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RAPID COMMUNICATION

Flexible triboelectric generator!

Feng-Ru Fan[a,b], Zhong-Qun Tian[b], Zhong Lin Wang[a,*]

[a]*School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA*
[b]*State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China*

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Abstract
Charges induced in triboelectric process are usually referred as a negative effect either in scientific research or technological applications, and they are wasted energy in many cases. Here, we demonstrate a simple, low cost and effective approach of using the charging process in friction to convert mechanical energy into electric power for driving small electronics. The triboelectric generator (TEG) is fabricated by stacking two polymer sheets made of materials having distinctly different triboelectric characteristics, with metal films deposited on the top and bottom of the assembled structure. Once subjected to mechanical deformation, a friction between the two films, owing to the nano-scale surface roughness, generates equal amount but opposite signs of charges at two sides. Thus, a triboelectric potential layer is formed at the interface region, which serves as a charge “pump” for driving the flow of electrons in the external load if there is a variation in the capacitance of the system. Such a flexible polymer TEG gives an output voltage of up to 3.3 V at a power density of ~10.4 mW/cm^3. TEGs have the potential of harvesting energy from human activities, rotating tires, ocean waves, mechanical vibration and more, with great applications in self-powered systems for personal electronics, environmental monitoring, medical science and even large-scale power.

Introduction

Energy harvesting and conversion devices using nanotechnology have received increasing interest recently because they are likely to play a vital role in building and driving self-powered nanodevices and nanosystems [1-7]. In 2006, our group demonstrated the first piezoelectric nanogenerator for successfully converting mechanical energy into electricity using ZnO nanowires [8]. Subsequently, various materials and designs of nanogenerators based on piezoelectric effect have been demonstrated [9-15]. The output power of a nanogenerator is high enough to drive a commercial light-emitting diode (LED), small liquid crystal display and even self-powered wireless data transmission system [7,16,17]. A power generation density of 1-10 mW/cm^3 has been achieved.

As a general principle, an approach that can generate electric charges, separate the charges with opposite signs

*Corresponding author. Tel.: +1 404 894 8008; fax: +1 404 384 3852.
E-mail addresses: zlwang@gatech.edu, zhong.wang@mse.gatech.edu (Z. Lin Wang).

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and use the potential generated by them to drive a flow of free electrons is termed as an electric generator, which can be based on electromagnetic, piezoelectric, pyroelectric [18,19] and even electrostatic effects. The nanogenerator relies on the piezoelectric potential generated by the ZnO nanowire to achieve the listed purposes. Alternatively, triboelectric associated electrostatic phenomena are most common phenomena in our daily life, from walking to driving, but it has been ignored as an energy source for electricity. It will be wonderful if one can use the electric charges/potential generated by a tribological process to generate electricity. The electrostatic microgenerators have been developed and applied in research area of microelectromechanical systems (MEMS) [20–22]. But the design is mainly based on inorganic materials and the fabrication of the device requires a complex process with sophisticated operation. In this paper, we report a simple, all-polymer based flexible generator for harvesting mechanical energy through a triobological process. By stacking two thin polymer films made of Kapton and polyester (PET), a charge generation, separation and induction process can be achieved through a mechanical deformation of the polymer film. A power output density of ~10.4 mW/cm^3 has been achieved at an output voltage of 3.3 V. This is a simple, low-cost, readily scalable fabrication process of generator that can convert random mechanical energy in our living environment into electricity using conventional flexible/foldable polymer materials. This technology has a great potential for scaling up to power mobile and personal electronics used in environmental monitoring, personal medical networks, electronic emergency equipment and other self-powered systems.

Experimental

Fabrication of the generator

A typical structure of a polymer based triboelectric generator (TEG) is schematically shown in Fig. 1a. The TEG is like a sandwiched structure with two different polymer sheets stacked alternatively without interlayer binding. One rectangular (4.5 cm × 1.2 cm) Kapton film (125 μm in thickness, Dupont 500 HN) was placed onto another flexible PET substrate (Dura-Lar, 220 μm in thickness). The two short edges of the device were sealed with ordinary adhesive tape and to ensure an adequate contact between two polymer sheets. Both the top and bottom surfaces of the structure were covered with a thin

