Highly Stretchable 2D Fabrics for Wearable Triboelectric Nanogenerator under Harsh Environments

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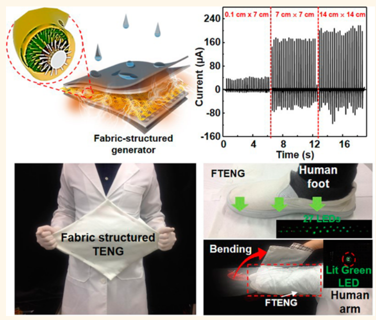
ABSTRACT Highly stretchable 2D fabrics are prepared by weaving fibers for a fabric-structured triboelectric nanogenerator (FTENG). The fibers mainly consist of Al wires and polydimethylsiloxane (PDMS) tubes with a high-aspect-ratio nanotextured surface with vertically aligned nanowires. The fabrics were produced by interlacing the fibers, which was bonded to a waterproof fabric for all-weather use for fabric-structured triboelectric nanogenerator (FTENG). It showed a stable high-output voltage and current of 40 V and 210 μA, corresponding to an instantaneous power output of 4 mW. The FTENG also exhibits high robustness behavior even after 25% stretching, enough for use in smart clothing applications and other wearable electronics. For wearable applications, the nanogenerator was successfully demonstrated in applications of footstep-driven large-scale power mats during walking and power clothing attached to the elbow.



KEYWORDS: fiber · fabric · triboelectric nanogenerator · strechable · wearable device

Harvesting mechanical energy from our surroundings has been of great interest in portable applications such as wearable electronics that require a steady and high output power.[1,2] The recent development in wearable technologies is changing our lives for the better and giving us information for crucial healthier lifestyle choices. However, the development and increased production of the wearable electronic devices bring increasing demands on power supply. In 2013, because many wearable devices such as Google Glass, Galaxy Gear by Samsung, and Smart Watch by Sony have been introduced to the market, the overall wearable electronics and technology market is expected to grow at a strong annual rate. These devices are now powered by rechargeable batteries, largely limiting their lifetime and sustainable operation. For seamless integration of the smart devices into clothing, the need for battery replacement or recharging should be eliminated, and the question of how to supply power in a stable and reliable manner is one of the most critical issues to increasing the commercialization success of the wearable devices.

Recently, a new type of power-generating device, called a triboelectric nanogenerator (TENG), was suggested; it is based on the contact electrification effect and electrostatic induction.[3−12] In the nanogenerator, energy generation is achieved by the charges transferred by a periodic physical contact between two materials that differ in the polarity of triboelectricity. Since 2012,[3] TENGs have been successfully demonstrated as a promising energy-harvesting technology for self-powered devices, for example, voice recognition devices,[13] a distress signal emitter,[10] a trace memory system,[14] and a velocity sensor[15] as well as self-electroplating technology.[16] Very recently, there were some reports on the TENGs integrated with fibers for smart clothing as promising applications.[2,17] In most works, the output power is generated from the contact between fibers; thereby, the output power of such triboelectric nanogenerators may be not sufficient and stable enough for powering the wearable devices, especially under a highly

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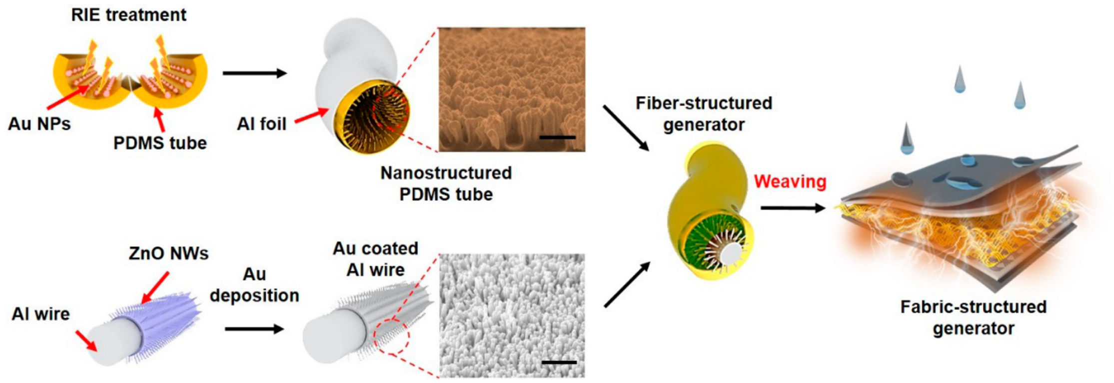

