Large-scale fabrication of robust textile triboelectric nanogenerators

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ABSTRACT

Smart energy textiles based on triboelectric nanogenerators (TENGs) are promising power supply and sensor arrays for wearable electronics and artificial intelligence. However, the challenges of the smart textile in large-scale industrialized production, facile and universal fabrication process, and enough robustness still remains. In this study, a textile-based triboelectric nanogenerator (t-TENG) is proposed through a facile and universal fabrication process. Liquid-metal/polymer core/shell fibers (LCFs) structure as the basic unit of TENG textiles, can be extensively achieved by pumping liquid metal into uniform ultrafine polymer hollow fibers, which contribute to the large-scale industrialized production of TENG textiles. In addition to gaining a high output, the t-TENG demonstrates excellent acid and alkali resistance, and high friction durability. Furthermore, profiting from the universal fabrication process, the polymer hollow fibers can be replaced by any type of fibers with various functions or colors according to practical applications (e.g., the silicone rubber could be an excellent choice for highly stretchable devices). Moreover, the fabricated t-TENGs demonstrate great capability in self-powered sensors for smart home controlling. All these advantages of the t-TENG exhibit its great potential for further application in wearable electronics and artificial intelligence and it will speed up the development of IoTs in the near future.

1. Introduction

Modern mobile electronic devices and wireless communication networks, the key role of the Internet of Things (IoTs) [1], humanoid robotics [2], big data [3] and artificial intelligence [4], have been prosperously developed with the advance toward the fourth industrial revolution [5]. At the same time, the energy supply problems of these tens of thousands of functional devices are becoming more and more apparent. On one hand, traditional energy supplies such as batteries, which are not sustainable power and cannot harvest energy from ambient energy sources, are not suitable and unreasonable for massively distributed, human-oriented and mobile functional devices [6,7]. On the other hand, in the new era, people have emergent requirements for energy power in environmental friendliness, wear-comfort and multifunction. Therefore, there are urgent demands to construct new energy conversion and supply means to address these issues [8].

The advent of triboelectric nanogenerator (TENG) in 2012 brings new hope and reengineering for distributed energy harvesting and self-powered sensing due to its unique working principle and environment friendly behaviors [9,10], TENG-based studies have sprung up like bamboo shoots after a spring rain and many researchers have now joined the TENG team [11–15]. TENGs with a wide range of material selectivity [16] and versatile structure [17] can be applied to harvest nearly all kinds of ambient mechanical energy, ranging from clean natural energy (wind [18], water flow [19], etc.) to ubiquitous mechanical power (slight acoustic wave [20], heart beating [21], etc.), showing their...
remarkable compatibility with severe environments and the human body. Possessing above merits, TENGs have been proven as up-and-coming candidates to complementarily solve the energy issue of randomly, massively distributed, human-oriented and mobile functional devices. Among different kinds of TENGs, textile TENGs (t-TENGs) bring new vitality and more possibilities for smart textile and have the highest matching degree with the demands of modern mobile electronic devices and artificial intelligence. The clothing or woven fabric by using the t-TENGs are not only wearable to meet the comfortability, but also can harvest human motion energies at anywhere and anytime to supply electric power. T-TENGs with different architecture dimensions (D) and fiber orientation (OD, 1D, 2D and more complex 3D), numerous materials (metal material, inorganic non-metal material, polymer material, composite material methods), diverse manufacturing techniques (knitting, weaving, braiding, and nonwoven), and widely applications (sensors and energy harvesting) have been extensively fabricated and studied.

Throughout all previous studies, there are still many challenges and difficulties to be overcome towards widespread applications. Large-scale industrialized production is a prominent challenge to hinder the broad commercial applications of t-TENGs. Although several efforts and attempts have been made to promote their rapid preparation, low-cost and large-scale industrialized production of t-TENGs is still hard to realize, especially in the perspective of the combination of contact layers and charge collectors. On one hand, it is impractical to scale up in the conventional textile manufacturing industry due to the sophisticated, complicated and cost fabrication procedures. For example, carbon nanotubes, Ag nanowires, stainless-steel wire, or liquid metal (charge collectors) must be uniformly and precisely dispersed on/in polymers (friction layers) to effectively harvest thetriboelectric energy. Secondly, the structure of the fabricated combination of friction layers and charge collectors is plane or uneven tubular in thickness, which is incompatible with commercial textile processing. Thirdly, although the size of the charge collectors such as stainless-steel wire can meet the requirement of commercial textile processing, because of the geometry (1D) of charge collectors, the polymer covers on their surface is very easy cracking/delamination.