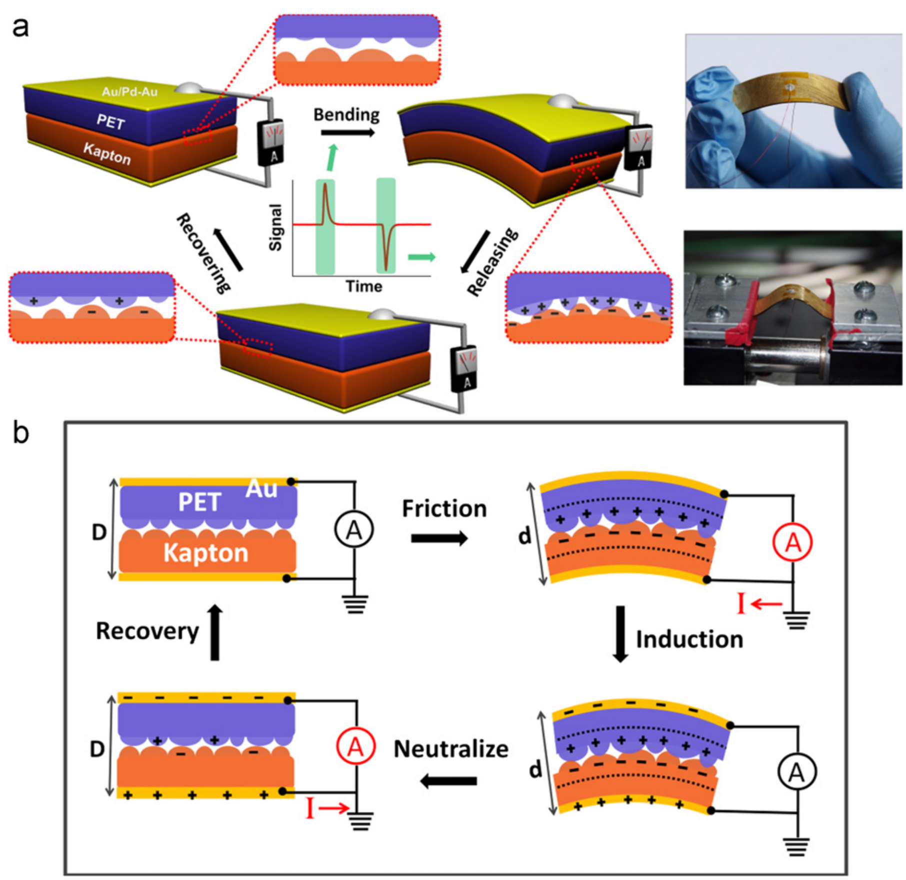

Figure 1 Schematic illustration of the structure and working principle of the triboelectric generator. (a) The structure of an integrated generator in bending and releasing process and related electrical measurement tests. Photographic images of a flexible TEG and mechanical bending equipment. (b) Proposed mechanism of a TEG (see text for details): charges are generated by frictioning two polymer films, which results in the creation of a triboelectric potential layer at the interfacial region (indicated by dashed lines); a mechanical compression results in a change in the distance between the two electrodes (from D to d), thus, under the driving of the triboelectric potential, a change in system capacitance leads to the flow of current in the external load which drives the flow of the free electrons across the electrodes to minimize the total energy of the system.

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layer of Au alloy film (100 nm in thickness) by sputter coating. The metal films play two important roles here (1) producing equal but opposite sign mobile charges via the electrostatic induction of the tribology generated potential at the interfacial region; (2) served as common electrodes for directly connecting the device with an external circuit. The entire preparation process of the device is simple, which make it easy to be upgraded for large-scale production. Consequently, our design uses less materials and process steps that will result in cost savings.

Results and discussions

Power generation mechanism of TEG

A TEG device and power generation mechanism is illustrated in Fig. 1a and b. As the external force is applied to the device during the deformation process, two insulating polymeric materials are touched and rubbed with each other. Although the surfaces of the two polymer films appear bright and smooth under light, they are in fact non-uniform with a different roughness of hundreds of nanometers (Fig. S1 in Supporting Information (SI)). Mechanical compression between the two layers of polymers leads to a relative sliding. As a result of small degree of friction, electrostatic charges with opposite signs are generated and distributed on the two surfaces of the polymer films due to the presence of the nanometer scale roughness, with the PET film positively charged and Kapton film negatively charged, and forming an interface dipole layer, which is called a triboelectric potential layer. Such a dipole layer forms an inner potential layer between the planar metal electrodes. The induced charges will not be quickly conducted away or neutralized owing to the insulative nature of the polymer films. To minimize the energy created by the triboelectric potential, electrostatically induced free-charges will flow across the external load between the two electrodes. Simultaneously, mechanical compression between the two layers of polymers leads to a small reduction in the interplanar distance (from D to d). If C is the capacitance of the system and V is the voltage across the two electrodes, a current generated across an external load is