Figure 1. Schematic diagrams of the fabrication process for the FTENG. The fiber-structured nanogenerator is a coaxial and fully sealed device containing an Al wire in the core and a PDMS tube in the shell. ZnO nanowires were first grown on the Al wire by a hydrothermal process, followed by the deposition of Au thin film, producing 3D Au/Al branched wires. The PDMS was etched away by using a reactive ions etching process, producing nanowire arrays with lengths of 1−2 μm inside the tube. The Au/Al wires were inserted into the PDMS tube, and the resultant fiber was wrapped around the Al foil. FTENG were then fabricated by weaving the fibers, followed by bonding to a waterproof fabric. Scale bars in SEM images are 1 μm (top) and 2 μm (bottom).

stretched condition. There were also very few reports on fabric-structured TENGs (FTENGs) composed of many fibers, which also generate stable output power. This approach should be considered as a promising candidate for high-performance and stable nanogenerators toward self-powered wearable electronics in the near future.

Here, for the first time, we demonstrate highly stretchable 2D fabrics for wearable triboelectric nanogenerators for powering wearable electronic devices that are based on a vertical-separation contact mode. First, Al wires and polydimethylsiloxane (PDMS) tubes with a high-aspect-ratio nanotextured surface with vertically aligned nanowires are prepared. The Al wires were then inserted into the PDMS tube, and the resultant fiber was wrapped around the flexible Al film, which acted as the other electrode, thus fabricating fiber-structured triboelectric nanogenerators. The 2D woven fabrics are fabricated by weaving several fibers that were then bonded to a waterproof fabric for all-weather use for FTENGs. This technique is simple and scalable, providing a promising solution for developing large-scale and practical self-powered wearable devices. A single fiber-structured nanogenerator showed an output power and current of 40 V and 10 μA, respectively, under a cycled compressive force of 50 N. There was no degradation in the output voltage and current at even 95% RH, meaning that the device can generate a stable output power under harsh environmental conditions such as high humidity. The output voltage and the output current from FTENGs reached a high current value of 210 μA, corresponding to an instantaneous power output of 4 mW under the same cycled compressive force. The fabric was also found to be quite stretchable up to over 25%, enough for use in smart clothing applications and other wearable electronics.[18,19] Additionally, the FTENG was successfully employed in applications for footstep-driven large-scale power mats and power clothing attached to the elbow.

RESULTS AND DISCUSSION

The schematic diagrams of the fabrication process of fiber- and fabric-structured triboelectric nanogenerators are shown in Figure 1, and detailed information described in Experimental section. Basically, the fiber-structured nanogenerator is a coaxial and fully sealed device containing an Al wire in the core and a PDMS tube in the shell. Before the fabrication process, ZnO nanowires were grown on the Al wire by a hydrothermal process, followed by the deposition of a Au thin film, producing 3D Au/Al branched wires that act as one electrode. The PDMS was etched away by using a reactive ions etching (RIE) process, producing nanowire arrays with a length of 1−2 μm inside the tube. The Au/Al wires were inserted into the PDMS tube, and the resultant fiber was wrapped around the flexible Al thin film, which acted as the other electrode. Because the fiber is fully sealed by a polymer, the inner wires are located in the middle between two walls inside the tube. Fabric-structured nanogenerators were then fabricated by weaving the fibers.

