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Ultrasonic-assisted Ultrafast Fabrication of Polymer Nanowires for High Performance Triboelectric Nanogenerators

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Abstract

Based on the coupling effect of triboelectrification and electrostatic induction, triboelectric nanogenerators (TENGs) can convert mechanical motions into electricity and electrical signals for mechanical energy harvesting and self-powered sensors, respectively. Polymer films with nanowires could significantly enhance the output performance of TENGs. Here, we introduce a novel ultrasonic-assisted ultrafast approach of fabricating vertical polymer nanowires for TENGs application. Benefited from the high temperature generated from ultrasonic-driven friction between the constituent materials, polymer can be fast melted and absorbed into the nanochannels of template. The vertical polymer nanowires will therefore be formed on the surface of polymer film by removing template for further serving as triboelectric materials. By changing the ultrasonication time, polymer nanowires with different length (0.5 to 58 μm) and aspect ratio (2 to 232) have been controllably prepared. The assembly TENGs based on PVDF film with nanowires are capable of generating open-circuit voltage of 230 V and transferred charge of ~ 79 nC. The devices are utilized to harvest mechanical energy with electric output of 153 V and 23 μA, which can power up 78 green LEDs and capacitors. This study not only presents a novel ultrafast fabrication approach of polymer nanowires with aspect-ratio controllability and universal suitability, but also demonstrates the polymer nanowires' application in mechanical energy harvesting of TENGs with enhanced performance.

Keywords: Triboelectric nanogenerator; Polymer nanowires; Mechanical energy harvesting; Ultrasonic-assisted.

Introduction

Triboelectric nanogenerators (TENGs) as novel energy harvesting technology can not only convert the ambient mechanical energy into electrical power,[1-5] but also be utilized to produce electronic signals for detection or high voltage applications.[6-10] By coupling triboelectrification and electrostatic induction, TENGs have been developed and categorized into four working modes, including vertical contact-separation, lateral sliding, single-electrode and freestanding triboelectric-layer modes.[11-17] In all these four working modes, polymers as important constituent materials of the device play a crucial role in energy harvesting and electric signal generation.[11-19]

Noticeably, the polymer surface morphology could greatly influence the performance of TENGs due to the change in triboelectric contact area of TENGs with the varied polymer surface area.[20-26] Wang et al firstly introduced inductively coupled plasma (ICP) technique to fabricate the polymer nanowires on the polymer surface to increase the contact area between polymer and electrode.[27, 28] The open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}) can achieve to the values of 110 V and 6 μA, respectively.[28] By following the similar strategy, many groups had prepared polymer nanowires on the surface of friction layer for enhancing the performance of TENGs.[29-36] Besides, Lee et al demonstrated a polymer self-assembly method to form polymer nanowires on the electrode, leading to the higher performance of TENGs.[37] Hao et al utilized the pattern transfer technique to introduce the PDMS microwires into TENGs.[38] Therefore, it is confirmed that the introduction of polymer nanowires on the triboelectric material surface could significantly improve the device's output and energy harvesting efficiency. However, traditional fabrication techniques require long time and complex processes to fulfill the expected vertical polymer nanowires. Wang et al demonstrate a technique to realize one-step, clean fabrication of patterned and aligned polymer nanowires at large scale.[27] Different gases such as Ar, O_2 and CF_4 were utilized as etchants in high vacuum to plasma-etch polymer film.[27] Liu et al presented vertical polypropylene nanowires fabrication based on polymer wetting mechanism.[35] To achieve polypropylene nanowires, the polypropylene film assembled with templates were placed at 200 ^{o}C for about 1 hr by wetting.[35] Therefore, it is important to develop rapid, simple and convenient fabrication processes of polymer nanowires to promote their applications in TENGs.

Herein, we introduce an ultrafast, controllable and low-cost approach to fabricate the polymer nanowires on various polymer films applied to TENGs. Specifically, under the assistance of ultrasonic vibration, the friction between the constituent materials can generate high temperature to melt the polymer. Based on the polymer wetting principle, polymer solutions or melts could be absorbed into the nanochannels of porous alumina templates due to the large difference in surface energy.[39] The polymer nanowires are therefore further formed on the surface after demolding the templates. Especially, the whole processes could be fast and controllably fulfilled from 10 to 65 s. The prepared polymer surfaces with nanowires are used to serve as the contact materials to fabricate TENGs. Our results show that, compared to the flat counterpart, the open-circuit voltage and transferred charge of TENG with PVDF nanowires are remarkably enhanced from 11 V and 6 nC to 230 V and 79 nC, respectively. The novel technique provides a promising approach to fast fabricate nanowires on polymer surface and extend application of polymer nanomaterial for TENGs.

