Nano Energy (▮▮▮▮) ▮, ▮▮▮-▮▮▮

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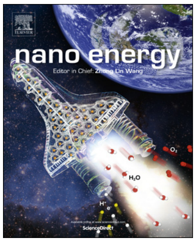

RAPID COMMUNICATION

Q3 Hybrid triboelectric nanogenerator for harvesting water wave energy and as a self-powered distress signal emitter

Yuanjie Su[a,b,1], Xiaonan Wen[a,1], Guang Zhu[a], Jin Yang[a], Jun Chen[a], Peng Bai[a], Zhiming Wu[b], Yadong Jiang[b],
Q1 Zhong Lin Wang[a,c,*]

[a]*School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA*
[b]*State Key Laboratory of Electronic Thin Films and Integrated Devices, School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC), Chengdu 610054, China*
[c]*Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing, China*

Received 15 June 2014; received in revised form 1 July 2014; accepted 10 July 2014

KEYWORDS
Energy harvesting;
Water wave;
Falling drops;
Self-powered distress signals emitter

Abstract

In this paper, a hybrid triboelectric nanogenerator (TENG) has been developed for simultaneously harvesting the electrostatic energy and mechanical impact energy from water wave. It is comprised of two parts: an interfacial electrification enabled TENG (IE-TENG) and an impact-TENG. The IE-TENG, composed of a fluorinated ethylene propylene thin film and an array of electrodes underneath, is used to harvest electrostatic energy arising from the water-solid interface. The impact-TENG, constructed with nanostructured polytetrafluoroethylene (PTFE) thin films and elastic wavy electrodes, is used to scavenge the mechanical impact energy from water wave. Under water waves propagating at a speed of 0.5 m/s, the short-circuit current of the IE-TENG and impact-TENG can reach 5.1 μA and 4.3 μA, respectively, which is able to drive nearly 50 LEDs simultaneously. Considering that natural water bodies may contain minerals and salt, the influence of NaCl concentration on the electric output of device has been investigated. Moreover, the hybrid TENG was developed as a self-powered distress signals emitter that may be used for life saving in water landing or swimming in evening. Considering the scalability of this

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Q4 [*]Corresponding author at: School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA.
E-mail address: zlwang@gatech.edu (Z. Lin Wang).

[1] These authors contributed equally to the work.

http://dx.doi.org/10.1016/j.nanoen.2014.07.006

Please cite this article as: Y. Su, et al., Hybrid triboelectric nanogenerator for harvesting water wave energy and as a self-powered distress signal emitter, Nano Energy (2014), http://dx.doi.org/10.1016/j.nanoen.2014.07.006

technology, this work demonstrates the great potential of TENG in areas of hydropower harvesting, environmental monitoring and maritime search and rescue.

Introduction

Owing to vast distribution of water systems and the tremendous mechanical energy possessed by water, hydropower is one of the most universal renewable energy resources on the earth. This energy, including ocean waves, tides and rivers, is released constantly and continuously, and it is almost unaffected by day or night, season, weather and climate [1]. According to statistical results, the viable offshore ocean wave resource in the United States is estimated at 255 TWh per year, about 6% of current national demand [2]. The ability to make use of this energy is significant in large-scale electricity generation for public utilities in order to replace the finite fossil fuels [3,4]. The water motion can be transformed into electricity based on various mechanisms, such as electromagnetic [5-8], and piezoelectric effect [9,10]. The fundamental technology is the electromagnetic generators, a main component of which is the permanent magnets that are considerably bulky, heavy and costly. As for the piezoelectric effect based generator [11,12], the relatively low output power density and complexity of fabrication may limit them only for powering small electronics. Consequently, a small-sized, lightweight, cost-effective approach that can effectively harvest energy from a variety of water motions is greatly desired.

Recently, triboelectric nanogenerators (TENGs), on the basis of coupling between triboelectrification and electrostatic induction, have been demonstrated as an effective and low-cost technology not only for harvesting various forms of mechanical energies [13-20], but also as self-powered chemical sensor [21,22], tracking system [23-25] and pollution degradation [26,27]. By converting ambient mechanical energy into electricity, the TENGs are capable of harvesting energy from human motion [28-30], vibration [31,32], wind [33], and water [34-36].

There two parts of energy that are provided by water wave: the electrostatic energy from the contact electrification between water and solid surface [34,36] and the mechanical impact energy. Here we present an all-in-one hybridized TENG based on the conjunction of liquid-solid interfacial electrification enabled TENG (IE-TENG) and impact-TENG to simultaneously scavenge the electrostatic energy and mechanical energy from water wave and falling water drops. The IE-TENG is composed of a fluorinated ethylene propylene (FEP) thin film and an array of electrodes underneath that is able to harvest the interfacial electrostatic energy from water. The impact-TENG consists of polytetrafluoroethylene (PTFE) thin films with nanostructures, two planar electrodes, and an elastic wavy electrode in between [30], which are utilized to scavenge mechanical impact energy from water wave. The hybridization of IE-TENG and impact-TENG enables fully harvest the water related energies in a complete cycle of water motion. Under water waves propagating at a speed of 0.5 m/s, the short-circuit current of the IE-TENG and impact-TENG can reach 5.1 μA and 4.3 μA, respectively, which is able to light up nearly 50 LEDs simultaneously. The influence of NaCl concentration in water on the electric output of IE-TENG has also been investigated. Furthermore, embedded in a life vest, the hybrid TENG is capable of powering portable electronics and emitting distress signals once landed in water. This work explicitly presents the practicability of the hybrid TENG for ocean wave/rain drops harvesting, self-powered navigation, maritime monitoring, and marine search and rescue.