Herein, we developed a large-scale and robust textile-based triboelectric nanogenerator (t-TENG). The t-TENG is constructed by liquid-metal/polymer core/shell fibers (LCFs) which can be substantively obtained by continuous pumping liquid metal into polymer hollow fibers. Such an exciting strategy, taking advantage of the fluid properties of liquid metal, makes mass production of the t-TENG possible. The excellent mechanical and chemical stability of PTFE shell enable the t-TENG to collect human motion energy steadily and continuously in various scenes, including some extreme conditions (desert saline area and acid rain-prone region, etc.). In addition to being used for energy harvesting, the t-TENG has been successfully applied to multi-finger sensing and smart home controlling systems as well. Furthermore, based on the strategy proposed above, the outer shell of LCFs could be replaced with different polymer hollow fibers to make LCFs have multiple functions, for example, modified PTFE fibers can offer various colors (black, red, blue), and soft silicone rubber fibers can enable large stretchability. It indicates that the approach in this paper is universal and suitable for a variety of polymer materials, which makes the t-TENG based smart clothes more fashionable, pretty and multifunctional while achieving high electrical output synchronously.

2. Results and discussion

As for TENG based energy harvesters, the most important two parts are tribo-materials and current collectors, they are the core elements affecting the performance of the TENG device. Especially for t-TENG, how to perfectly integrate the contact layer with suitable electrode and construct appropriate weaving blocks is the key technology for the whole energy harvesting textiles. As illustrated in Fig. 1a, Fig. S1 and Video S1 (Supporting Information), the flexible and stretchable gallium-based liquid metal electrode (which is environmentally friendly and harmless to human) were successfully integrated with ultrafine PTFE hollow fibers by a simple pumping process. The photographs of the original PTFE hollow fiber and fully liquid-metal filled fiber after pumping were shown in Fig. 1b and c, respectively. Moreover, the PTFE hollow fiber adopted in this study is ultrafine with a size of 600 μm OD (Outer diameter) & 300 μm ID (Inner diameter), which is approximately half the diameter of a universal pencil lead. It needs to be emphasized that the commercial process of the polymer based hollow fibers is very mature in large-scale production. Therefore, the size and material selection of hollow fibers are very wide and depend on the requirements of the applications. The electrical conductivity performance of the LCF was demonstrated in Fig. S2 and the resistance of the LCF can keep stable under various mechanical deformations like bending or knotting. To visually verify the conductivity of the LCF, the wires of a commercial earphone were replaced by LCFs and it indicated that the earphone still can work normally in Fig. S3 (Supporting Information). Supplementary video related to this article can be found at https://doi.org/10.1016/j.nanoen.2020.104605.

Weaving is a kind of handicraft with long history, which has important sense to the development of human civilization. The model diagram of a traditional Chinese weaving machine was displayed in Fig. S4 (Supporting Information). Based on the obtained LCFs, a piece of breathable and soft TENG textile was designed by weaving. The photos of the as-fabricated TENG textiles with different colors and sizes were demonstrated in Fig. 1d and e. In previous studies, most of energy harvesting textiles were usually developed and constructed on a commercial fabric. Such a design will inevitably affect the overall breathability of the device and reduce the comfortability. Nevertheless, the TENG textiles in this study were directly fabricated by the LCF-basic blocks without any fabric substrate, further illustrating its great potential in achieving mass production and applying to the next-generation smart clothes.

2.1. Working principle and electrical output of the t-TENG

Taking the contact-separation between the TENG textile and a piece of commercial silk fabric as an example, the working mechanism of the t-TENG under vertical contact-separation mode is illustrated in Fig. 2a. Based on coupling effects of contact triboelectrification and electrostatic induction, the working cycle of the t-TENG can be demonstrated from four basic states as follows. Firstly, when the device is loaded with a mechanical force (e.g., human walking), the surface of the TENG textile and silk fabric would be negatively charged and positively charged due to the different contact electrification polarities, respectively (state I). Once the applied pressure was released, the distance of the two fabrics would be gradually changed from microscale to macro-scale and got the maximum separation eventually; at the same time, there would be a potential between the liquid metal and fabric electrodes. Then the electrons would transfer from the liquid electrode to the fabric electrode through an external circuit and eventually reach a balance (state II and state III). When the external force was applied again, the electrons would return to the liquid metal due to the potential difference and finally recover to the initial state (state IV and state I).

