Heart-pulse driven FNGs can serve as ultrasensitive sensors for monitoring the behavior of the human heart, which may possibly be applied to medical diagnostics as sensors and measurement tools.

Air pressure is a very common physical parameter that affects our daily life in many ways. Air/liquid flow induces dynamic pressure changes, which can drive a lot of things. How to use the energy induced by air pressure/flow is important for today's energy technologies. Fluctuations in air pressure are rather irregular phenomena with a large degree of change in amplitude and frequency, which makes them rather difficult to be harvested directly using conventional technologies. Taking the piezoelectric cantilever approach as an example, its energy-harvesting efficiency is optimal if the external mechanical stimulating frequency matches the resonance frequency of the cantilever. If the stimulating frequency is lower, the required size of the resonator has to be larger, so that the energy can only be harvested if the magnitude of the applied force is strong enough. If the applied frequency is higher, the size of the resonator can be smaller, however, high-frequency mechanical signals are not as popular as the natural low-frequency agitations found in our living environment, especially in biological systems, such as that of breathing and heart beating.

Recently, piezoelectric nanowires have been applied to harvest mechanical energy.[1–7] Multimaterial piezoelectric fibers have been developed as acoustic wave motors/receivers/transmitters.[8] The advantage of the nanowire-based nanogenerator is that it *does not* rely on resonance, but rather on strain-induced dynamic deformation. The force required to induce the mechanical deformation is small considering the small size of the nanowires. However, these nanogenerators (NGs) are wrapped by a polymer layer, which may damp the applied mechanical stimulation and largely reduce the energy-conversion efficiency. More importantly, most of the nanogenerators demonstrated so far use direct forces in the contact mode for agitation. Air/liquid pressure is different from force in a way that pressure is an isotropic scalar quantity, but force is a vector. A new approach needed to be developed in order to use pressure to generate electricity.

Previously, ZnO nanowires (NWs) grown on Kevlar 129 fibers have been demonstrated as an approach for FNGs, in which gold-coated ZnO NWs on one fiber act as an array of atomic force microscopy (AFM) tips, and the NWs on the other fiber are the acting piezoelectric components for energy conversion.[9] Alternatively, poly(vinylidene fluoride) (PVDF) fibers have also been applied to harvest energy using the piezopotential created in the fiber by straining.[10] However, the output of the two designs was rather low so that they could not be used to drive practical devices. In this paper, we report an alternative design for NGs using carbon fibers that are coated with a textured ZnO thin film. Using the flexibility of the fiber and the cylindrical coating of the film, an applied pressure can induce compressive strain around the ZnO shell. The textured structure of the ZnO film results in a macroscopic piezopotential that can produce a peak output voltage of 3.2 V and an average current density of 0.15 μA cm^{-2}. The NG can not only harvest the energy from the

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DOI: 10.1002/adma.201003161

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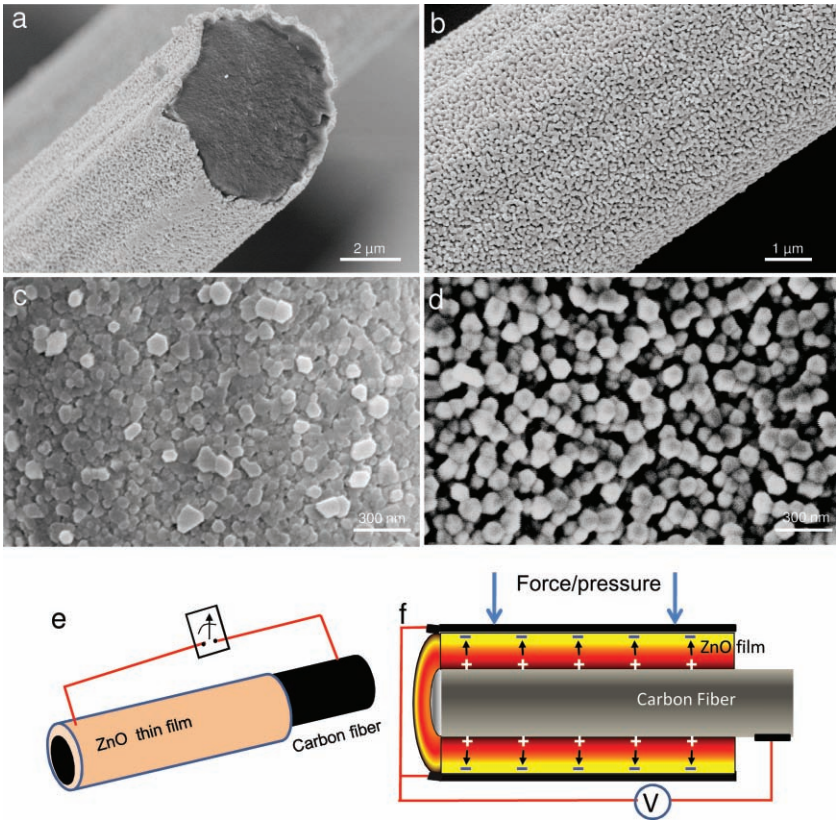