Experimental Section

The polymer materials, including Polyethylene (PE, Tm = 129 ^{o}C), Acrylonitrile butadiene styrene (ABS, Tm = 140 ^{o}C), Poly(methyl methacrylate) (PMMA, Tm = 160 ^{o}C), Polyvinylidene fluoride (PVDF, Tm = 177 ^{o}C), Polycarbonate (PC, Tm = 230^{o}C), phosphoric acid, perchloric acid, and other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. By conventional hot-pressing, the polymer films with dimensions of 200 mm×200 mm×0.5 mm were fabricated and cut for further experiments.

Porous Anodic Alumina were fabricated by electrochemical oxidation methods as follows.[40, 41] Briefly, the pure Al sheets were thermal annealed for 4 hrs at 500 ^{o}C to eliminate the inner stress. After removing the alumina oxide in a mixture of phosphoric acid and ethanol (1:1) solution for 0.5 hrs, the sheets were electrically polished in alcohol and perchloric acid (3:1) mixture for 5 min at 10 V. The first anodization was conducted in a 0.3 M oxalic solution for 4 hrs at 40 V under the temperature of 0 ^{o}C. To remove alumina oxide, the sheets were then rinsed by a phosphoric acid and ethanol (1:1) solution for 1 hrs. The second anodization was conducted in 0.3 M oxalic solution for 12 hrs at 40 V. To widen the pore, the prepared sheets were immersed into 0.1 M phosphoric acid solution for 30 min.

The ultrasonic-assisted fabrication system was set up with a commercial ultrasonic welding machine from DG South Nekon Co., Ltd. The apparatus provides strong ultrasonic vibration with the frequency of 15 KHz. Scanning electron microscopy (JEOL Model JSM-6490) was utilized to characterize the nanowires on the surface of polymer. The open-circuit voltage (V_{oc}), short-circuit current (I_{sc}) and transferred charge (Qc) of TENGs were measured by LeCroy Wave Runner Oscilloscope (44MXI) with probe resistance value of 10 Mn, SR570 low noise current amplifier (Stanford Research System) and 6514 system electrometer (Keithley), following literatures.[38, 42, 43]

Results and discussion

The ultrasonic-assisted fabrication processes of polymer nanowires are schematically illustrated in **Figure 1a**. The ultrasonic vibration source, Cu film, polymer film and porous anodic alumina were firstly assembled. Under high compression, Cu film, polymer film and porous anodic alumina were fully contacted with each other. By the application of 15 kHz ultrasonic sinusoidal vibration from an ultrasonic source, the strong frictions are occurred between different materials which form two interfaces including interface of ultrasonic vibration source/Cu film and one of polymer film/Cu film. The friction further converts mechanical energy from vibration source into thermal energy to heat the materials. As the ultrasonic vibration source and Cu film are metal materials, the friction in this interface can contribute most of heat. Given the polymer film can be melted, the friction between polymer film and Cu film is much less. When the temperature arrives at the melting range of the polymer, the polymer starts melting, leading to the thermal bonding of the interface between Cu electrode and polymer film. Meanwhile, the polymer melts will be absorbed into the nanochannels of porous anodic alumina due to the large difference in surface energy between porous anodic alumina and polymer melts. After removing the porous anodic alumina by saturated NaOH aqueous solution for about 10 mins, the polymer nanowires could be released from the template. **Figure 1b** and **1c** present the top-view and cross-sectional SEM images of porous anodic alumina which was prepared by electrochemical oxidation method. The diameter of nanochannel is around 250 nm which is consistent with the literatures.[40, 41] Correspondingly, **Figure 1d** and **1e** present the morphology of the prepared PVDF nanowires on the surface of PVDF film. It is observed that, under the ultrasonic time of 15 s, the length and diameter of PVDF nanowires are around 4 μm and 250 nm, respectively. The diameter of nanowires is consistent with that of nanochannels in porous anodic alumina.