$$I = C\frac{\partial V}{\partial t} + V\frac{\partial C}{\partial t}$$

The first term is the variation in the potential across the top and bottom electrodes owing to the electrostatically induced charges. The second term is the change in the capacitance of the system as the distance between the top and bottom electrodes being changed when the unit was being mechanically deformed. This process contributes to the current only if there is a potential drop being maintained across the two electrodes, which is caused by the tribo-electric effect. A change in system capacitance is due to a variation in the inter-plane distance between the two electrodes as a result of mechanical compression. These are the contributions made to the observed first peak in the output voltage/current (see Fig. 2). A detailed description of the entire power generation process is presented in Fig. S2.

Once the tribology force is removed and the structure is released, the two polymer films recover their original shapes, and the tribologically generated positive and negative charges may neutralize, and the electrostatic induced charges across the two electrodes recombine.

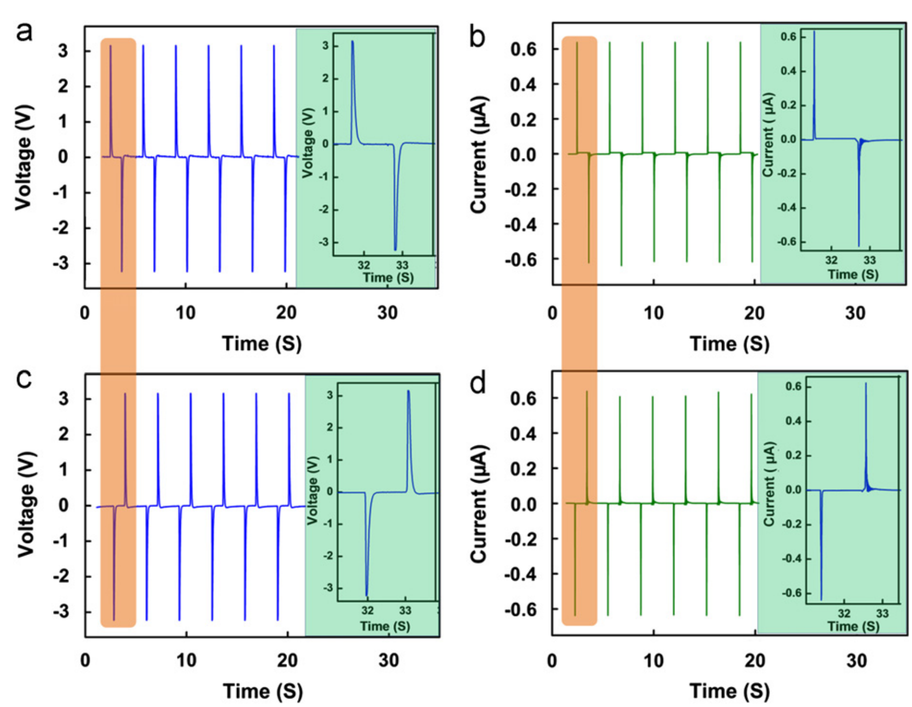

Figure 2 Electric output of a typical triboelectric nanogenerator. (a) Open circuit voltage and (b) short circuit current when forward-connected to measurement system. (c) Open circuit voltage and (d) short circuit current when reverse-connected to measurement system. The insets are enlarged views of single signal peak in the voltage and current outputs. Note the forward and reverse connections are defined in reference to the measurement voltmeters for testing if the output signal is truly from the TEG.

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This is the process for outputting a current peak in opposite direction. The electricity generation process presented above is analogous to that of the piezoelectric AC nanogenerator [11] except the driving force here is the triboelectric potential rather than piezopotential. It is important to note that the triboelectric effect was not present in the piezoelectric nanogenerators we had developed previously, as discussed in details at the end.