Experimental section

Nanowire-based surface modification of PTFE film

Nanowires on the surface of PTFE were formed by using inductively coupled plasma (ICP) reactive ion etching. The PTFE film with a thickness of 50 μm was clean with isopropyl alcohol and deionized water, then blown dry with nitrogen gas. In the etching process, Au particles were deposited for 45 s by using DC sputter on the PTFE surface as a mask. Subsequently, a mixed gas including Ar, O_2, and CF_4 was introduced in the ICP chamber, with corresponding flow rate of 15.0, 10.0, and 30.0 sccm, respectively. The PTFE film was etched for 15 s to obtain nanowire structure on the surface. One power source of 400 W was used to yield a large density of plasma, while another 100 W was used to accelerate the plasma ions.

Fabrication of IE-TENG

A 1.5 mm-thick acrylic sheet was cut into a hollow mask by precision laser cutting. The patterns in the mask were the same as electrodes. Then the mask was mounted on to the FEP film. The Cu layer was deposited onto the exposed PET surface by physical vapor deposition (PVD) to prepare the parallel electrode. Lead wires were connected to the electrodes as output terminals with one-to-one correspondence. Subsequently, a 75 μm-thick FEP film was attached to the PET substrate.

Fabrication of the impact-TENG

Cu layer was deposited on the nanostructured PTFE using physical vapor deposition (PVD) to form the back electrode. The PTFE film was coated with PDMS and adhered onto the PET substrate. A Kapton film fixed by an array of steel sticks was heated to form wavy shape in the oven at the temperature of 100 °C for 4 h. Cu layers were deposited

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on both sides of the wavy-shaped Kapton film by E-beam evaporation to form the wavy electrode in between. Lead wires were connected to the electrodes as output terminals.

Characterization and electrical measurement of the SE-TES

The morphology and nanostructure of etched PTFE film were characterized by Hitachi SU8010 field emission scanning electron microscopy (SEM) operated at 3 kV. The output performance of TENG was measured using Stanford Research Systems. SR560 and SR570 low noise current amplifiers were used to record voltage and current, respectively.

Experimental setup for quantitative measurement

A 6 mm-thick acrylic sheet was mounted on the electrical linear motor. The sheet was immersed into the water and perpendicular to the water surface. The reciprocating motion of the linear motor forms waves of tap water in the container.

Results and discussion

The structure diagram of the fabricated hybrid TENG is shown in Figure 1a, which is composed of two different types of TENGs that are vertically integrated: the upper one is the IE-TENG and the bottom one is the impact-TENG. The IE-TENG is based on a fluorinated ethylene propylene (FEP) thin film, four parallel strip-shaped electrodes with a fixed gap in between, and polyethylene terephthalate (PET) as the substrate. FEP is selected as the contact material for its hydrophobic property and high negativity in the triboelectric series [1]. As the area of the device submerged cyclically varies with the water wave, free electrons are driven to flow alternatingly between electrodes, leading to an AC output on the external load. The impact-TENG is comprised of PET substrates, polytetrafluoroethylene (PTFE) thin films with nanostructure, two planar electrodes, and an elastic wavy electrode in between. Copper was deposited on both sides of a wavy Kapton thin film to constitute the inner wavy electrode as indicated in Figure 1b (Figure S1, Supporting information). PTFE and copper were chosen as contact materials due to their large difference in electron affinity. The impact resulting from the surrounding water motion repetitively compresses the elastic wavy electrode and shortens the distance between PTFE film and wavy electrode, leading to electrons flow between wavy electrode and planar electrode. Surface modification on the PTFE film was adopted to create vertically aligned polymer nanowires as sketched in Figure 1c. By using inductively coupled plasma (ICP), the dry etched nanowires have an average diameter of 170 nm and lengths ranging from 450 nm to 730 nm, as shown in Figure 1d. The nanowires on the PTFE surface increase the effective contacting area with wavy electrode, enhancing the triboelectric charge density in the friction process triggered by water impact. The prepared hybrid TENG features advantages such as flexibility, robustness, lightweight, and small volume with a uniform size of 15 cm × 6 cm × 0.8 cm, as revealed in Figure 1e.