The length of polymer nanowires and the morphology of polymer surface can be controlled by ultrasonic time. As shown in **Figure 2**, the PVDF short nanowires of ~500 nm could be formed on the surface of PVDF film at a short ultrasonic time of 10 s. With the elongation of ultrasonic time, the length of PVDF nanowires increases and arrives at – 63 μm within the ultrasonic time of 65 s. The formation mechanism of polymer nanowires could be attributed to the polymer wetting principle.[44-47] When the temperature originated from the ultrasonic-driven friction arrives at the melting temperature of polymer, the polymer starts melting. Comparing with the porous anodic alumina, the polymer melts possess lower surface energy. Therefore, when the polymer melts contact with porous anodic alumina, the melts could be absorbed into the nanochannels of porous anodic alumina under strong capillary force. According to the Lucas-Washburn equation[48]

$$\mathrm{d}z/\mathrm{d}t=(Ry\cos 0)/(41z) \tag{1}$$

where z is the length of polymer nanowires in the nanochannels of porous anodic alumina, t is the wetting time of polymer melts in the nanochannels, R is the hydraulic radius equal to the diameter of nanochannel, y is the surface tension of polymer melts, 0 is the contact angle between polymer melt and subtract, 1 is the viscosity of liquid equal to viscosity of polymer melt. For the fixed polymer (1 and y are fixed) and diameter (R) of nanochannel, the length (z) of polymer nanowires could be controlled by changing the wetting time (t) of polymer melts in the nanochannels of porous anodic alumina. The longer ultrasonic time, the longer polymer nanowires are achieved, which leads to different surface morphology. As shown in **Figure 2a**, when the polymer nanowire is as short as 500 nm, the polymer nanowires keep vertical stand. Accompanying with the increment of length of polymer nanowires, the nanowires will collapse with each other and form special micro/nano-patterns as shown in **Figure 2b-2f**. The formation mechanism of micro/nano-patterns on the polymer surface could be contributed to the elastocapillary self-assembly of 1-D polymer nanomaterial. For nanowires with the length L, there is a critical pillar length, namely L_c. when $L < L_c$, two adjacent nanowires could keep upright, while once $L > L_c$, the upright state among adjacent nanowires will not be maintained. The L_c has a close relationship with the force to bend nanowires to contact with each other ($Fb \sim Bd/L^3$) and the force originated from the capillary force ($F_c \sim yr$). Here, the diameter of nanowire is r, interfacial tension is y, d is the distance between nanowires, bending stiffness of nanowire B can be expressed by $B \sim Er^4$, where E is Young's modulus of nanowires. As shown in **Figure 2a**, the length of nanowires is below the L_c, leading to the vertical nanowires on the surface. Accompanying with the longer ultrasonic time, the length of polymer nanowires is larger than L_c, which induces the collapse of nanowires and the formation of nano/micro-pattern on the surface of polymer film as shown in **Figure 2c-2f**.

Besides PVDF, the ultrasonic-assisted fabrication technique of polymer nanowires can also be expanded to a range of other polymers, including PE, ABS, PMMA and PC, with melting temperature range from 130 °C to 230 °C. The features of these polymer nanowires are shown in **Figure 3a-3d**. Under identical ultrasonic-assisted fabrication condition, interface friction between ultrasonic vibration source and Cu film could output the same heat which has no relationship with polymer film. Therefore, the length of polymer nanowires can be mainly affected by the viscosity (1) and surface tension (y) of polymer and wetting time (t). PE, ABS, PMMA and PC have different polymer structures and molecular weight distribution, leading to change viscosity (1) and surface tension of polymer melts (y) under identical temperature. Therefore, even fixing the diameter (R) of porous anodic alumina and wetting time (t), varied length of polymer nanowires still could be fabricated on the surface of different polymer film according to Lucas-Washburn equation, as shown in **Figure 3**. Among them, PE has the lowest melting temperature and surface energy which lead to the longest nanowires illustrated in **Figure 3a**. PC has the highest melting temperature, which leads to the higher viscosity (I) and surface tension of melts (y), and achieve the shortest nanowires in **Figure 3d**. As aforementioned, distinctive nano/micro-patterns therefore were formed on the surface of different polymer film due to elastocapillary self-assembly phenomenon. Consequently, nano/micro-patterns and surface morphology can be varied and arrived in a short time.