The output voltage and the output current of the fiber-structured TENG of approximately 5 cm in length were measured under a cycled compressive force of around 50 N at an applied frequency of 10 Hz, as shown in Figure 2a. The fiber-structured TENG shows typical ac-type electrical output performance of approximately 40 V and 10 μA. We found that the output performance was enhanced by the nanowires (Figure S1). The output performance in the triboelectric nanogenerator is strongly dependent on the gap distance and the contact area between two materials; thus, it is also dependent on the radius of the PDMS tube and the Al wire. The COMSOL simulation in Figure 2b shows that the triboelectric potential increases with the radius of

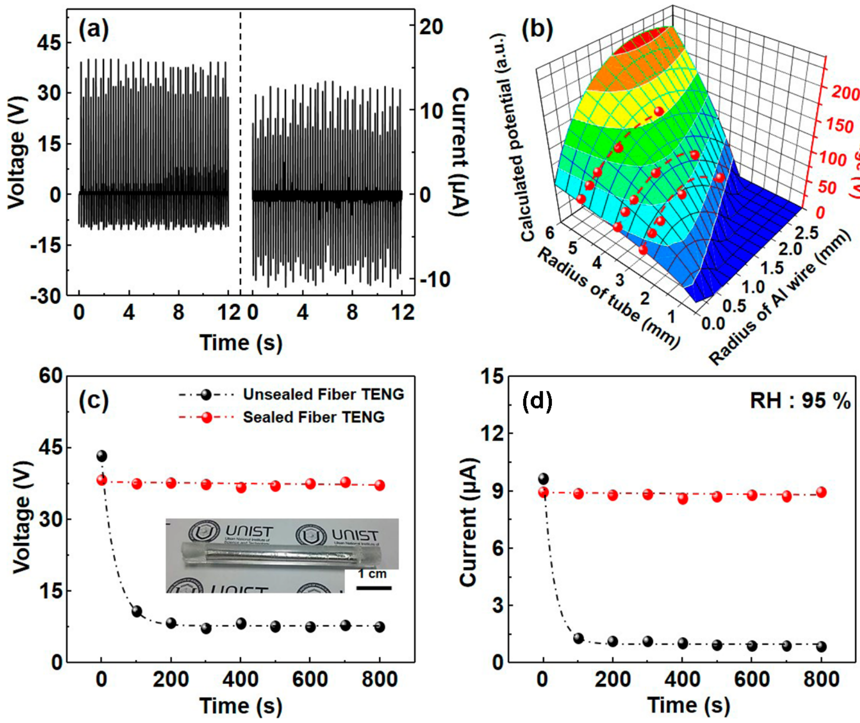

Figure 2. (a) Output voltage and current of fiber-structured TENG. (b) Calculated electrostatic potential with radius of Al wire and PDMS tube simulated by the COMSOL multiphysics software. The output voltages measured experimentally are also drawn as dotted lines. Change in (c) output voltage and (d) current of the unsealed and sealed fiber-structured TENG at relative humidity of 95% RH.

both materials, and there is a maximum potential at a radius of 6 and 2.0 mm in tube and wire, respectively. This is evident by the change in output voltages measured experimentally, drawn as dotted lines in Figures 2b and S2. However, here we used the PDMS tube with a radius of 2.5 mm and the Al wire with a radius of 0.1 mm to increase flexibility of the fiber, an important parameter for flexible practical wearable applications. The fiber was then sealed at both edges, as shown in the inset of Figure 2b. It is clearly seen that the sealed device shows enhanced performance under extreme conditions of high humidity (>95% RH), whereas the output signals in the unsealed device are degraded within approximately 1 min in Figure 2c. The experimental set up for measuring electrical output performances under high humidity conditions is shown in Figure S3.

The charge generation of the fiber-structured nanogenerator can be understood by the coupling effect between triboelectrification and electrostatic induction in Figure S4. At the original state, the PDMS tube and the Al wire are fully separated by sealing both edges (Figure S4a), and there is no charge transfer between them. When the PDMS tube is in full contact with the wire, a charge transfer is brought about, resulting in positive charges on the wire and negative ones on the PDMS (Figure S4b). When the external force recedes, the negative charges and the positive charges cannot be compensated. As a result, the positive charges are induced on the outer Al electrode attached onto the tube by the flow of electrons from the outer Al electrode to the Al wire through the external circuit (Figure S4c). As the PDMS tube reverts back to the original position, the negative charges on the PDMS tube can be fully screened, inducing an equal amount charges on the Al electrodes (Figure S4d). Subsequently, when the external impact is applied once again, the PDMS tube is reverted to the Au/Al wires. The induction of positive triboelectric charges on the Al electrode decreases. Consequently, the free electrons flow in a reversed direction from the Au/Al wire to Al electrode in order to eliminate the difference of electric potential (Figure S4e).