The working mechanism of the fabricated hybrid TENG can be illustrated independently as an IE-TENG (Figure 2a) and an impact-TENG (Figure 2b). The contact electrification between triboelectrically negative materials and water gives rise to the negative triboelectric charges on the surface of FEP thin film (Figure 2a, I). These surface charges do not dissipate in an extended period of time due to the insulating property of the polymer material [37]. The hydrophobic surface of FEP thin film repels water immediately after emerging from water surface. When electrode A is increasingly submerged by the rising water wave, positive ions in water are attracted by the negative triboelectric charges on the FEP surface to form an interfacial electrical double layer (EDL). This asymmetric distribution of charges

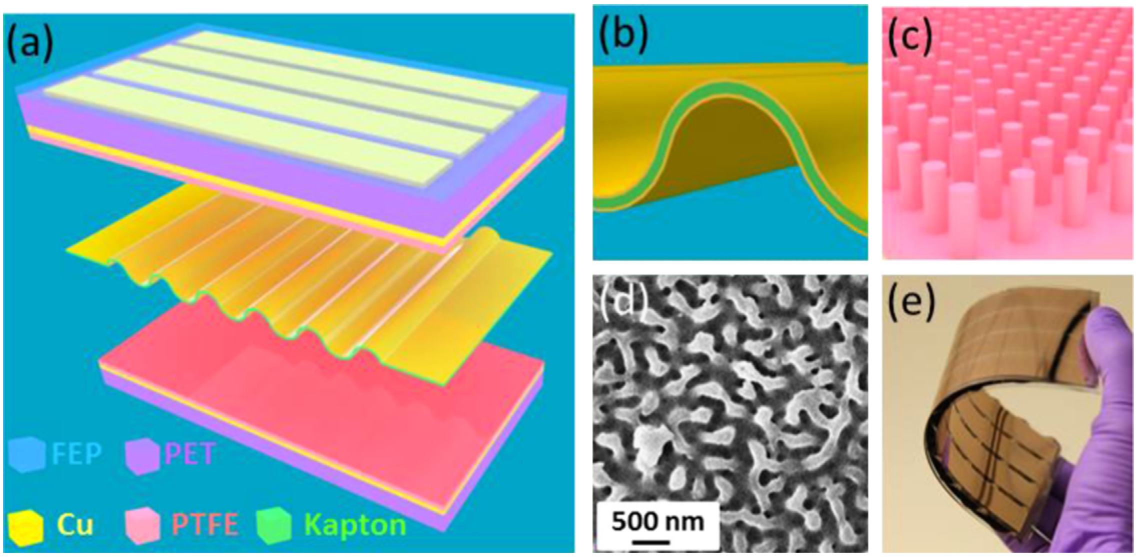

Figure 1 Structural design of the hybrid TENG. (a) Schematic diagram of the fabricated hybrid TENG. (b) Schematic of the inner elastic wavy electrode. (c) Schematic of the PTFE surface with etched nanowire structure. (d) Scanning electron microscopy (SEM) image of the PTFE surface with etched nanowire structure. (e) Photograph of the prepared hybrid TENG.

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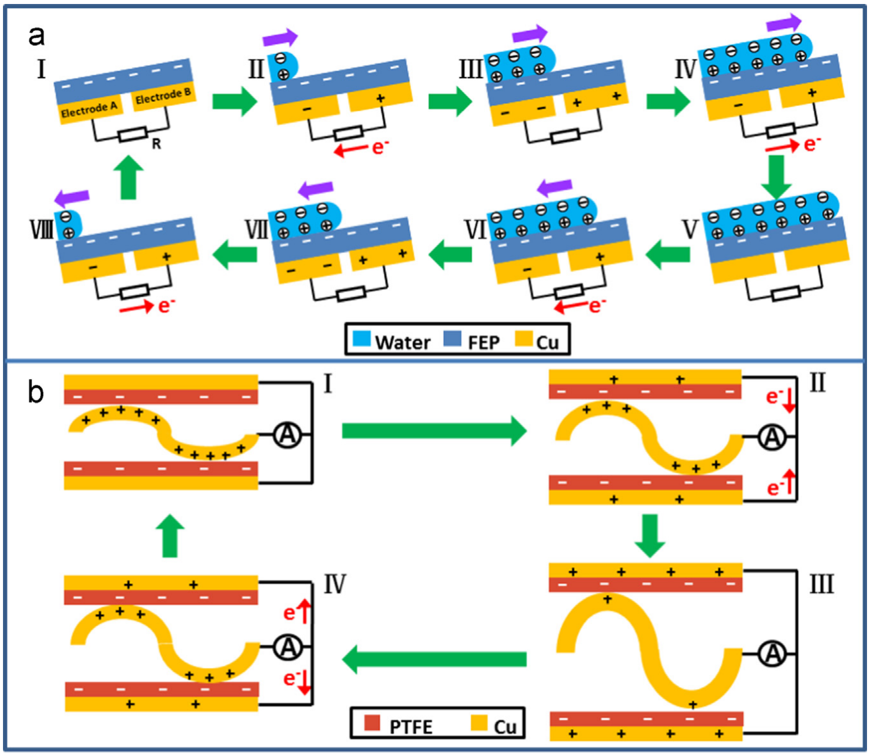

Figure 2 Working mechanism of the fabricated hybrid TENG. (a) Working mechanism of the prepared IE-TENG. (b) Working mechanism of the prepared impact-TENG.