As previous studies, polymer films with nano/micro-patterns are good candidate as the triboelectric materials of TENGs. After systematic researching the controllability of nanowire's morphology, here, we take the as-prepared PVDF surface with nanowires employed for triboelectric material to fabricate a vertical contact-separation TENG as illustrated in **Figure 4a**. The working principle of TENGs to generate electricity is schematically illustrated in **Figure 4b-4e**. The polymer film with nanowires could contact and separate with the aluminum electrode under external forces, such as mechanical stimuli. With the compression of the TENG (**Figure 4c**), the nanowires on the surface of polymer film could fully contact with the surface of aluminum electrodes. Because of the difference in triboelectric series between the polymer and aluminum, electrons may migrate from aluminum to polymer surface. The negative and positive triboelectric charges will be generated on the surface of polymer film and aluminum electrode, respectively, as shown in **Figure 4c**. At the moment of separation between polymer film and aluminum, the electrical potential difference between aluminum and copper electrodes will drive electrons flow from copper electrode to aluminum electrode, which leads to the generation of instantaneous current as shown in **Figure 4d**. Because of the insulation properties of polymer, the electrons can stay on the surface of polymer nanowires. When the aluminum electrodes contact with polymer surface again, the electrons on the aluminum electrodes will flow back to the copper electrodes as shown in **Figure 4e**. By repeating the contact and separation processes between triboelectric materials, alternating current (AC) will be generated in external circuit and the mechanical energy will be transferred into electricity.

The prepared TENGs in our experiments can successfully convert mechanical motions into the electricity output as shown in **Figure 5**. Meanwhile, it is observed that the length of polymer nanowires can affect the performance of TENGs. As shown in **Figure 5a** to **5c**, accompanying with the increment of polymer nanowires length, both V_{oc} and transferred charge obviously increase. For the device based on the flat polymer film, the V_{oc} and transferred charge are ~ 11 V and ~ 6 nC, respectively. While polymer nanowires with 500 nm were fabricated on the surface of polymer film, V_{oc} and transferred charge have about 2 times enhancement and reach up to ~ 21 V and ~ 8 nC, respectively. When the length of polymer nanowires is around 30 μm, V_{oc} and transferred charge of TENGs device could arrive at ~ 230 V and ~ 79 nC. While further increment of the nanowires length (58 μm) will lead to the decrement of V_{oc} and transferred charge to 206 V and 68 nC. This may be attributed to that the length of polymer nanowires could influence their aspect ratio as shown in **Figure 5d**, and further change the triboelectric contact area and performance of TENG. Through adjustment of ultrasonic time, the length and aspect ratio of polymer nanowires could be controlled as shown in **Figure 5e**. Therefore, the performance of as-prepared TENG device will be tunable and optimizable.

Followed by the investigation of the fabrication controllability of polymer nanowires and the relationship between polymer nanowires and TENG performance, a TENG device with dimension of 4 cm × 4 cm and 2 mm gap was fabricated with PVDF nanowires of 30 μm and utilized to harvest the walking energy of human. The device was installed into the shoes and linked with instruments to measure the output performance. The generated V_{oc} and I_{sc} could achieve at 153 V and 23 μA, respectively, as shown in **Figure 6a** and **6b**. The relative current density is about 1.43 μA/cm^2. The resistance dependences of V_{oc} and I_{sc} of TENG device are shown in **Figure 6c**. The value of V_{oc} increases with the increment of loading resistance, while I_{sc} shows converse trend that the value decreases with increment of loading resistance. The maximum output power of device could achieve at 0.46 mW with external resistance of - 10 Mn as illustrated in **Figure 6d**. The whole device can power up 78 green LEDs connected in series without external energy storage devices. AC generated by TENG can be transferred into DC by utilization of inverter to charge a capacitor. Its voltage can achieve at 10 V in 3 seconds.

Conclusions

In summary, we demonstrate a novel ultrafast ultrasonic-assisted fabrication approach of vertical polymer nanowires for making TENGs. Due to the high temperature originated from ultrasonic-driven friction between materials, polymer melts could be formed and absorbed into nanochannels of template to fast prepare polymer nanowires on the surface of polymer film by removing template. The length and aspect ratio of polymer nanowires are controllable simply by changing the ultrasonication time. The prepared polymer surface with nanowires serves as the triboelectric materials of TENGs. The assembly triboelectric nanogenerator with PVDF nanowires can offer the output of 230 V in open-circuit voltage and ~ 79 nC in transferred charge. The prepared device could be utilized to harvest human walking energy with electric output of 153 V and 23 μA. 78 green LEDs and storage capacitor can be easily powered. More importantly, the approach of controllable and ultrafast fabrication can be expanded to synthesizing various kinds of polymer nanowires which are essential parts of diverse energy devices.[48] This study presents a novel fabrication approach of polymer nanowires with ultrafast property, controllability, universal suitability, and demonstrates the polymer nanowires' application in energy harvesting of TENGs with enhanced performance.