Woven fabrics are then produced by the interlacing of the fibers and bonded to a waterproof fabric for all-weather use of the FTENG under vertical contact-separation mode, as shown in Figure 3a. When the electrical output performance was measured in parallel under the same mechanical force, the nanogenerator can generate an output voltage and current of up to 40 V and 210 μA, respectively. The current increases as the number of the fibers increases, as shown in Figure 3b. To investigate the output power of the nanogenerator, resistors were used as external loads from 1 Ω to 1 GΩ; the instantaneous power of the external resistance reaches a peak value of 4 mW at a resistance of 10 MΩ, as shown in Figure 3c,d.

In the FTENG, which is a 2D network with the fibers, the fibers may be pressed together to produce a smooth-surfaced, stiff, dense material during the weaving

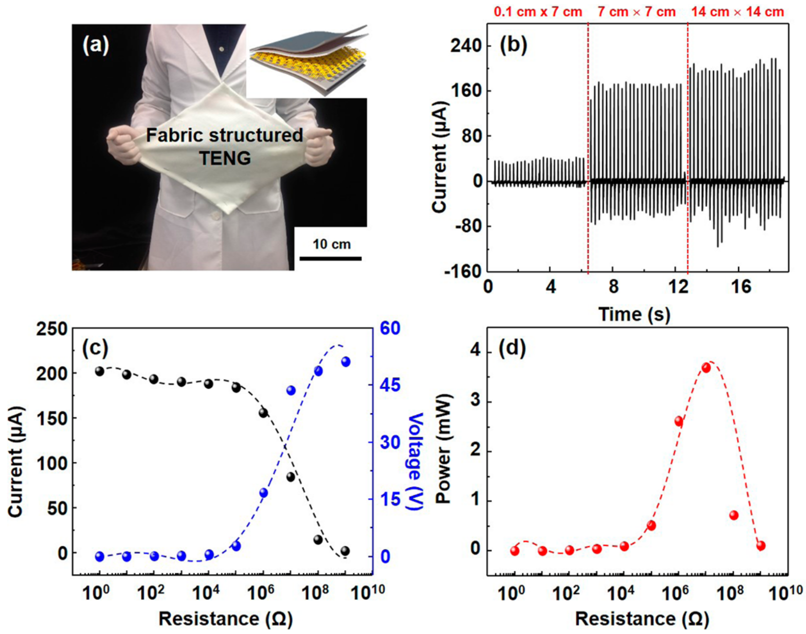

Figure 3. (a) Photograph and schematic image of FTENG. (b) Output current of the FTENG with the active area. (c) Output current and voltage and (d) instantaneous power of the FTENG as a function of resistance from 1 Ω to 1 GΩ.