To further simulate the output performance of the t-TENG, the TENG textile with an area of $6 \times 8 \text{ cm}^2$ was attached to a linear motor, and a corresponding size of silk fabric was chosen as the counter tribo-layer and the operating frequency was 1 Hz. Through the electrical testing system, an open-circuit voltage $(V_{OC})$ of $\sim 105$ V and a short-circuit current $(I_{SC})$ of $\sim 6 \mu A$ were measured as shown in Fig. 2b and c, respectively. Then the load voltage and the average power density $(P_{ave})$ as a function of resistance were investigated by connecting an adjustable resistor box (range from 1 kΩ to 1 GΩ) in the external circuit. As the load resistance increased, the voltage on the load was raised, and a peak power density of $30.4 \text{ mW/m}^2$ was obtained at a $7 \text{ MΩ}$ external
Fig. 1. Schematic illustration, fabrication procedure of the textile-based TENG (t-TENG). a) Fabrication process of the liquid-metal/polymer core/shell fibers (LCFs). b-e) Photograph of b) the original ultrafine polymer hollow fibers, c) polymer hollow fibers after pumping into liquid metal, d) large piece of TENG textile and e) t-TENG based on black-blue-red tricolor PTFE fibers.

Fig. 2. Working principle and triboelectric output of the t-TENG. a) Mechanism description of the device under vertical contact-separation mode. b-d) Electric performance of the t-TENG, including b) \( V_{\text{OC}} \), c) \( I_{\text{SC}} \), d) variation of output voltage and power density of the t-TENG as a function of load resistance.
2.2. Stability and robustness test

2.2.1. Chemical stability measurement of acid/alkali resistance

The TENG with characteristic of acid & alkali resistance has rarely been reported before, but it can really extend the application lifetime of the device in special environments such as acid rain-prone areas and alkaline seaside environment. Here, a closed structure was adopted and the PTFE was chosen as the shell friction fiber, so the device is theoretically resistant to acid & alkali and then it was verified through experiments. Fig. 3a shows the schematic illustration of the dipping test.

Fig. 3. Stability and robustness test. a-c) Chemical stability test of acid/alkali resistance. a) Treating process of the t-TENG. b) The resistance of the TENG textile after various dipping treatments. The photograph of a TENG textile in water is shown as the inset. c) The $V_{OC}$ of the t-TENG which has been dipping in different liquid mediums. d,e) Mechanical robustness test. d) Output durability under ~10000 cycles. e) wear test of the t-TENG through walking on a ring sandpaper (600 mesh) road. The optical photograh of the wear test was shown as the inset.
The detailed dipping procedures and after-treatments were depicted in the experimental section. The resistance and output $V_{OC}$ of the TENG textile after various treatments were shown in Fig. 3b and c, where the output $V_{OC}$ was simulated by a linear motor under the same conditions with a reference silk fabric tribolayer. As it can be seen from these data, the resistance and output performance of the t-TENG have not been affected after the treatment of either acid or alkali, further demonstrating that the t-TENG has outstanding chemical stability and it is promising to apply in harsh environments.

2.2.2. Mechanical stability and robustness test

To further verify the mechanical stability of the t-TENG, the output $V_{OC}$ of the device was continuously measured under ~10,000 contact-separation cycles and it can remain stable as shown in Fig. 3d, indicating that the device could collect biomechanical energy continuously and steadily. In addition, a wear-resistant experiment was designed by placing the TENG textile under one shoe and then walking on a ringsandpaper path. In Fig. 3e, the output $V_{OC}$ value of the t-TENG after 10 min walking (~600 steps) was almost the same as the output before wear. Therefore, the t-TENG possesses enough mechanical stability and robustness and it could be an ideal energy source for wearable electronics in the near future.