Figure 1. Textured ZnO thin films grown around a carbon fiber. a,b) Low-magnification SEM image of the ZnO/fiber structure. c) A ZnO film made of densely packed ZnO nanorods showing the uniaxial alignment of their *c*-axes. d) A ZnO film made of aligned ZnO nanorods with parallel *c*-axes. e) Schematic of a fiber nanogenerator based on a carbon fiber coated by a ZnO thin film. f) Working principle of the fiber nanogenerator, where the '+/–' signs indicate the polarity of the local piezoelectric potential created on the inner and outer surfaces of the ZnO thin film.

air/liquid pressure/flow, but it can also serve as a pressure sensor for detecting a heartbeat. It will find important applications in smart clothes, flexible electronics, and medical sciences.

Growth of Radial Textured ZnO Thin Film on Fibers: Our design of the FNG is based on a radial textured ZnO thin film that is grown around carbon fibers (**Figure 1a**). In principle, any conductive fiber can be used for this purpose. The fiber is not only used as the flexible soft substrate onto which a ZnO thin film is grown at high temperature but it also acts as an electrode for charge transport. Previous work has shown the growth of a ZnO thin film on carbon fibers by electrospray deposition,[11] zinc film oxidation,[12] hydrothermal growth in solution,[13] and RF magnetron sputtering.[14] The key advantage of our method is that it produces a textured film that is made of densely packed nanowires with [0001] orientations, which completely surrounds the fiber to form a radially textured, cylindrical, and shelled structure.

The growth of the ZnO thin film that cylindrically covers the surface of a carbon fiber was carried out using a physical vapor deposition method (Figure 1a,b). The as-grown thin film is composed of nearly parallel aligned ZnO nanorods that form a textured film (ca. 250 nm in thickness) with the normal direction along [0001] (Supplementary Information (SI), Figure S1). This can be seen from the scanning electron microscopy (SEM) image presented in Figure 1c in which the hexagonal flat tops of the densely packed ZnO nanorods are clearly shown. These nanorods can have a random orientation in the planar film, but here a good alignment in the normal direction is achieved so that the entire film has a uni-polar structure along the *c*-axis. The distribution of the nanorods around the fiber can be clearly seen if the density of the nanorods is not high (Figure 1d). The density of the NWs could be controlled by tuning the ratio of ZnO to carbon nanowire in the physical vapor deposition process. Our previous study using X-ray diffraction shows that ZnO tends to form epitaxial thin films on any surface, such as on polymer and silicon surfaces.[15] This provides a unique advantage not only to accommodate the curvature as defined by the shape of the substrate, which is a fiber, but also provides a uni-polar structure for piezoelectric applications.

The Working Principle of the Fiber Nanogenerator: For the fabrication of the fiber nanogenerator (FNG), the ZnO thin film at one side of carbon fiber was etched off locally by a NaOH solution to expose the fiber electrode for making contact. The other electrode of the FNG was contacted to the top surface of the ZnO thin film using a silver tape/paste (Figure 1e). As shown in Figure 1 and our previous study,[5] wurtzite-structured ZnO nanorods form a densely packed and polar-direction aligned thin film,[15] with the polar direction pointing radially outward. The FNG was constructed by aligning the ZnO-coated carbon fibers in parallel, with an electrode connected to the carbon fibers and one electrode connected to the top surface of the ZnO film. A plastic substrate was used to support the aligned fibers, and all of the fibers were fixed to the substrate. The working principle of the FNG is as follows. For simplicity, the textured film can be treated as a "single-crystal" for the purpose of the FNG. When the film is compressively strained under an applied external pressure through air/liquid flow, a separation between the static ionic charge centers in the tetrahedrally coordinated Zn-O units results in a piezoelectric potential gradient along the *c*-axis. The strain on the textured structure of the thin film results in a macroscopic piezoelectric potential across the thickness of the film (Figure 1f). As the *c*-axis is pointing outward of the fiber substrate, the negative side of the piezopotential is the external surface of the film, which gives a rise in the conduction band and the Fermi level of the electrode,[16] forcing the electrons to flow from the surface of the film to the other electrode (the carbon fiber) through the external load because of the existence of the Schottky barrier at the interface (SI, Figure S2) until equilibrium is reached. As the external force is removed and the compressive strain is released, the piezoelectric potential inside the film diminishes. The electrons accumulated at the other electrode flow back via the external circuit, creating an electric pulse in the opposite direction. The role of the Schottky barrier is to prevent those mobile charges from passing through the film-metal interface. The piezoelectric potential acts as a