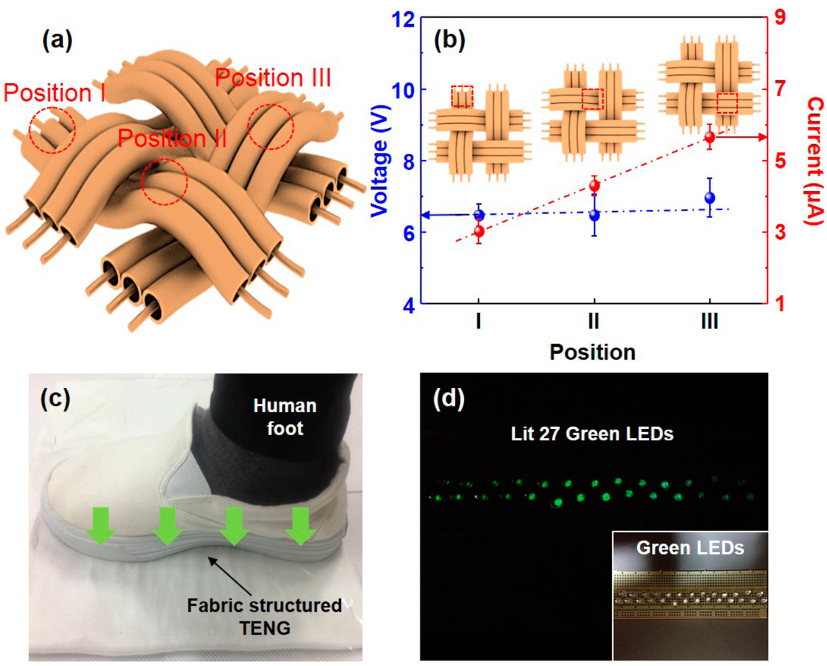

Figure 4. (a) Schematic image of FTENG composed of 6 × 6 fibers. The fibers may be pressed together to produce a smooth-surfaced, stiff, dense material during the weaving process, driving morphological change of the fibers. (b) Output voltage and output current from the fibers in each position. The photographs of (c) a footstep on the FTENG and (d) 27 commercial green LED lit up during walking.

process. This implies that the output signals from the FTENG depend on the position (I, II, and III) in the fabric, as shown in Figure 4a. Each position has flat fibers, curved fibers, and crossed fibers, respectively. Figure 4b shows the output voltage and the output current of the FTENG from the position (area = 0.5 cm × 0.5 cm). From positions I and II, an output current of about 3 μA was generated, although the output current in position II is a little larger. The output current is the highest (~6 μA) in position III, almost twice the output current from flat fibers. This indicates that the output power generation from each fiber in the FTENG is quite uniform and that there is no significant influence on the output power of the fibers, although the fibers may be pressed a little bit by the weaving process, showing the possibility of a large-area nanogenerator that is based on the woven