Electric output performance characterization

To investigate the performance of the polymer TEG, we made a detailed electrical characterization of the system. Owing to the presence of the polymer insulation between the two metal electrodes, the device exhibited clearly an open-circuit behavior in *I–V* measurement (Fig. S3). During periodical bending and releasing of TEG using a linear motor in a cyclic agitation (at 0.33 Hz and 0.13% strain), the maximum output voltage and current signal were up to 3.3 V and 0.6 μA, respectively (Fig. 2). A peak output power density of ~10.4 mW/cm^3 has been achieved, which is compatible to that received based on a more complex design [7]. The electric energy produced by polymer TEG was stored and used to light up a commercial LED (Video S1 in SI). The generated charges can be stored using a rectifier and storage device connecting 10 capacitors (22 μF) in parallel [16,23]. The voltage across a single capacitor was monitored in the charging process and reached 0.2 V at the last. The entire charging process only requires the device to run 450 cycles of mechanical deformation (Fig. 3e and f). The device also showed good durability and stability even 30 days after being fabricated and tested for ~10^5 cycles (Fig. S4).

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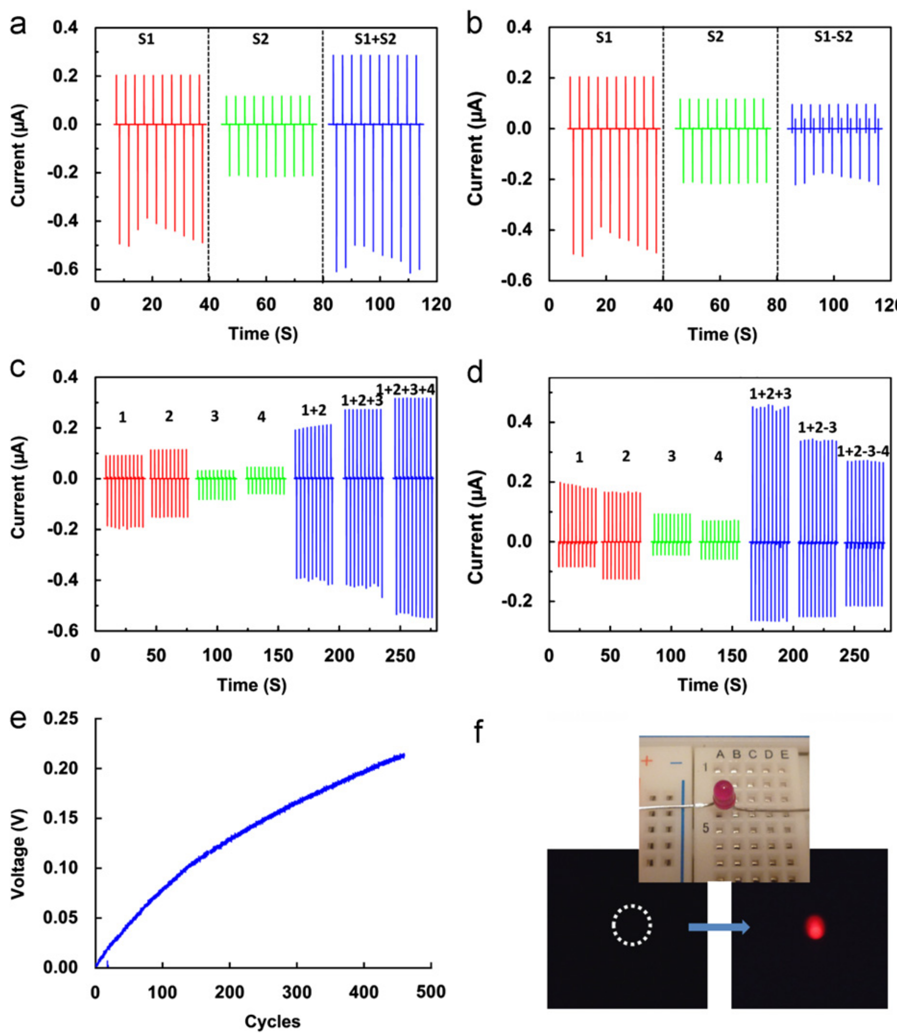

Figure 3 Linear superposition tests and storage of the TEG generated electrical energy and its application for driving a commercial LED. The total output currents of two TEGs connected in parallel with (a) the same polarity (S1 + S2) and (b) reverse polarity (S1 − S2), showing linear superposition as expected. The total output currents of four TEGs in various forms of connections when (c) forward-connected or (d) reverse-connected to the measurement system. These sets of tests are to prove that the observed signals are truly generated by TEGs, and their output obeys the basic principle of linear circuit. (e) The charging curve across a single capacitor when pumped by a TEG, showing a steady increase in the storage charges with the increase of charging time. (f) Images of a commercial red LED in dim background before and the moment of being lit up by the stored energy.