'charging pump' that drives the electrons to flow.[9] A cycled strain induced in the film by alternating the externally applied pressure results in an AC output. The key role played by the fiber is to effectively use the pressure from all directions.

Experimentally, a linear motor was used to periodically deform the FNG in a cyclic stretching-releasing agitation. The short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) were measured to characterize its performance. When the current meter was connected in a forward position to the FNG, a positive current pulse was recorded during fast stretching of the substrate (see SI), and a corresponding negative pulse for fast release (where 'fast' means an angular bending rate of ca. 260° s^{-1} at a radius of 2 cm for the substrate). For a FNG made of 150 carbon fibers of around 10 μm in diameter and about 20 mm in length each, the maximum output voltage received was 2.0 to 2.2 V and the output current was 60 to 120 nA. Although the heights of the current peaks for the stretch and release appear to be different, possibly because of different straining rates, the areas under the peaks remain about the same to within 5%. Similar experiments were carried out whereby the FNG was under compressive strain.

To exclude the effect of a change in capacitance in the mechanical pressing and releasing processes, which could potentially introduce output signals related to effects within the measurement system, we used carbon fibers without ZnO films for comparison. The electric signal generated by such a device was too small to be detected (SI, Figure S3 cyan lines). In a different experiment, we also allowed the mechanical arm of the linear motor stimulator to vibrate back and forth to a distance very close to the top surface of the packaged FNG, but without making direct physical contact. Again, the output was so low that it could not be distinguished from the noise (SI, Figure S3 pink lines).

To verify that the measured signal was indeed generated by the FNG rather than by the measurement system, a 'linear superposition' test of output voltages and currents for two FNGs was carried out. The output voltage of the two FNGs, as triggered by a mechanical motor in a synchronized matter, was the sum of the two when they were connected in series (**Figure 2a**). The output current density could be added up when the two FNGs were connected in parallel (Figure 2b).

Air-Pressure-Driven Fiber Nanogenerator: As air pressure can act on every part of an object that is exposed without a specific direction, we packaged the ZnO-film-coated carbon