Acknowledgements

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FIGURE CAPTIONS:

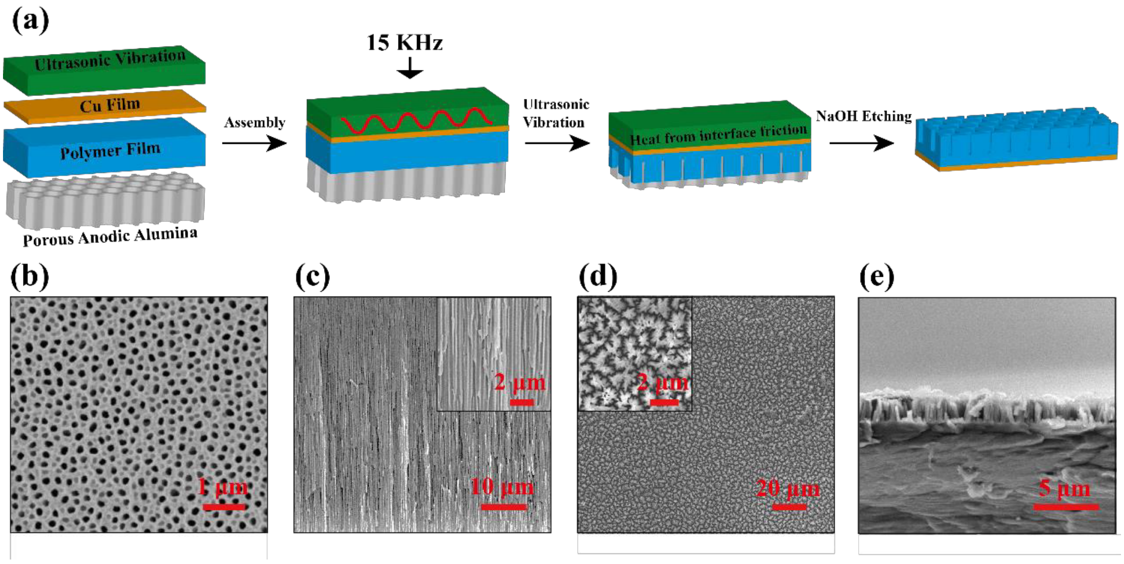

Figure 1. (a) Schematically illustration of fabrication processes of polymer nanowires under ultrasonic assist; (b) and (c) Top-view and cross-section of porous anodic alumina; (d) and (e) Top-view and cross-section of PVDF nanowires under 15 s of ultrasonic time and 15 kHz of ultrasonic vibration frequency.