on FEP surface establishes the positive electric potential difference from electrode A to electrode B and thus drives electrons to flow from electrode B to electrode A (Figure 2a, II). Once the rising water reaches the gap between two electrodes, a maximum quantity of induced charges on the electrodes will be attained with no electrons transferred (Figure 2a, III). As the rising water continues to inundate the electrode B (Figure 2a, IV), induced electrons flow back to electrode B since the electric potential difference between the two electrode decreases until the electrode B is fully submerged by water. When the device is completely covered by water (Figure 2a, V), a symmetric screening of triboelectric charges is achieved, and therefore the electric potential difference decays to zero with no electrons transfer between electrodes. Then the wave begins to recede and expose electrode B and the increasing electric potential difference drives electrons to flow from electrode B to electrode A (Figure 2a, VI). Once the water surface returns to the gap between two electrodes, a maximum quantity of induced charges on the electrodes will be obtained again without electron flowing (Figure 2a, VII). Subsequently, the water level falls down and exposes the electrode A and the decreasing screening area results in electron flow from electrode A to electrode B (Figure 2a, VIII). Finally, the device fully emerges from water and completes a whole cycle (Figure 2a, I). Consequently, as the device submerges and emerges from the waving water, two pairs of alternating electron flows are brought about between the two adjacent electrodes, leading to power generation.

The working principle of impact-TENG is described in Figure 2b. In the initial state, the PTFE and wavy Cu electrode are brought into intimate contact by the external impact from water wave. Owing to the triboelectrification properties [1], the PTFE attracts electrons from Cu electrode, leaving net negative charges on the PTFE surface and equal net positive charges on the surface of Cu layer (Figure 2b, I). Once the wave recedes, the compressed wavy electrode will revert to its original shape due to the restoring force from elastic deformation of the designed structure. As a result, the contact surface area separates and creates an electric potential difference between planar electrode and wavy electrode, driving electrons to flow from planar electrodes to wavy electrode to screen the positive triboelectric charges on the wavy electrode (Figure 2b, II). When the impact-TENG reverts back to its original position, positive triboelectric charges on the wavy electrode are mostly screened, leaving a maximum amount of induced charges on the planar electrode (Figure 2b, III). Subsequently, mechanical impact from the water wave once again shortens the separation and increases the contact area, producing an electric potential difference with reversed polarity. Therefore, electrons flow from wavy electrode to planar electrodes to eliminate the electric potential difference (Figure 2b, IV). Finally, the PTFE thin film and wavy electrode are brought into intimate contact again and complete a whole cycle of electricity generation (Figure 2b, I).

For quantitative characterization of the output performance, the electric output of the hybrid TENG in response to motions of water wave was systematically measured, as shown in Figure 3. In order to obtain uniform water waves, a linear motor was used to introduce a periodical impact. The setup of the quantitative measurement system is shown in Figure S2 (Supporting information). The hybrid TENG was

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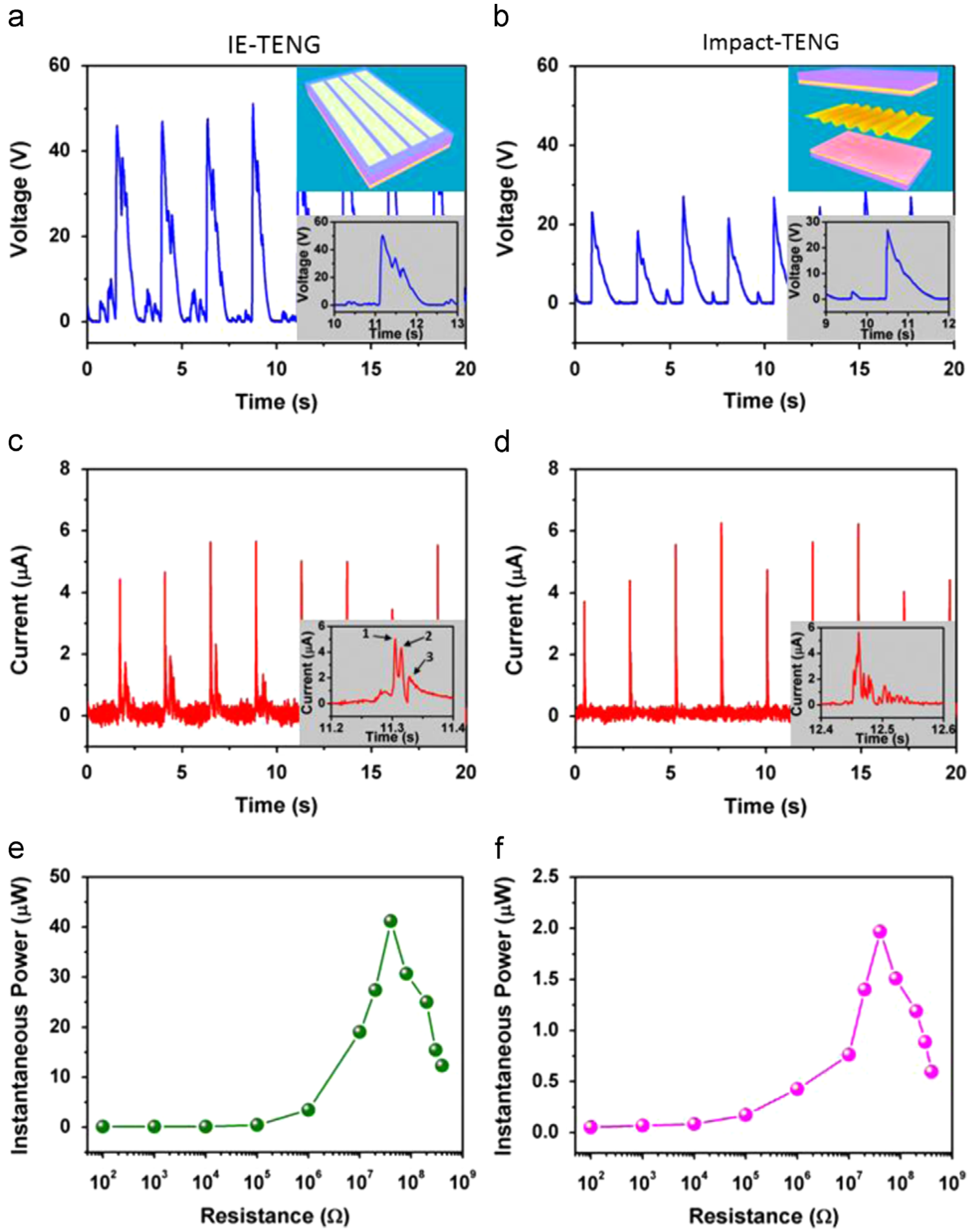