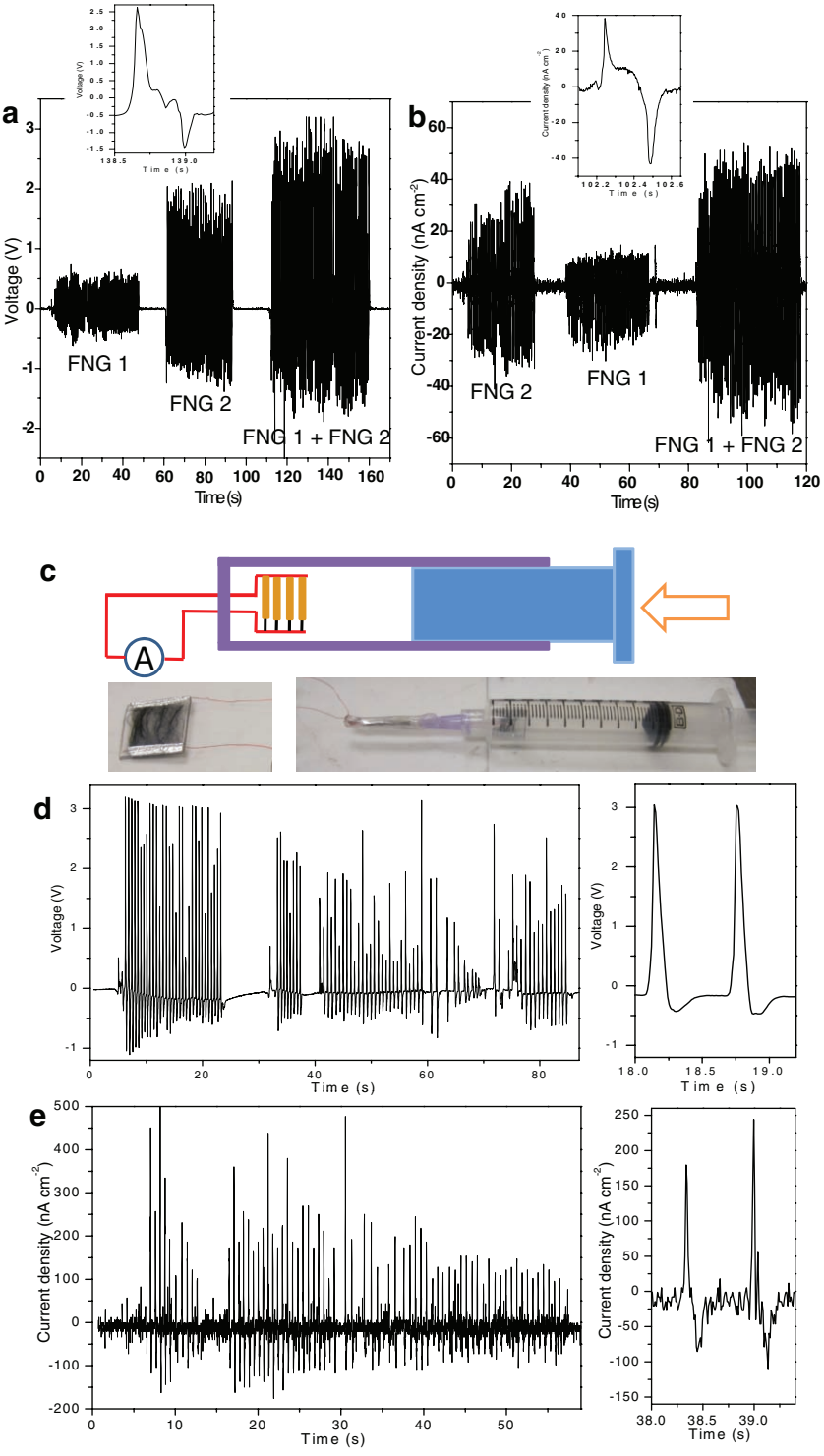

Figure 2. Two normal good working FNGs for a 'linear superposition' test of output current densities (a) and voltages (b), The output voltage of the two FNGs (FNG1+FNG2) was the sum of FNG1 and FNG2 when they were connected in series. The output current density was the sum of the two FNGs when they were connected in parallel. The insets show the details of the output signals. c–e) Integration and performance of an air-pressure driven fiber nanogenerator. c) Schematics for the air pressure driven FNG when it is placed inside a syringe. The variation in the air pressure is created by the piston of the syringe. d,e) Open-circuit output voltage (d) and short-circuit output current (e) measured for a FNG structure comprising 100 carbon fibers. The maximum output voltage peak reaches 3.2 V. The graphs on the right-hand side of (d) and (e) show one cycle of the output voltage and current, respectively.

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fibers loosely on a flexible substrate, as shown in Figure 2c using the connections as shown in Figure 1e. A uni-radial compression by the air pressure around the fiber creates a piezoelectric potential as shown in Figure 1f. A dynamic variation in pressure creates a compression-release process to the cylindrical shaped ZnO film; the corresponding generated piezoelectric potential drives the flow of the electrons back and forth in the external load in response to the fluctuation in air pressure.

By placing the FNG inside a syringe (Figure 2c) and applying a periodic pressure through compression of the piston, an AC output was achieved (Figure 2d,e and Supplementary Video 1). The generated electricity output was not quite symmetric because the pressure and rate were different for compressing and releasing of the piston. The output peak voltage reached up to 3.2 V and the average current density reached 0.15 μA cm^{-2}. The surface area was calculated as the area of the working carbon fibers in the nanogenerator. The output was significantly higher than our previous reports possibly because there was no packaging material to cover the FNG so that the pressure acted directly onto the ZnO film without being damped by the packaging material or substrate.