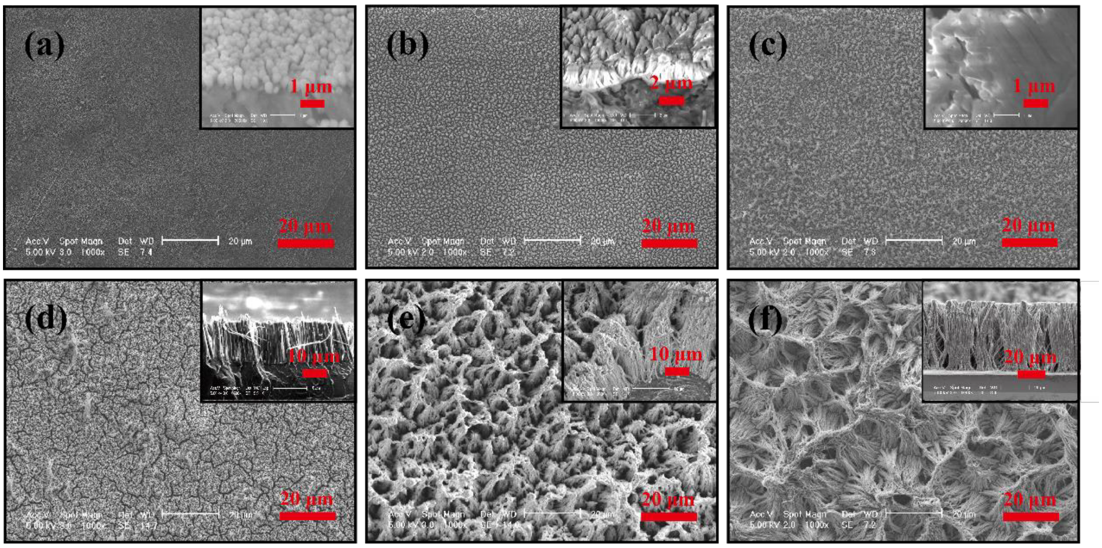

Figure 2. The surface morphology of PVDF film under different ultrasonic time: (a) 10 s; (b) 20 s; (c) 30 s; (d) 40 s; (e) 50 s; (f) 65 s.

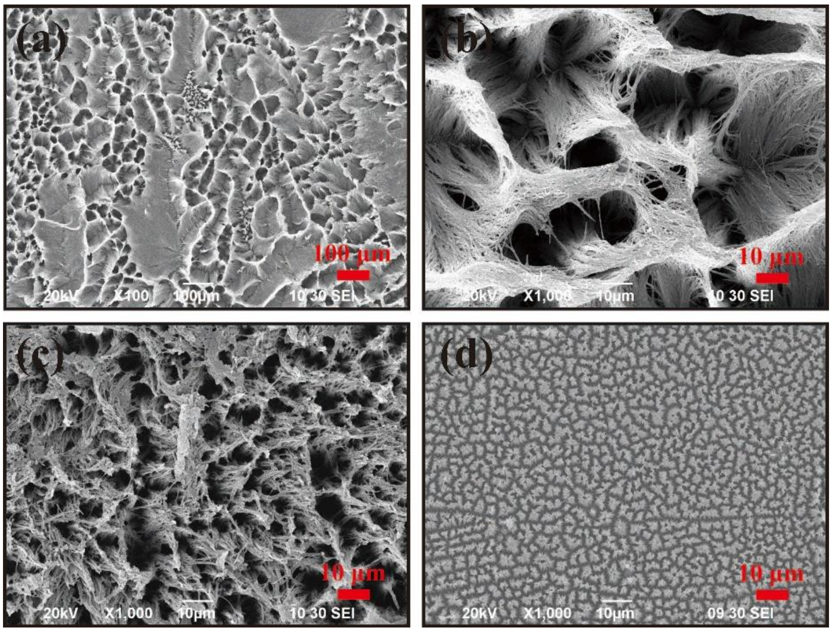

Figure 3. Nano/micro-patterns of different polymer under 15 s ultrasonic treatment. (a) Polyethelene; (b) Acrylonitrile butadiene styrene; (c) Poly(methyl methacrylate); (d) Polycarbonate.