Figure 3 Electrical measurement results of the hybrid TENG in respond to water waves. The open-circuit voltage of the IE-TENG (a) and the impact-TENG (b). The short-circuit voltage of the IE-TENG (c) and the impact-TENG (d). Instantaneous power dependences of the IE-TENG (e) and the impact-TENG (f) on the load resistance.

vertically fixed in a water container. The tap water surface was leveled with the bottom edge of the device. For all measurements, the linear motor is working at a frequency of 0.4 Hz, an impulse length of 80 mm, a moving speed of 0.5 m/s. The height of water waves propagating at 0.5 m/s reaches 11.7 cm, which can fully interact with the device fixed on the container. Given the four parallel electrodes used for electricity collection, a total of three basic units were established by any pair of adjacent electrodes, where each pair of unit was rectified through an electric bridge and then superimposed through a parallel connection. The electric output of the IE-TENG and impact-TENG were measured independently. Under a group of water waves, the open-circuit voltage values of the IE-TENG and impact-TENG can reach 43.2 V and 23.6 V, respectively, as shown in Figure 3a and b. The insets represent the magnification views of a single voltage pulse. The short-circuit current values of the IE-TENG and impact-TENG are up to 5.1 μA and 4.3 μA as shown in Figure 3c and d, respectively, where three peaks on a single current pulse can be observed in the inset of Figure 3c, corresponding to the amount of units. This is because the three units interact with the waving water sequentially instead of simultaneously, resulting in three current peaks in a single pulse. In contrast, the short-circuit current curve of the impact-TENG reveals only one peak for each pulse in the inset of Figure 3d. By combining the IE-TENG and impact-TENG in the same output direction, the hybrid TENG can simultaneously light up 48 LEDs driven by water waves created by hand-shaking (Movie 1 and Figure S3, Supporting information). It is worth to note that compared to previously reported TENG for water energy harvesting [33,34], this all-in-one design requires no extra movable components for capturing and transmitting mechanical energy, and thereby extends its applicability, such as offshore areas and ocean surface.

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.nanoen.2014.07.006.

To investigate the dependence of the output power of the two kind of TENG on load resistance, the output power values of the IE-TENG and the impact-TENG were measured in response to water waves at the external resistance ranging from 100 Ω to 400 MΩ as plotted in Figure 3e and f, respectively. For the IE-TENG, the instantaneously maximum power of 41.2 μW is achieved at a load of 40 MΩ. For the impact-TENG, the instantaneously maximum power of 2.03 μW is achieved at a load of 40 MΩ.

Apart from the energy harvesting from water wave, the hybrid TENG also demonstrates the ability of energy scavenging from falling water or rain drops. The hybrid TENG was still fixed