Exhalation-Driven Fiber Nanogenerator/Sensor: Gentle air flow has the following characteristics. First, the direction of the air flow varies unpredictably. Second, the force of the air flow acting on a small device is rather weak so that it may not drive a generator if the stiffness and damping of the packaging material are too high. Lastly, the frequency of the air flow also varies. To enhance the effectiveness of a gentle breeze for driving the FNG, we used carbon fibers that were long and flexible enough to respond to that air breeze, as shown in the inset in **Figure 3a**. A looped FNG was fixed on a glass substrate. One electrode was connected to the carbon fibers and the other one was joined to the ZnO film. When blowing onto the FNG by a gentle exhalation, the breezing wind made the FNG to change shape and vibrate, resulting in an electricity output (Figure 3). Repeated exhaling resulted in an AC output. The average output voltage was 1.5 mV and the average output current was 0.5 nA. The low output is possibly due to the low strain created in the film by exhalation. Such low output may not be useful for energy harvesting, but it can be used as a breathing sensor in biomedical and health-care applications (Supplementary Video 2).

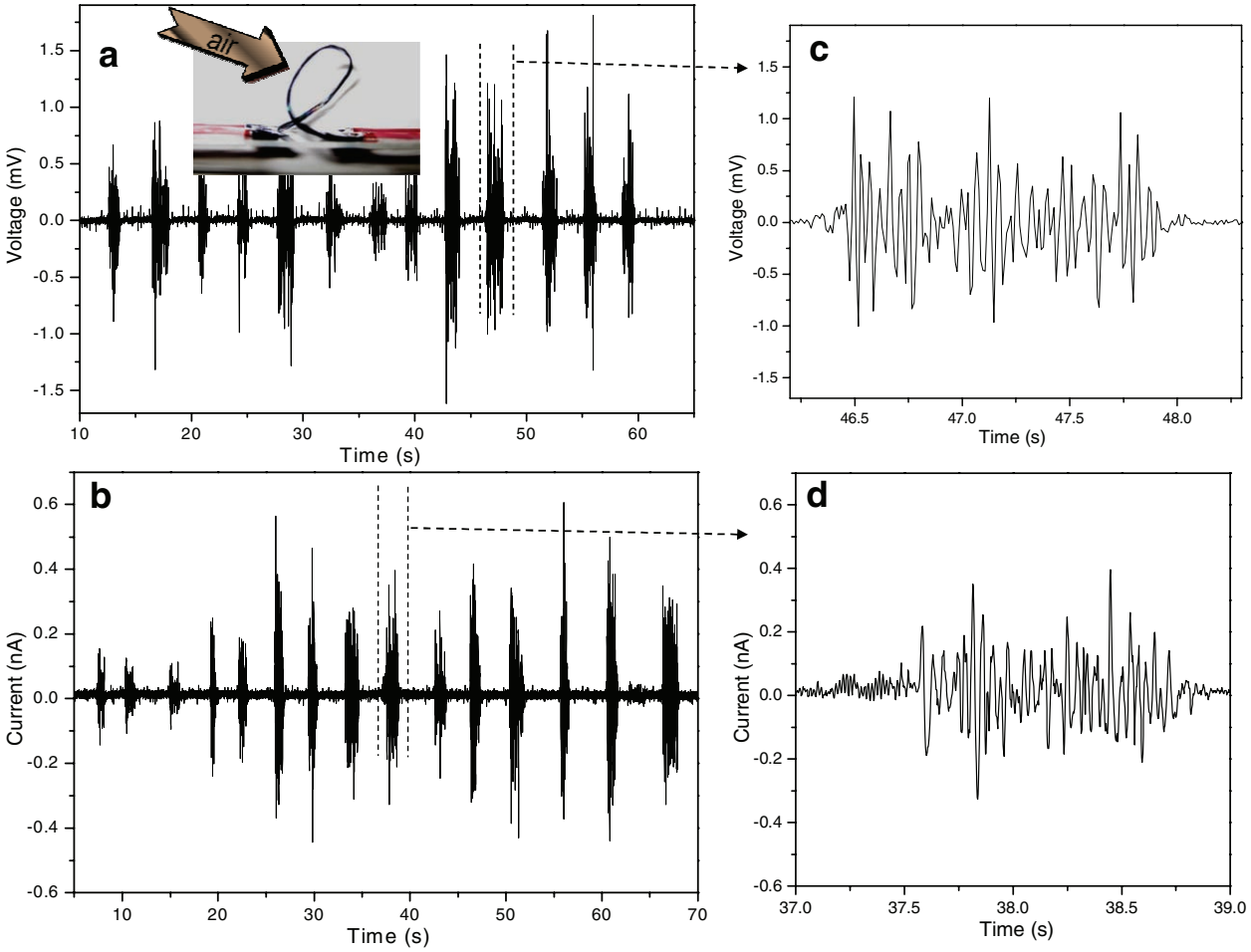

Figure 3. a–d) Performance of an air-flow driven fiber nanogenerator. The inset in (a) is a loop-shape FNG made of 50 carbon fibers, which was fixed to a glass substrate. By exhaling onto the FNG (and thus creating an air flow) an open-circuit output voltage (a,b) and short-circuit output current (c,d) were achieved.

Heartbeat-Pulse Driven Nanogenerator as Pressure Sensor: The pulse pressure (PP) is one of the output signals of a human heart system, which is a complex time–dependent and non-linear signal reflecting the fluctuation of one's motion and health situation.[17,18] A quantitative measurement of the pulse signal provides important information for medical monitoring especially in medical diagnostics.