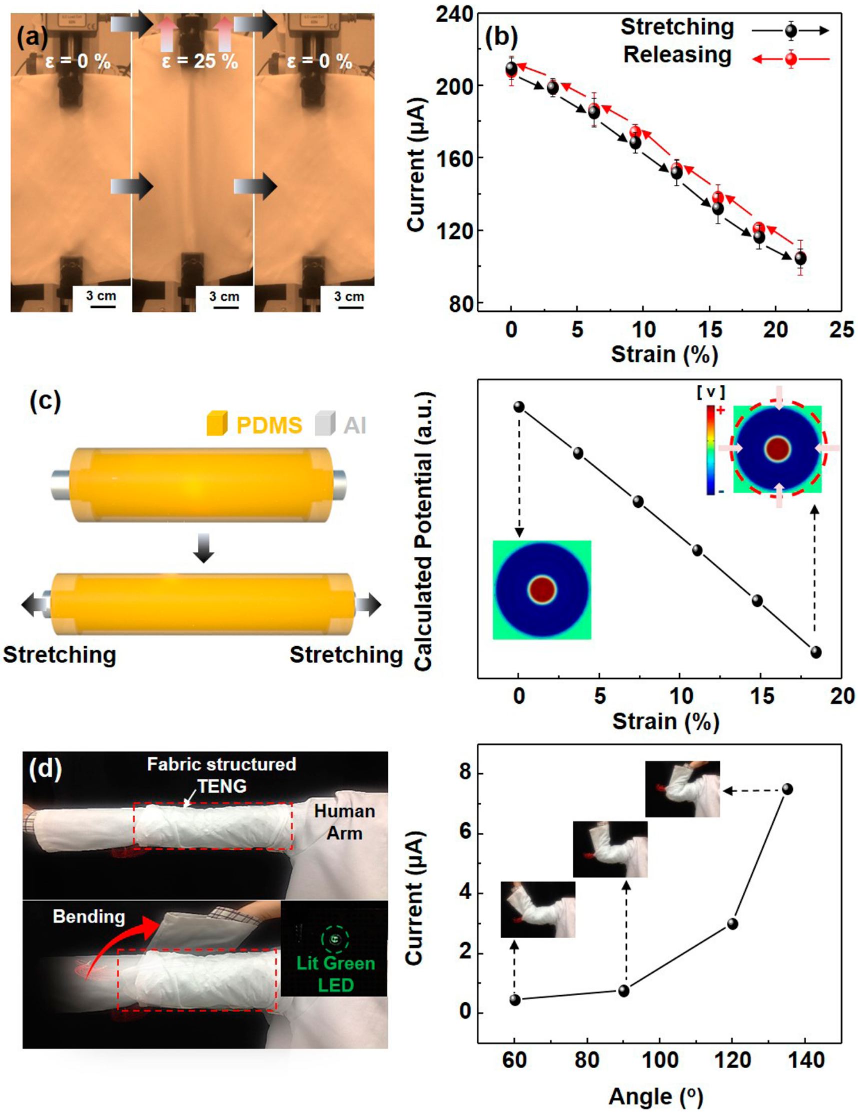

Figure 5. (a) Optical image of uniaxial tensile sample. (b) Change in the output current of the FTENG measured when it is stretched and released. The output current decreases with the strain up to 25%, but when it is released, the current returns the original value. (c) Schematic image of the fiber when it is stretched and the calculated potential with the strain. (d) Output current of the FTENG integrated in coats as a power-generating arm patch, as a function of bending angle from 60 to 135°.

fibers without any degradation. Actually, 27 green LEDs can be lit up by a human foot walking as shown in Figures 4c,d. Although a human's foot does not fully cover the active area of the device, it shows that the FTENG can effectively harvest energy from the human motion. Moreover, the FTENGs with larger dimensions, easily fabricated by weaving more fibers, can be extended to square and subway.

Knowing the stretch and recovery characteristics of the fabric is also a very important first step in determining the possible applications. Figure 5a shows the photographs of a stretching test with a length increase of over 25%. It shows that the fabric can almost perfectly recover its original shape after release of the tensile force. This is clearly seen in the movie included in the Supporting Information. It means that plastic deformation does not occur in fabric, and elastic deformation and recovery occur during the process. When the fabric was stretched up to strain of about 22% along the both sides, the output current decreases by about 47.6%, from 210 to 110 μA (Figure 5b). We ascribe this to the decrease in the radius of the PDMS tube induced by the stretching of the fiber. Actually, we showed the output power decreased as the radius of tube decreases in Figures 2b and S2. However, when it was released, the output power reversibly recovered its original value, showing stable electrical output performance. The FTENG is then integrated to coats as a power-generating arm patch, becoming a power cloth. The generated current from nanogenerator can reach 1 μA when the FTENG bends at 60 °. When the bending angle increases to 130 °, the current increases to 7 μA, lighting up the green LED during motion of the elbow in Figures 5d and S6.

CONCLUSIONS

We demonstrated highly stretchable 2D fabrics as a wearable triboelectric nanogenerator for powering wearable electronic devices. First, fibers were prepared, which mainly consist of Al wires and PDMS tubes with a high-aspect-ratio nanotextured surface with vertically aligned nanowires. The fiber-structured nanogenerator showed an output power of 40 V and 10 μA, a stable output performance even under a high humidity environment condition and under a cycled compressive force of 50 N. The FTENG was then fabricated by weaving the fibers, followed by bonding to a waterproof fabric for all-weather use. It showed a high output voltage and current value of 40 V and 210 μA, respectively, corresponding to an instantaneous power output of 4 mW under same cycled compressive force. The fabric was also found to be quite stretchable up to over 25%, enough for use in smart clothing applications and other wearable electronics. Finally, we achieved a stable output performance from the nanogenerator even under a highly stretched condition. Additionally, the FTENG was employed in applications for footstep-driven large-scale power mats during walking and power clothing attached to the elbow. It is believed that this approach provides a promising candidate for high-performance and stable nanogenerator toward self-powered wearable electronics in the near future.

EXPERIMENTAL METHODS

Fabrication of the Fiber-Structured Triboelectric Nanogenerator. PDMS (Sylgard 184, Dow Corning), aluminum wires and foils were used for the fabrication of the fiber-structured triboelectric nanogenerator. The base monomer and curing agent are mixed in a mass ratio of 10:1, followed by vacuum drying for 1 h, producing a PDMS solution. To make the PDMS tubes, aluminum wires with various radii were immersed in the solution and pulled out very slowly for uniform wall thickness (~400 μm) of the tube. The resultant tubes were dried in atmosphere at 90 °C for 20 min. If they were immersed in acetone for 20 min, then the PDMS could be easily peeled off from the aluminum wire, producing PDMS tubes. The inner wall of the tube is etched by using the RIE process with 37 sccm CF_4 and 13 sccm O_2 mixtures at 270 W for 20 min, producing PDMS wires with an average length of 1 μm and a radius ranging from 80 to 125 nm.