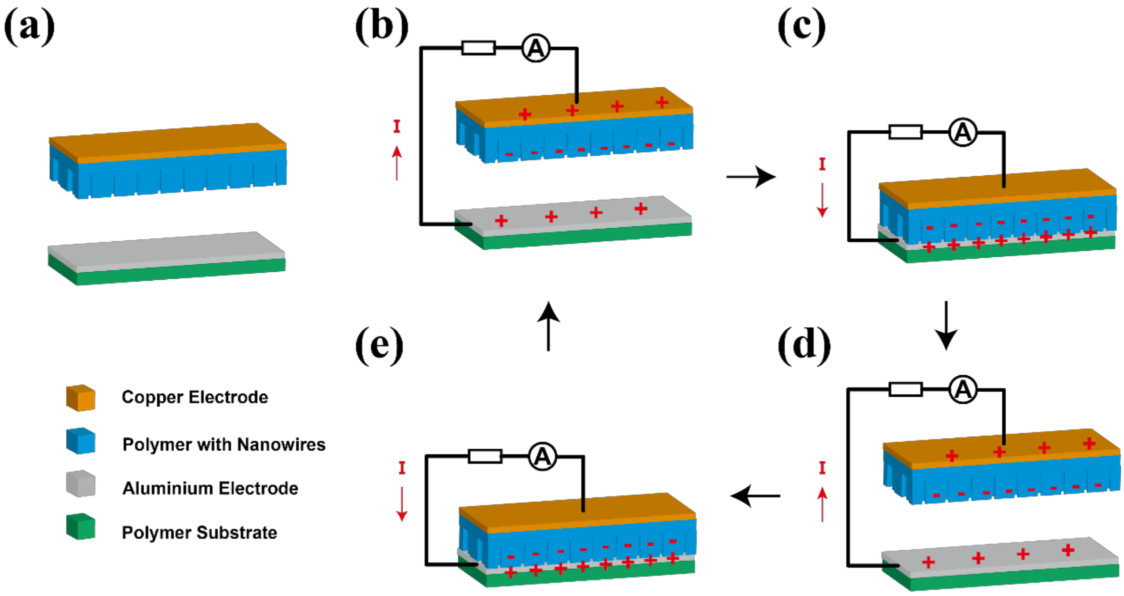

Figure 4. (a) Structure illustration and (b)-(e) working principle of the triboelectric nanogenerator.

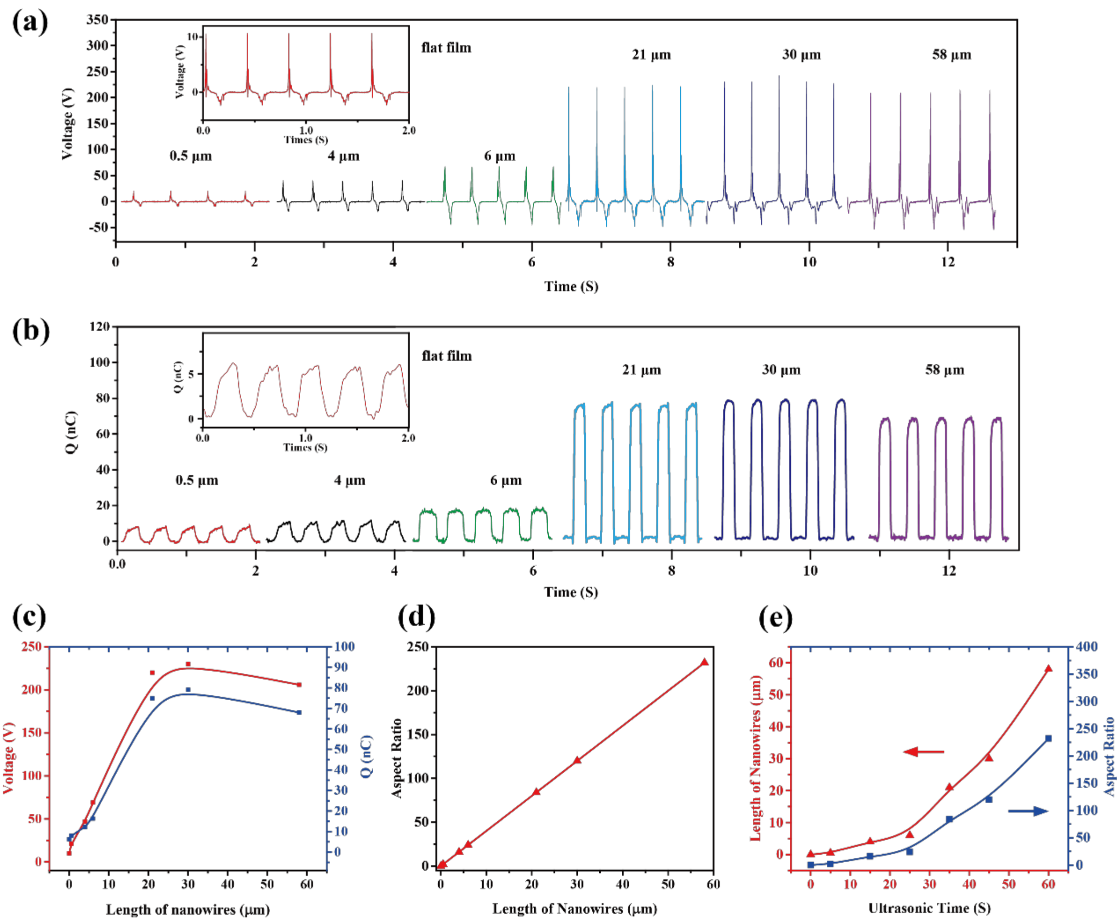

Figure 5. (a) The open-circuit voltage of TENGs with different length of polymer nanowires; (b) The transferred charges of TENGs with different length of polymer nanowires; (c) The influence of length of polymer nanowires on the open-circuit voltage and transferred charge; (d) The relationship of nanowires length and aspect ratio; (e) The influence of ultrasonic time on the length and aspect ratio of polymer nanowires, respectively.