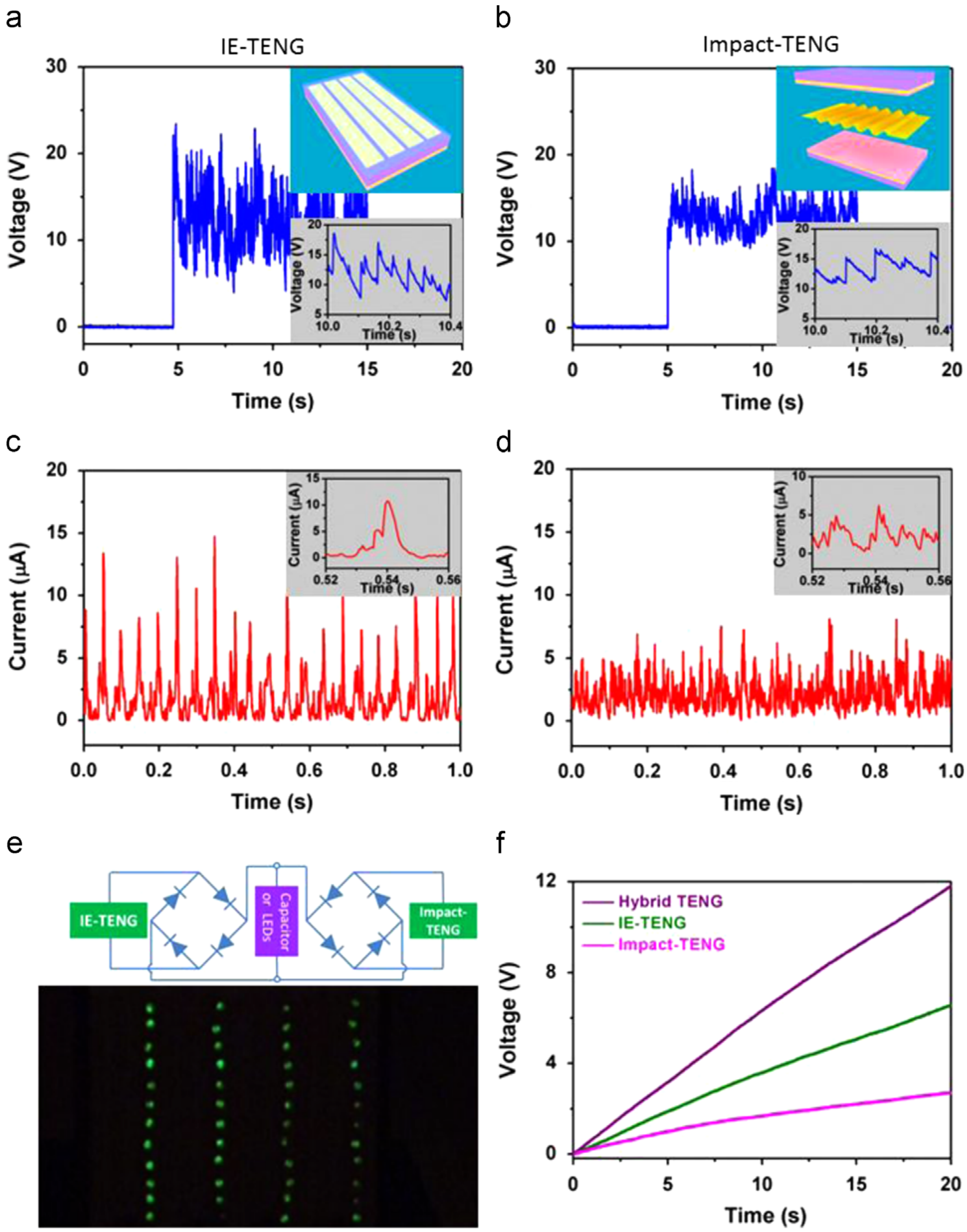

Figure 4 Electrical measurement results of hybrid in respond to falling drops. The open-circuit voltage of the IE-TENG (a) and the impact-TENG (b). The short-circuit voltage of the IE-TENG (c) and the impact-TENG (d). (e) Photograph of 48 commercial LEDs bulbs driven by the hybrid TENG at a water flowing rate of 65 mL/s, and inset shows the diagram of rectifying circuit. (f) Charging curves of 2 μF capacitor by the hybrid TENG and a single part of the hybrid TENG at a water flowing rate of 65 mL/s.

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on the container and a shower head was used to spray water onto the device (Figure S4, Supporting information). The falling water drops hit on the device surface and then slide down across the electrode array, which is accompanied with the collection of the impact mechanical energy and the water-solid interfacial electrification energy in sequence. At first, the water drops fall on the surface of the device and immediately lose the impulse, which exerts an impact force towards the device. Since the water flowing from the shower head has some fluctuation, the impact force on the device surface is not fully constant, which results in repetitive cycles of deformation and recovery of impact-TENG. The positively charged droplets then slide across the parallel electrodes and thus induce free electron transfer between adjacent electrodes. With plentiful moving droplets, a large amount of current pulses were brought about together, rendering an apparent continuous dc output. The open-circuit voltages (V_{oc}) of the IE-TENG and impact-TENG can reach 17.4 V and 13.1 V, respectively, as shown in Figure 4a and b. The V_{oc} of impact-TENG in response to water drop is smaller than that from water wave. This is attributed to the fact that the wave carries larger impulse and thereby causes greater deformation compared to the falling water. As revealed in Figure 4c and d, the short-circuit current of the IE-TENG and impact-TENG can reach 9.1 μA and 3.9 μA, respectively. The falling water drops induce much denser current pulse than the water waves do, which gives rise to a higher output power density. To demonstrate the practical applications in driving LEDs or charging a capacitor, the IE-TENG and the impact-TENG are connected in parallel to deliver pulse output in the same direction by using two full-wave rectifying bridges, as displayed in Figure 4e (Supporting information, Figure S4). Under the falling water at a flow rate of 65 mL/s, the hybrid TENG can be used as a sustainable source to light up 48 LEDs continuously, as shown in Figure 4e and supporting movie 2. Moreover, a 2 μF capacitor is charged by the hybrid TENG at the presence of falling water, as shown in Figure 4f.