For the metallic wires inserted into the PDMS tube, ZnO nanowires were grown on the aluminum wires by a hydrothermal process. For the growth, the aluminum wires were immersed in a 2.5 mM ethanolic solution of zinc acetate (ZnAc) dehydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$], and the wires were then annealed at 300 °C in a furnace for 30 min. The wires were loaded into Teflon-sealed stainless autoclave and immersed in the nutrient growth solution with 1:1 ratio of zinc nitrate and 20 mM hexamethylenetetramine (HMTA) and were kept in an oven at 90 °C for 3 h. The 100 nm thick Au film was deposited on the ZnO nanowires by e-beam evaporation at a base pressure 3.0×10^{-6} Torr.

The Au/Al wires were inserted into the PDMS tubes and were then sealed at both sides. The resultant fiber was wrapped around the flexible Al thin film, which acted as the other electrode.

Characterization. We measured the output voltages and currents of the fiber- and fabric-structured triboelectric nanogenerators under a vertical compressive strain, measured by a Tektronix DPO 3052 Digital Phosphor Oscilloscope and low-noise current preamplifier (model no. SR570, Stanford Research Systems, Inc.). A pushing tester (Labworks Inc., model no. ET-126-4) was used to create vertical compressive force in the nanogenerator. The morphologies of the fibers were characterized by a Nano 230 field-emission scanning electron microscope (FEI, USA). Stretchability tests were carried out with Mecmesin Multitest i-1 (Slinfold, United Kingdom).

A homemade apparatus was employed to examine the effect of the humidity on the output current of the triboelectric nanogenerators. The humid air from a humidifier was introduced into the chamber under 1 atm of dry air background. The nanogenerators were then placed in the chamber and the output voltage and current was measured under extreme conditions of high humidity (~95% RH).

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

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Supporting Information Available: Output voltages and currents of fiber which consists of PDMS tube and Al wire with and without nanowires; output performance with various radius of metal wire and PDMS tube; schematic image of homemade apparatus in order to measure the output performance under harsh environment; working mechanism of the FTENG under external force at short-circuit condition; video showing a uniaxial tensile test of the FTENG over 25% and the change in output current as a function of the strain when it is stretched and released; and photographs and generated current of FTENG when the FTENG is bent at an angle of 135°. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b02010.

REFERENCES AND NOTES

1. Zhou, T.; Zhang, C.; Han, C. B.; Fan, F. R.; Tang, W.; Wang, Z. L. Woven Structured Triboelectric Nanogenerator for Wearable Devices. *ACS Appl. Mater. Interfaces* **2014**, *6*, 14695–14701.
2. Zhong, J.; Zhang, Y.; Zhong, Q.; Hu, Q.; Hu, B.; Wang, Z. L.; Zhou, J. Fiber-Based Generator for Wearable Electronics and Mobile Medication. *ACS Nano* **2014**, *8*, 6273–6280.
3. Fan, F.-R.; Tian, Z.-Q.; Wang, Z. L. Flexible Triboelectric Generator. *Nano Energy* **2012**, *1*, 328–334.
4. Yang, Y.; Zhang, H.; Zhong, X.; Yi, F.; Yu, R.; Zhang, Y.; Wang, Z. L. Electret Film-Enhanced Triboelectric Nanogenerator Matrix for Self-Powered Instantaneous Tactile Imaging. *ACS Appl. Mater. Interfaces* **2014**, *6*, 3680–3688.
5. Wang, S.; Niu, S.; Yang, J.; Lin, L.; Wang, Z. L. Quantitative Measurements of Vibration Amplitude Using a Contact-Mode Freestanding Triboelectric Nanogenerator. *ACS Nano* **2014**, *8*, 12004–12013.
6. Yang, J.; Chen, J.; Yang, Y.; Zhang, H.; Yang, W.; Bai, P.; Su, Y.; Wang, Z. L. Broadband Vibrational Energy Harvesting Based on a Triboelectric Nanogenerator. *Adv. Energy Mater.* **2014**, *4*, 1301322–1301330.
7. Bae, J.; Lee, J.; Kim, S.; Ha, J.; Lee, B.-S.; Park, Y.; Choong, C.; Kim, J.-B.; Wang, Z. L.; Kim, H.-Y.; et al. Flutter-Driven Triboelectrification for Harvesting Wind Energy. *Nat. Commun.* **2014**, *5*, 4929–4937.
8. Yang, Y.; Zhu, G.; Zhang, H.; Chen, J.; Zhong, X.; Lin, Z.-H.; Su, Y.; Bai, P.; Wen, X.; Wang, Z. L. Triboelectric Nanogenerator for Harvesting Wind Energy and as Self-Powered Wind Vector Sensor System. *ACS Nano* **2013**, *7*, 9461–9468.
9. Zhu, G.; Su, Y.; Bai, P.; Chen, J.; Jing, Q.; Yang, W.; Wang, Z. L. Harvesting Water Wave Energy by Asymmetric Screening