The electricity output of the TEGs should satisfy linear superposition criterion in the basic circuit connections [11]. We did the current measurement when two or four TEGs were connected in parallel to examine the linear superposition of currents. The results show that when two TEGs were connected in the same direction, the total output current is enhanced and approximately equal to the sum of the individual output currents (Fig. 3a). In comparison, when two TEGs are connected in parallel but in reverse directions, the total output current is decreased (Fig. 3b). The same conclusion was also obtained when four TEGs were tested. The total output current can be enhanced (in the same direction) or reduced (in reverse direction) in various forms of connections, whether when forward-connected or reversely-connected to the measurement system (Fig. 3c and d). The above results not only rule out possible artifacts, but also indicate that we can greatly improve the output current and power per unit area by connecting multiple TEGs in parallel and assembling them layer by layer due to their thin flat-panel structures.

The power generation performance of the TEG is affected by the bending frequency and strain as well as straining rate. Fig. 4a shows the output current signal of a TEG under various bending frequencies ranging from 0.33 to 5 Hz for a given strain (0.13%). The output of the TEG was not affected significantly by an increase in the low frequency range (0.33–1 Hz). When the frequency is higher than 1 Hz, the electrical outputs increase with the frequency. A possible cause of this phenomenon is that the positive and negative potentials on the polymer surfaces are not completely neutralized under the high-frequency mechanical agitation, leading to an accumulation of residual charges on the electrodes. For a given frequency (0.33 Hz), an increase in the strain generally increased the magnitude of the electrical output (Fig. 4b). It should be noted that the TEG is able to work in a range of low frequencies and low strain (Videos S2–4). This means that it can effectively harvest energy from slow and gentle mechanical movement, such as human walking, light wind blowing and water waving.

Effect of the materials in the triboelectric series

The performance of TEG is also affected by the nature of the materials used. In general, organic materials may be arranged in a table according to the amount of positive charge that can be transferred, which is known as the triboelectric series (Fig. S5) [24]. It is usually analogous to the electrochemical series of materials that describes the tendency of a material to gain or loss electrons. The series lists materials towards the bottom of the series in an order of decreasing tendency to charge positively (lose electrons), and increasing tendency to charge negatively (gain electrons). Further away two materials are separated apart from each other in the series, the greater the charge transferred, and vice versa. We selected three types of polymer materials for the study, Kapton, PET and PVC (polyvinyl chloride), which are at different positions in the triboelectric series. Both Kapton and PVC (negative) are far away from the location of PET (positive) in the list. As shown in Fig. 4c and d, using the combination of Kapton-PET or PVC-PET, we can achieve high-output power generation. In contrast, Kapton and PVC are near to each other in the series that will only exchange a small amount of charges, resulting in low-output voltage and current. Our study indicates that to achieve a higher performance, we should select materials that are further away from each other in