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To verify the capability of the hybrid TENG in harvesting energy from sea water, the influence of NaCl concentration on the output performance has been studied. The NaCl concentration of 0.6 M is similar to that in sea water. The saline water was driven by linear motor to form a repeated wave motion. According to the measurement results plotted in Figure 5a and b, the output of IE-TENG is reversely proportional to the NaCl concentration while the output of impact-TENG almost stays at a fixed value. This result indicates that the output voltage and output current of the IE-TENG are affected by the electrolytes in water (Figure S5, Supporting information). This is due to the fact that FEP film cannot completely eliminate the adhesion of water droplets after it emerges from water.

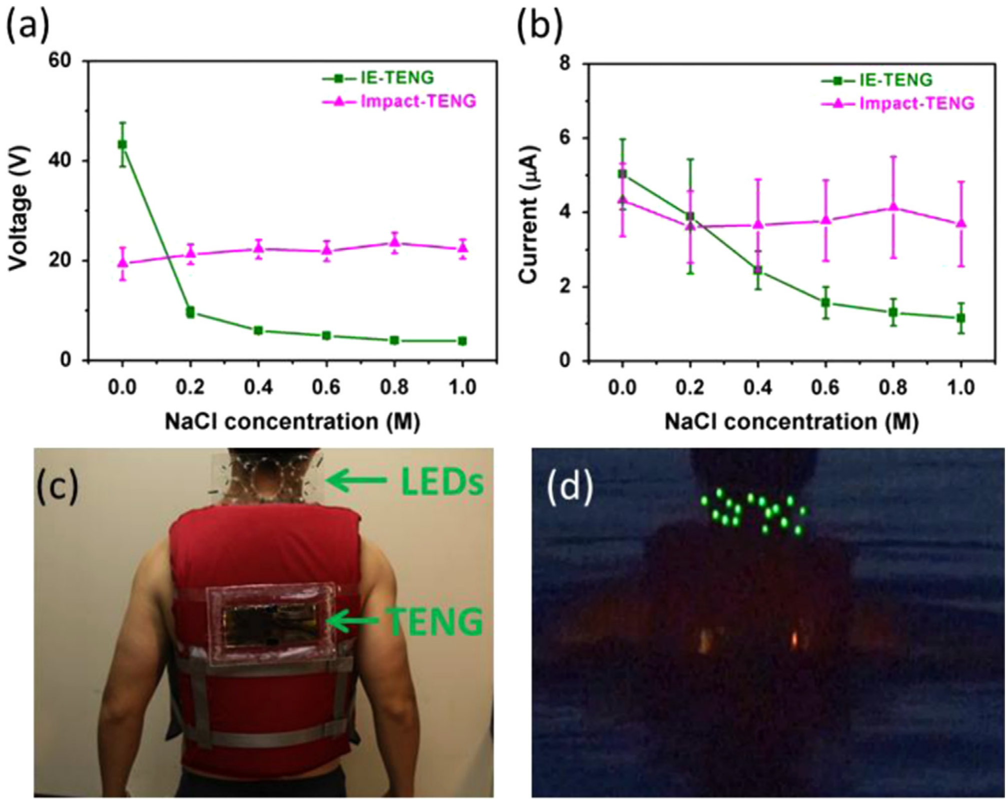

Figure 5 (a) The dependence of output voltage of IE-TENG and impact-TENG on the NaCl concentration. (b) The dependence of output current of IE-TENG and impact-TENG on the NaCl concentration. (c) Photograph of the hybrid TENG imbedded on a life vest as a distress signal emitter connected to tens of LEDs. (g) Photograph of the distress signal LED bulbs driven by the hybrid TENG during the process of swimming.

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The residual electrolytical solution, including positive dissolved ions, remains on the surface and will partially screen the triboelectric charges on the FEP film, reducing the electrostatic induction and thus the electric output [33]. The higher NaCl concentration renders more positive ions in electrolytical solution. It should be noted that the impact-TENG generates a constant value of electric output even when the output of the IE-TENG decreases with the increasing NaCl concentration, indicating the necessity of impact-TENG in harvesting mechanical energy from sea water.

Furthermore, we demonstrated another application of hybrid TENG to be used as a self-powered distress signals emitter on water. Figure 5c shows the self-powered distress signal emitter imbedded on a life vest. The hybrid TENG was fixed on the back of life vest and connected with tens of LEDs as distress signal lights. The IE-TENG and the impact-TENG are connected in parallel to drive the distress LEDs on a life vest at the same time by using two full-wave rectifying bridges, as displayed in Figure 4e. In the process of swimming or floating on the water, the hybrid TENG submerges and emerges from the water surface in responding to a human motion and interacts with the water waves, producing an AC current that can light up the LEDs and deliver a visible signal, as shown in Figure 5d (see Supporting information, Movie 3). It is worthwhile to note that this self-powered distress signals emitter is powered by the direct interaction with water instead of batteries or power supplies. Therefore, the longevity and applicability of the distress signal emitter will be largely extended compared to the ones that are only driven by batteries. Once these designed hybrid TENGs are equipped on life vests, a great deal of expense and time can be saved on inspection and maintenance of power supplies, which is ideal for the survival equipment on the crafts that prepare for unpredictable small probability event.