2.3. Energy harvesting from human motions by the t-TENG

To prove that the device is capable of collecting various human motion energy, the electrical output of the t-TENG was investigated in some common states under a single electrode mode. In detail, the $V_{OC}$ and $I_{SC}$ of the t-TENG by tapping with a cotton glove, walking on it, tapping with human hand and swinging arm were comprehensively evaluated in Fig. 4a. Specifically, the generated peak $V_{OC}$ are 206 V, 185 V, 135 V, 48 V, respectively; and peak $I_{SC}$ are 28.7 $\mu$A, 25.0 $\mu$A, 20.9 $\mu$A, 1.35 $\mu$A, respectively. The cotton glove is softer and more flexible than human skin, so it can be fully contacted with the TENG textile during the tapping process and then a higher output was produced. It indicates that the t-TENG not only can harvest energy from skin, but also can collect energy in combination with other commercial fabrics.

Furthermore, the t-TENG has been successfully applied to driving small electronic products directly and indirectly. By hand patting, the pulse voltage generated by t-TENG can directly light 129 LEDs in series (Fig. S5a and Video S2 in the Supporting Information). Through a power management circuit described in Fig. 4b, the pulse AC voltage of the t-TENG was converted to DC voltage and then stored in a commercial capacitor, and finally it was applied to drive portable electronics. As illustrated in Fig. 4c, a 10 $\mu$F capacitor was charged to 3 V in ~184 s (including break time) by tapping the TENG textile, and the charged capacitor has successfully powered a commercial calculator. In addition, an enlarged view of the inset of Fig. 4c is shown in Fig. S5b (Supporting Information).

Supplementary video related to this article can be found at https://doi.org/10.1016/j.nanoen.2020.104605.

2.4. T-TENG for multi-finger sensing and smart home controlling

As shown in Fig. 5, in addition to being an energy harvester, the t-TENG could be applied in self-driven sensing systems as well. By utilizing the sewability of the fabric, we sewed the TENG textiles onto each fingertips part of a cotton glove. The conceptual drawing and optical photograph of the smart glove were shown in Fig. 5a and Fig. S6, respectively. Based on the principle of single electrode TENG, a contact response signal could be detected while the finger touching the dielectric surface, as shown in Fig. 5b. And the material of the dielectric surface is phenolic resin, which show different triboelectric properties from PTFE in triboelectric sequence. Note that we only connected four fingers to the oscilloscope due to the limitation of the number of channels, which does not limit the further application of t-TENG. Fig. 5c displayed the touching signals with different fingers and the signal of each finger connected can be well distinguished. Besides, the display of multi-finger real-time contact detection was demonstrated in Video S3 (Supporting Information). To further exhibit the application of the smart sensing system, a microcontroller system was integrated with the glove by a management circuit as illustrated in Fig. 5d (Supporting Information). Taking the controlling of LEDs as an example, the switching of LEDs was managed by touching the middle finger and the index finger respectively (Fig. 5d; Video S4 in Supporting Information). Note that, the trigger voltage of each sensing unit is 0.3 V in this work. In the era of home automation, the t-TENG as a self-powered sensor with the merits of easy-integration, strong-signal and light-weight, will provide reliable control.
services for smart home electronics.

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2.5. Multiple choices of the polymer hollow fibers for t-TENG

To exhibit the universality of the pumping-design strategy for various LCFs with different polymer hollow fibers, the external materials were replaced with translucent silicone rubber, red PTFE and blue PTFE, respectively. Fig. 6a depicted the as-fabricated TENG textiles with abovementioned LCFs. Then the output performance (including $V_{OC}$ and $I_{SC}$) of different t-TENGs was measured by hand tapping in the lower part of Fig. 6a. After replacing the shell materials, we found that the t-TENG can still be served as a high-efficiency energy harvester. In addition, the mechanical properties of silicone rubber-based LCFs and corresponding knitted TENG fabrics were displayed in Fig. 6b–e. A single silicone...
rubber-based LCF can be stretched to over 200%, and a knitted fabric can be stretched to ~250% in both the X and Y directions. In a word, all kinds of LCFs and TENG textiles could be designed according to our own demands, e.g., multiple materials, colors and sizes. It is greatly in line with the development of the next-generation smart energy garments.