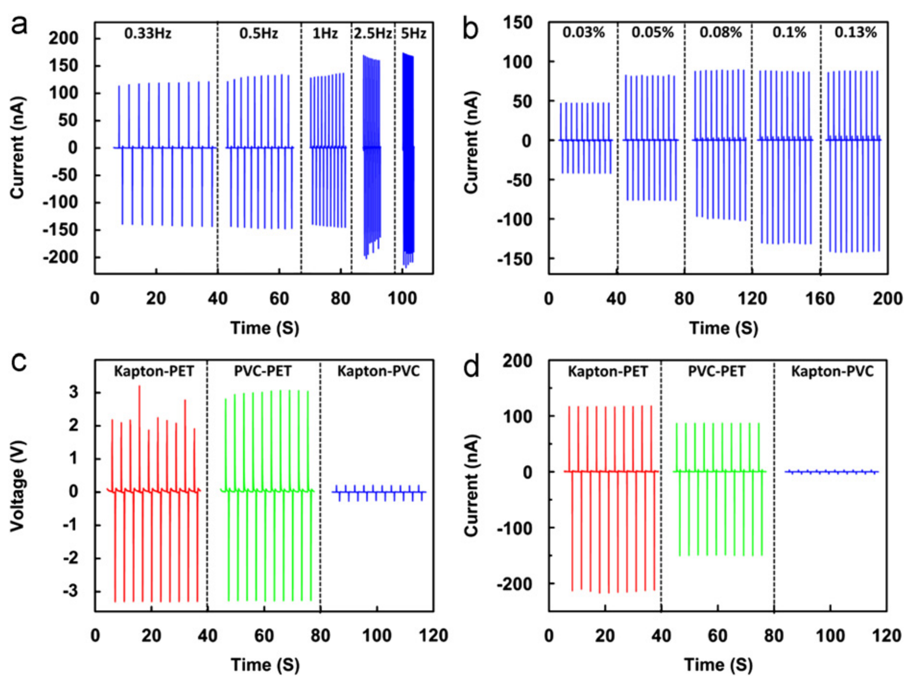

Figure 4 Performance characterization of the TEGs under different experimental conditions and made using different materials. Output current measurements of a TEG subject to increasing bending-release (a) frequencies and (b) strains. (c) Output voltage and (d) output current of TEGs based on different combinations of three materials, Kapton, PVC and PET. This set of experiments proves that the output of the TEGs is closely related to the difference in triboelectric property of the polymer materials.

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the series due to their different ability to attract electrons. In other words, the output efficiency can be controlled using different materials as the components of the device.

Difference between TNG and PNG

The triboelectric generator presented here is different from the piezoelectric nanogenerator (PNG) in design. An PNG is built based on a single layer of polymer substrate, on which structures of ZnO nanowires are fabricated. The entire structures are fully packaged as one piece without any internal friction between the components. Further, owing to the finite conductivity of ZnO nanowires, there is little triboelectric effect present. The TEG is made of a simply stacked polymer films of different triboelectric characteristics (Figs. S5 and S7), between which there is no binding and possibly a small gap with freedom of relative small sliding. A working TEG must have two electrodes on the top and bottom surfaces of the stack; the two electrodes are at open-circuit state due to the insulative nature of the polymer layers (Fig. S3). A completely sealed double-layer structure with little freedom of sliding shows a rather low output (Figs. 5a and b). A structure made of a single polymer layer shows no electric output (Figs. 5c and d). Our controlled experiments show that the triboelectric effect was not responsible for the electric output observed in PNGs. Therefore, the triboelectric nanogenerator offers an alternative way for harvesting mechanical energy, and it by no means contradicts in principle with the PNG. Both approaches use different physical mechanisms for generating electricity, although there are some similarity in physical pictures [11], such as charge generation, charge separation and potential driven flow of induced electrons in external load.

Conclusions

Although we normally believe that charging of organic materials are a negative effect for scientific research and even practical application, in this paper, we have demonstrated an innovative and effective approach for harvesting energy using the tribology process. The TEG relies on the charge pumping effect of the triboelectric potential, and it is a simple, low-cost, scalable engineering approach. Based on a two layered structure, the electrical output achieved a peak voltage of 3.3 V and current of 0.6 μA with a peak power density of ~10.4 mW/cm^3. The reported TEG has several unique advantages in comparison to the existing energy harvesting methods. First, this is a new class of generators based on a novel principle and method, which is likely to open up new areas of research in using organic materials for energy harvesting. Second, the entire fabrication process does not require expensive raw materials or sophisticated equipments, which would benefit mass industrial production and practical applications of the technology. Lastly, the device is based on flexible polymer sheets, which have manufacturability, durability and capability of integration with other processing technologies. The TEG exhibits a potential of harvesting energy from human activities, rotating tires, ocean waves, mechanical vibration and more, with great applications in self-powered