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Conclusions

In summary, we developed an all-in-one hybrid TENG that can simultaneously harvest the electrostatic energy and mechanical energy from water wave or falling water drops. The variation of contact area between FEP film and water induces electrons flow between adjacent electrodes in IE-TENG. The separation and contact of wavy electrode and PTFE film by the impact of water motion result in the AC output of impact-TENG. In the presence of falling water drops at a rate of 65 mL/s, the short-circuit current of the IE-TENG and impact-TENG can reach 9.1 μA and 3.9 μA, respectively. By connecting the IE-TENG and the impact-TENG in the same output polarities, the hybrid TENG can be used as a sustainable power source to drive LEDs or charge capacitors. The influence of NaCl concentration on the electric output has also been evaluated to reveal the potential for harvesting energy from sea water. Furthermore, integrated in a life vest, the hybrid TENG demonstrate the capability in self-powered distress signals emitter on water. This work pushes forward a significant step towards the application of triboelectric generator in energy harvesting from ocean wave and rain drops, self-powered distress call system, monitoring, navigation and maritime search and rescue.

Acknowledgments

This work was supported by U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-07ER46394), and the “thousands talents” program for pioneer researcher and his innovation team, China. Y. Su, Z. Wu, and Y. Jiang acknowledge the support of the National Natural Science Foundation of China via Grant no. 61101029. Y. Su also would like to acknowledge the fellowship from the China Scholarship Council (CSC).

Appendix A. Supporting information

Electric output of the hybrid TENG under varied NaCl concentration, schematic of setup for quantitative measurement, photographs of copper wavy electrode for impact-TENG and parallel electrodes for IE-TENG. This information is available free of charge via the Internet at http://pubs.acs.org/.

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2014.07.006.

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Yuanjie Su received his Bachelor's degree in the School of Optoelectronic Information, University of Electronic Science and Technology of China. He is a Ph.D. candidate in the School of Optoelectronic Information, University of Electronic Science and Technology of China. He is currently a visiting student in Prof. Zhong Lin Wang's group at Georgia Institute of Technology. His research interests include piezo-phototronics, triboelectric nanogenerator, nanostructured semiconductor and optoelectronic device.

Xiaonan Wen received his B.S. degree in Physics from Peking University, China in 2010. He is currently a Ph.D. student in the School of Materials Science & Engineering, Georgia Institute of Technology. His research interests include synthesis of functional nanomaterials, energy harvesting using piezoelectric and triboelectric generators, self-powered nanosystems, piezo-electronics and piezo-optoelectronics based on ZnO, GaN etc. for novel transistors, devices and integration of them into functional systems.

Guang Zhu is a postdoctoral fellow in Professor Zhong Lin Wang's group at Georgia Institute of Technology. He received his B.S. degree in Materials Science and Engineering from Beijing University of Chemical Technology in 2008, and his Ph.D. degree in Materials Science and Engineering from the Georgia Institute of Technology in 2013. His research areas include synthesis and characterization of nanomaterials, mechanical energy harvesting, self-powered electronics, and micro-fabricated transducers for energy applications.

Jin Yang received the BE, ME and Ph.D. degrees in instrumentation science and technology from Chongqing University in 2002, 2004, and 2007, respectively. He is currently a professor with the College of Optoelectronic Engineering, Chongqing University. He is currently a visiting scholar in the group of Professor Zhong Lin Wang at Georgia Institute of Technology. His research interests include self-powered sensor and system, measurement and instrumentation.

Jun Chen received his B.S. and M.S. in Electrical Engineering from the Department of Electronics and Information Engineering at Huazhong University of Science and Technology in 2007 and 2010, respectively, and a second M.S. in Biological Engineering from College of Agricultural and Environmental Science at The University of Georgia in 2012. He is currently a Ph.D. candidate in the School of Materials Science and Engineering at the Georgia Institute of Technology, working under the guidance of Prof. Zhong Lin Wang. His research focuses primarily on the synthesis and characterization of semiconducting nano-materials, nanomaterial-based piezotronic and piezo-phototronic devices as well as triboelectrification based energy harvesting and self-powered micro-/nano-systems.

Peng Bai received his Bachelor's degree in Mechanical Engineering from Tsinghua University, China, in 2010. He is a Ph.D. candidate at Department of Mechanical Engineering, Tsinghua University. From 2012 to 2014, he was a visiting student in Prof. Zhong Lin Wang's group at Georgia Institute of Technology. His research interests include energy harvesting, nanogenerators, and self-powered systems.

Zhiming Wu received his Ph.D. from Huazhong University of Science and Technology in 1993. He is now the professor of School of Optoelectric Information in University of Electronic Science and Technology of China. His research interests include electronic polymeric material and devices, piezoelectric materials and ferroelectric materials, smart materials and sensors.

Yadong Jiang received his Ph.D. from University of Electronic Science and Technology of China in 2001. He is now the professor of School of Optoelectric Information in University of Electronic Science and Technology of China. His research interests include optoelectronic thin film and integrated devices, organic electronic materials and devices, smart materials and sensors.

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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.

Please cite this article as: Y. Su, et al., Hybrid triboelectric nanogenerator for harvesting water wave energy and as a self-powered distress signal emitter, Nano Energy (2014), http://dx.doi.org/10.1016/j.nanoen.2014.07.006