[19] The origins of the PP are complex because it is more than just cardiac output and total peripheral resistance. In the literature[20,21] the PP is increasingly being recognized as an indication for cardiovascular and other diseases. Our first experiment consisted of just using the pulse at the wrist of a human to drive our FNG. The FNG in this case was made using relatively long fibers of about 4 cm and was attached to the wrist with cloth athletic tape. The FNG was placed over the pulse point as schematically shown in **Figure 4a**. In order to get the in-situ original blood pressure signal, a medical blood-pressure gauge was affixed over the FNG. The output of the FNG was recorded in response to the heart-beating behavior (Supplementary Video 3). Figure 4a to c show three different output patterns of the heartbeat as measured by the output current of the FNG. These curves contain information about the dynamics of the heart beating. Applying data analysis techniques can derive specifics about possible health conditions of a person.[22,23] The normal pulse-pressure wave should look like that in Figure 4b. A young person has a smooth pulse as shown in Figure 4c. An older person would have a pulse wave like the one shown in Figure 4d. We anticipate that the technique demonstrated here can be new quantitative diagonostic techniques for healthcare.

In summary, we have presented a new approach for fabricating a flexible-fiber-based nanogenerator that can be used for smart shirts and flexible electronics. The NG is based on carbon fibers that are covered cylindrically by a textured ZnO thin film. Once subjected to uni-compression by applying a pressure, the cylindrical ZnO thin film is under a compressive strain, resulting in a macroscopic piezopotential across its inner and exterior surfaces, which is the driving force for generating an electric current in the external load. Using such a structure, an output peak voltage of 3.2 V and an average current density of 0.15 μA cm^{-2} have been demonstrated.

The reported NG has a number of advantages over the NGs based on vertically or laterally aligned nanowire arrays. First, the NG uses flexible fibers so that it has the potential to be integrated within the fabric used for smart clothes. Second, the NG does not need to be protected by a thick polymer layer, which usually damps the magnitude of the mechanical triggering, thus, the output voltage is substantially high. Last, the design relies on air pressure, so that it can work in a non-contact mode