3. Conclusion

In summary, a general but novel approach for large-scale, multi-functional, and robust LCFs based t-TENG has been developed, which can efficiently collect biomechanical energy and directly serve as a self-powered tactile sensor. More importantly, the facile manufacturing can efficiently collect biomechanical energy and directly serve as a self-powered smart energy garments. The t-TENG with an area of 6 × 8 cm² can produce a peak VOC of 206 V and a peak Ioc of 28.7 μA by tapping with a cotton glove. Furthermore, it can charge a 10 μF commercial capacitor to ~3 V in ~184 s (including break time) by tapping which can power a calculator. Besides, A multi-finger smart system by using the t-TENGs as self-powered sensor units was designed which could realize intelligent controlling of LED bulbs. It is worth mentioning that the electric performance of the PTFE based t-TENG remains the original value even after a treatment of acid or alkali leaching. Due to the excellent mechanical and chemical stability, the t-TENG can be a reliable and promising energy source that could adapt to various environments. Last but not least, the choice of shell material is diverse and flexible, which could combine other functions based on the specific application requirement.

4. Experimental section

Materials: The gallium-zinc liquid metal (zinc accounts for 3.5–5 wt %) was purchased from Shenyang Jiabei Trading Co., Ltd. (Shenyang, China). The hydrochloric acid (HCl, 36–38 wt%) and Sodium hydroxide (NaOH, 97 wt%) was provided by Sinopharm Chemical Reagent Co., Ltd. (Beijing, China), Shanghai Mclean Biochemical science and Technology Co., Ltd. (Shanghai, China), respectively. In the acid & alkali resistance test, the applied acid solution was undiluted concentrated hydrochloric acid and the concentration of lye was 2 M (NaOH). The PTFE hollow fibers (with the outside diameter of 600 μm and the inside diameter of 300 μm) and silicone rubber hollow fiber (with the outside diameter of 800 μm and the inside diameter of 300 μm) are commercial products purchased from Alibaba.

Fabrication of LCFs and t-TENGs: Firstly, the liquid metal was put in an open container for use and a vacuum pump (GM-0.33A, Jinteng Co., Ltd, China) was prepared; then insert one end of the ultrafine polymer hollow fiber into the liquid metal and connect the other end to the vacuum pump. Finally, the liquid electrode was fully pumped into the polymer fiber and one LCF could be successfully obtained. Besides, the testing electrode is a 350 μm enamel-insulated copper wire and it was inserted into one end of the LCF. Based on the above-mentioned LCFs, the t-TENG was fabricated by a simple weaving machine. As for the t-TENG based multi-finger sensing system, the construction method is to sew each textile sensing unit to the corresponding position of glove.

Acid & Alkali Resistance Test: The acid and alkali resistance test was carried out in four steps as follows. Firstly, the TENG textile with an area of 5 × 5 cm² was dipping in the corresponding liquid medium for 30 min (step I). Then, the textile was taken out and washed by the deionized water (step II and III). Lastly, the textile was dried at 40 °C for 30 min in an air-dry oven (step IV). All the dipping processes were carried out in a fume hood for safety reasons.

Wear Test: We first put a piece of TENG textile on the sole. Then we carry out the test by walking on a sandpaper road (600 mesh) road. And the sandpaper road was constructed by eight sheets of sandpaper (230 mm × 280 mm, 600 mesh). The tester weighs 60 kg and the size of the shoes is Eurocode 40.

Electrical Measurement: A linear motor (Linmot E1100) was used to generate regular and stable contact-separation to imitate human motions. During the test, the TENG textile and the commercial silk fabric were attached to a corresponding size acrylic substrate by one piece of foam tape. The output open-circuit voltage and short-circuit current were measured by a programmable electrometer (Keithley 6514). The data was transferred to the computer via a DAQ system (NI PCI-6259) in real time and recorded by a LabVIEW software. A four-channels oscilloscope (LeCroy 610ZI, 1 GHz) was adopted to test the signal of multi-finger sensors and the voltage intensity of smart home controlling system was characterized by Keithley 6514. The data communication between LEDs and the sensing system is done by a microcontroller system (Arduino UNO). In the experiment of human motions harvesting, the corresponding human body was considered to be electrically connected to the ground. All human-involved experiments were carried out under the informed consent of the participants.

Declaration of competing interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.nanoen.2020.104605.

References


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