of Electrostatic Charges on a Nanostructured Hydrophobic Thin-Film Surface. *ACS Nano* **2014**, *8*, 6031–6037.
10. Su, Y.; Wen, X.; Zhu, G.; Yang, J.; Chen, J.; Bai, P.; Wu, Z.; Jiang, Y.; Wang, Z. L. Hybrid Triboelectric Nanogenerator for Harvesting Water Wave Energy and as a Self-Powered Distress Signal Emitter. *Nano Energy* **2014**, *9*, 186–195.
11. Zhu, G.; Lin, Z.-H.; Jing, Q.; Bai, P.; Pan, C.; Yang, Y.; Zhou, Y.; Wang, Z. L. Toward Large-Scale Energy Harvesting by a Nanoparticle-Enhanced Triboelectric Nanogenerator. *Nano Lett.* **2013**, *13*, 847–853.
12. Bai, P.; Zhu, G.; Lin, Z.-H.; Jing, Q.; Chen, J.; Zhang, G.; Ma, J.; Wang, Z. L. Integrated Multilayered Triboelectric Nanogenerator for Harvesting Biomechanical Energy from Human Motions. *ACS Nano* **2013**, *7*, 3713–3719.
13. Yang, J.; Chen, J.; Su, Y.; Jing, Q.; Li, Z.; Yi, F.; Wen, X.; Wang, Z.; Wang, Z. L. Eardrum-Inspired Active Sensors for Self-Powered Cardiovascular System Characterization and Throat-Attached Anti-Interference Voice Recognition. *Adv. Mater.* **2015**, *27*, 1316–1326.
14. Chen, X.; Iwamoto, M.; Shi, Z.; Zhang, L.; Wang, Z. L. Self-Powered Trace Memorization by Conjunction of Contact-Electrification and Ferroelectricity. *Adv. Funct. Mater.* **2015**, *5*, 739–747.
15. Jing, Q.; Zhu, G.; Wu, W.; Bai, P.; Xie, Y.; Han, R. P.S.; Wang, Z. L. Self-powered Triboelectric Velocity Sensor for Dual-Mode Sensing of Rectified Linear and Rotary Motions. *Nano Energy* **2014**, *10*, 305–312.
16. Zhu, G.; Pan, C.; Guo, W.; Chen, C.-Y.; Zhou, Y.; Yu, R.; Wang, Z. L. Triboelectric-Generator-Driven Pulse Electrodeposition for Micropatterning. *Nano Lett.* **2012**, *12*, 4960–4965.
17. Zhong, J.; Zhang, Y.; Zhong, Q.; Hu, Q.; Hu, B.; Wang, Z. L.; Zhou, J. Fiber-Based Generator for Wearable Electronics and Mobile Medication. *ACS Nano* **2014**, *8*, 6273–6280.
18. Kim, J.; Lee, M.; Shim, H. J.; Ghaffari, R.; Cho, H. R.; Son, D.; Jung, Y. H.; Soh, M.; Choi, C.; Jung, S.; et al. Stretchable Silicon Nanoribbon Electronics for Skin Prosthesis. *Nat. Commun.* **2014**, *5*, 5747–5757.
19. Xie, Y.; Liu, Y.; Zhao, Y.; Tsang, Y. H.; Lau, S. P.; Huang, H.; Chai, Y. Stretchable All-Solid-State Supercapacitor with Wavy Shaped Polyaniline/Graphene Electrode. *J. Mater. Chem. A* **2014**, *2*, 9142–9149.