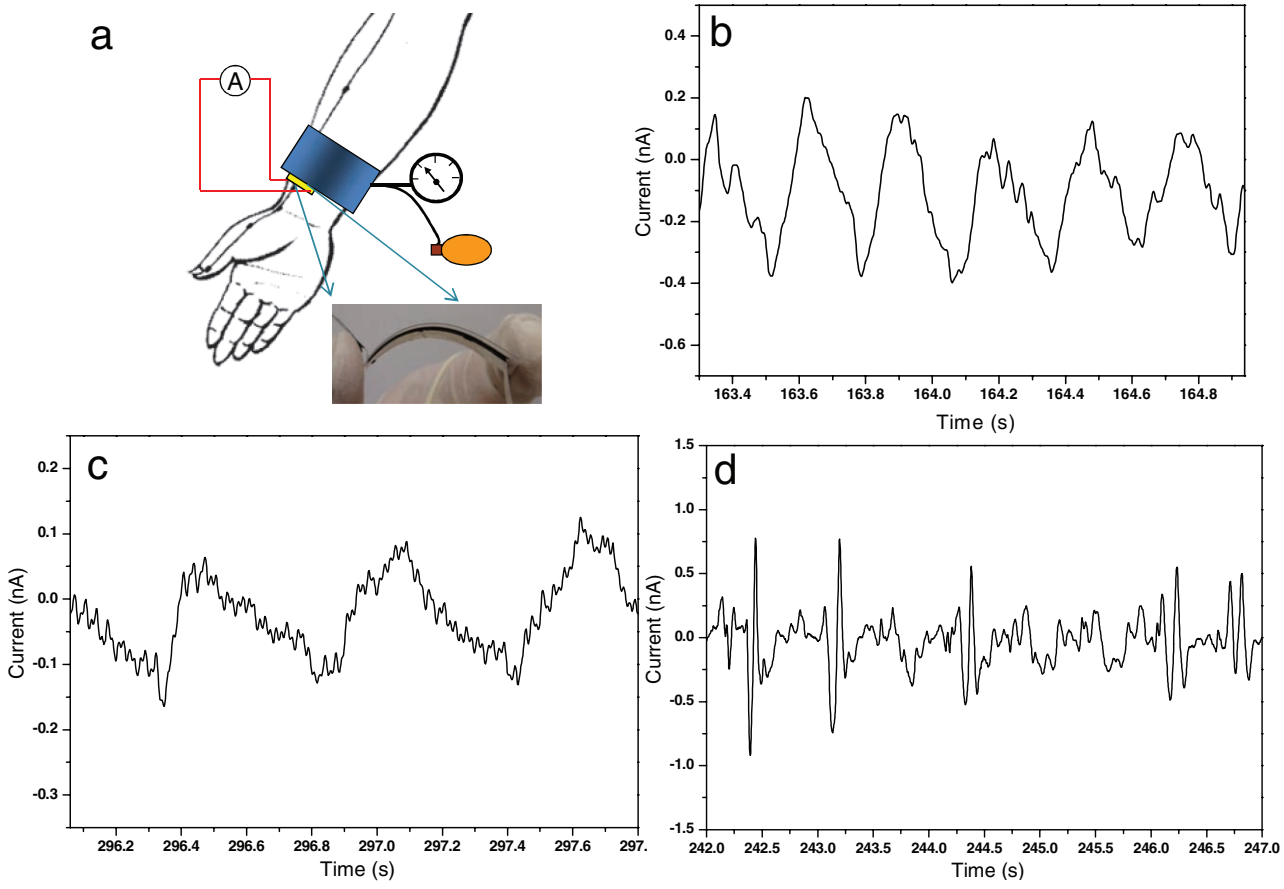

Figure 4. Pulse-driven fiber nanogenerator for energy harvesting or strain sensor. a) Schematics of the experimental set-up. b–d) Three typical electric current outputs from a FNG generated by heartbeat pulses, which not only demonstrates the possibility of energy conversion from small physical motion, but also the use of a FNG as bio-strain-sensor.

on all of the available surface area, so that it can also be used as a 3D sensor in rotating tires, flowing air/liquids, and even in blood vessels. The pressure-driven NG when put in a syringe shows potential to harvest energy within a blood vessel, gas pipe, or oil pipe, as long as there is a fluctuation in pressure (or turbulence). The energy generated can be used to monitor the status and operation of the fluid/gas. The heart-pulse-driven NG can serve as an ultrasensitive sensor for monitoring the behavior of the human heart, which may possibly serve for medical diagnostics.

Experimental Section

The source materials used for the growth of the ZnO film on the carbon fibers were ZnO powder (Alfa Aesar, 99.9%, 200 mesh), activated carbon particles (Alfa Aesar, steam activated, acid washed) with equal ratio in mass, which were placed at the center of a tube furnace with a quartz tube to be able to monitor the carbon fibers and the flow of the gas. The carbon fibers were freely suspended in the tube, which was located at about 10 cm from the end of the tube furnace, by the carrier gas. The carrier gas was made of oxygen and nitrogen gas (99.9%, Georgia Tech) at a ratio of 1:4 at a flow rate of 40 sccm. The growth temperature was 960 °C.

Supporting Information

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

Acknowledgements

This research was supported by the NSF, DARPA, Airforce, BES DOE, and NSFC(No.50878114). Zetang Li is grateful for the fellowship from the China Scholarship Council (CSC) (No. 2009621143).

Received: August 31, 2010
Revised: September 25, 2010
Published online:

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