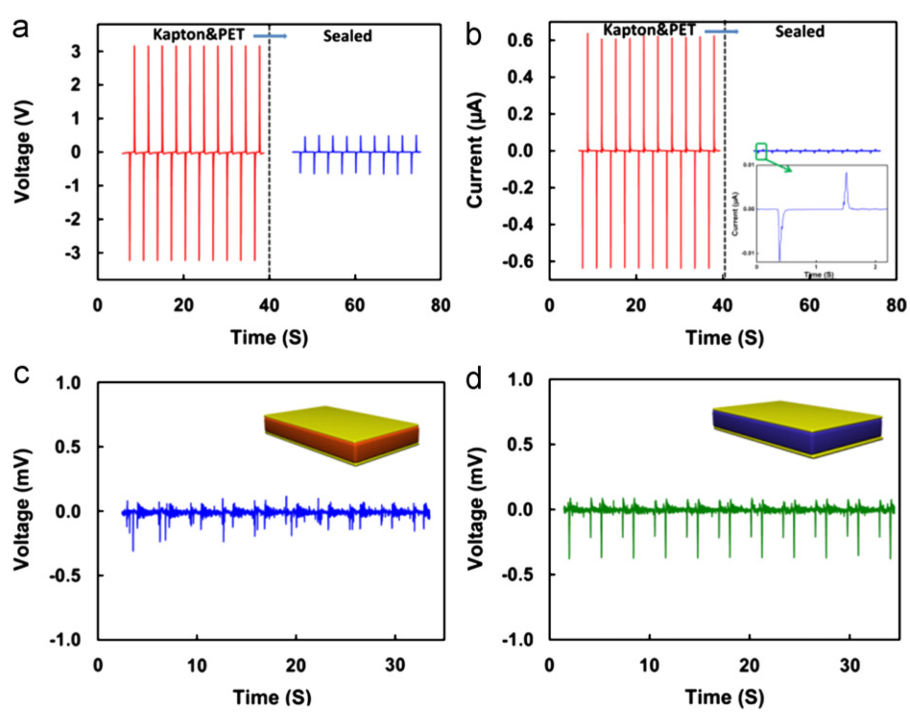

Figure 5 Performance characterization of the polymer TEGs with different materials (a–b) Kapton and PET before and after the internal friction layer is stuck with glue. (c) One Kapton film and (d) one PET film coated with metal electrodes. (a) and (b) indicate that a small gap with freedom of relative small sliding is necessary in TEG, which does not exist in PNG. (c) and (d) indicate that if there is only one polymer film coated with metal electrodes on the top and bottom surfaces, the triboelectric effect will not exist. The PNG usually just adapted this design. All of these results suggest that the triboelectric effect was not responsible for the electric output observed in PNG.

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systems for personal electronics, environmental monitoring, medical science and even possibly large-scale power.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2012.01.004.

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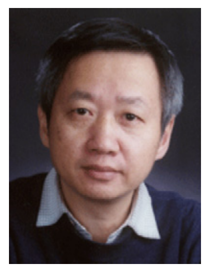
Feng-Ru Fan received his B.S. degree in Chemistry from Xiamen University, China in 2006. He is a Ph.D. candidate at College of Chemistry and Chemical Engineering, Xiamen University. From 2008 to 2011, he was as a visiting student in Zhong Lin Wang's group at Georgia Institute of Technology. His research interests include nanogenerators and self-powered nanosystem, preparation and applications of metal-semiconductor hybrid devices, synthesis and characterization of novel nanostructures with functional materials.



Zhong-Qun Tian received his B.S. degree in Chemistry from Xiamen University, China in 1982. He moved to University of Southampton in 1983 and worked on surface-enhanced Raman spectroscopic studies on electrochemical deposition and adsorption with Prof. Martin Fleischmann. After obtaining a Ph.D. from University of Southampton in 1987, he returned to Xiamen University. He was promoted to full professor in 1992 and is serving as the director of State Key Laboratory for Physical Chemistry of Solid Surfaces since 2003. His main research interests are surface-enhanced Raman spectroscopy, spectro-electrochemistry and nano-electrochemistry. He has received several major grants and prestigious awards in China. He is a Member of Chinese Academy of Sciences, Fellow of the Royal Society of Chemistry, Titular Member of Division of Physical and Biophysical Chemistry of IUPAC and the Chairman of the Chinese Electrochemical Society.

Zhong Lin (ZL) Wang received his Ph.D. from Arizona State University in physics. He now is the Hightower Chair in Materials Science and Engineering, Regents' Professor, Engineering Distinguished Professor and Director, Center for Nanostructure Characterization, at Georgia Tech. Dr. Wang has made original and innovative contributions to the synthesis, discovery, characterization and understanding of fundamental physical properties of oxide nanobelts and nanowires, as well as applications of nanowires in energy sciences, electronics, optoelectronics and biological science. His discovery and breakthroughs in developing nanogenerators established the principle and technological road map for harvesting mechanical energy from environment and biological systems for powering a personal electronics. His research on self-powered nanosystems has inspired the worldwide effort in academia and industry for studying energy for micro-nano-systems, which is now a distinct disciplinary in energy research and future sensor networks. He coined and pioneered the field of piezotronics and piezo-phototronics by introducing piezoelectric potential gated charge transport process in fabricating new electronic and optoelectronic devices. Details can be found at: http://www.nanoscience.gatech.edu.