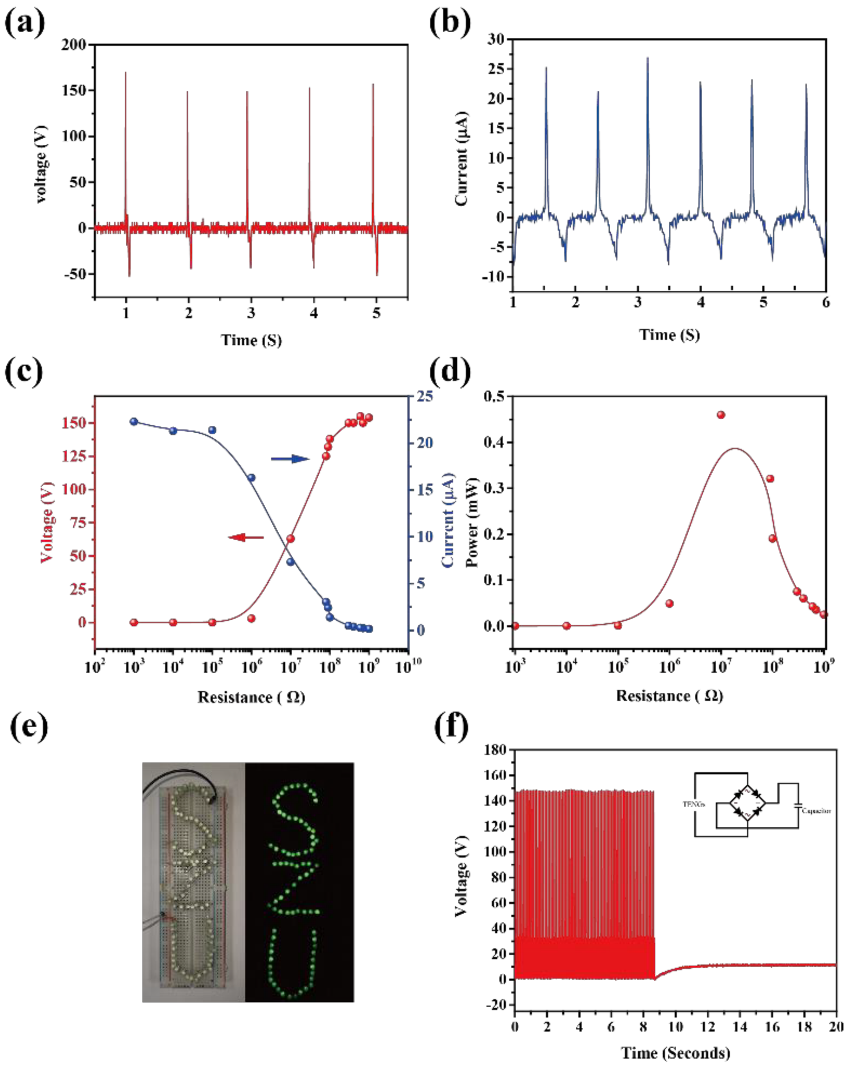

Figure 6. (a) and (b) Open-circuit voltage and short-circuit current of the TENG, respectively; (c) and (d) The dependence of output performance and peak power of TENG on the resistance of external load, respectively; (e) Photo images showing 78 green LEDs driven by TENG device without external circuit loads; (f) DC voltage of TENGs with inverter and connected with capacitor (5 μF).

Table of Content

A novel, ultrafast, ultrasonic-assisted fabrication technique of polymer nanowires has been developed for triboelectric nanogenerator. By controlling the ultrasonic times, the length and aspect-ratio of polymer nanowires on the surface of polymer can be tunable from 2 to 232. The assembly TENGs are capable of harvesting mechanical energy with electric output of 153 V and 23 μA. This study not only presents a novel ultrafast fabrication approach of polymer nanowires with aspect-ratio controllability and universal suitability, but also demonstrates the polymer nanowires' application in energy harvesting of TENGs with enhanced performance.