Environmentally Friendly Hydrogel-based Triboelectric Nanogenerators for Versatile Energy Harvesting and Self-Powered Sensors

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Abstract:

Triboelectric nanogenerators (TENGs) as a promising energy harvesting technology have been rapidly developed in recent years. However, the research based on fully flexible and environmentally friendly TENGs is still limited. Herein, we demonstrate, for the first time, a hydrogel-based triboelectric nanogenerator (Hydrogel-TENG) with high flexibility, recyclability and environmental friendliness simultaneously. The standard Hydrogel-TENG can generate a maximum output power of 2 mW at a load resistance of 10 Mn. The tube-shaped Hydrogel-TENG can harvest mechanical energy from various human motions, including bending, twisting and stretching. Furthermore, the system can serve as self-powered sensors to detect the human motions. Additionally, the utilized Polyvinyl Alcohol (PVA) hydrogel employed in this study is recyclable to benefit for fabricating the renewable TENG. The open-circuit voltage of renewed hydrogel-TENG can reach up to 92% of the pristine output voltage. This research will pave a potential approach for the development of flexible energy sources and self-powered motion sensors in environmentally friendly way.

1. Introduction

As an emerging electronics with excellent deformability and reliability, the flexible electronics is attracting extensive interest, enabling various applications in wearable devices, epidermal electronics and bendable display etc.[1-5] Meanwhile, the massive applications of these modern electronics inevitably causes environment issues due to their non-degradability in the environment. As a solution, green electronics with high biodegradability and biocompatibility has emerged with growing focus.[6-8] The advance in flexible electronics and green electronics put forward severe challenges on the traditional power source.[9-11] In this regards, developing sustainable, flexible and environmentally friendly power generation devices is highly desired to drive these emerging electronics and deserves more attempts.[12, 13]

Recently, triboelectric nanogenerators (TENGs) as a sustainable power source have been achieving rapid progress from both academia and industry.[14-16] Based on the conjunction of triboelectrification and electrostatic induction, TENGs can efficiently convert ambient mechanical energies into electricity with simple fabrication process and expected sizes.[3, 16-18] Most importantly, TENGs can be designed and fabricated with flexibility, elasticity, bio-degradation and bio-compatibility through the choice of constituent materials,[3, 8, 14] and therefore they becomes promising candidates to drive flexible electronics and green electronics. Nowadays, considerable efforts have been contributed to develop flexible TENGs,[19-23] such as fiber-based TENG, rubber-based TENG, TENG coat and TENG based on conductive liquid. Compared with the rigid TENGs, flexible TENGs can harvest ambient mechanical energy in various modes and thus gain continuous concern from relevant industries.[5, 20] Accompanying with the widespread applications of flexible TENGs in the new-generation electronics, it is highly necessary to develop novel TENGs with high flexibility and environmental friendliness simultaneously to meet dual demand of both flexible electronics and green electronics. To our knowledge, very limited research has been reported in the related field.[24]

Hydrogel, an environmentally friendly material with 3D crosslinking network of polymer

chains,[25-27] could be an ideal material to realize flexible and environmentally friendly TENGs. The 3D network structure of hydrogel leads to excellent mechanical properties, including high softness, flexibility and elasticity.[26-29] In addition, the hydrogel also remains excellent properties of environmental friendly, such as biodegradability and biocompatibility.[25, 27, 30] These advantages may result in the extensive applications of hydrogel in flexible electronics and green electronics.[29-31] Although some attempts have been made in innovating hydrogel-based electronics for energy storage and conversion applications,[31-34] there has been no report on applying hydrogel to TENGs.

Herein, we presented a novel hydrogel-based triboelectric nanogenerator (Hydrogel-TENG) with full flexibility and environmental friendliness by using physical-crosslinking Polyvinyl Alcohol (PVA) hydrogel as substrate materials. For the standard Hydrogel-TENG which consists of a polydimethylsiloxane (PDMS) film attached on hemispheric-shaped hydrogel and an aluminum foil, a peak output power of 2 mW can be achieved at a load resistance of 10 Mn. The tube-shaped Hydrogel-TENG can harvest mechanical energy from various human motions, including bending, twisting and stretching, and serve as self-powered human motion sensor. Besides, the utilized PVA hydrogel with biodegradability and biocompatibility presents the recyclability, which provides the Hydrogel-TENG with advantages of environmental friendliness and low-cost.

2. Results and discussions

As shown in **Figure 1a,** the structure of Hydrogel-TENG consists of two parts: the top contact layer with hemispheric shape and the bottom contact layer with flat structure. For the top contact layer, a hemisphere-shaped PVA hydrogel with a nickel fabric electrode was encapsulated by a PDMS film. Due to the high elasticity of PVA hydrogel and PDMS film, the top contact layer shows excellent expansibility, flexibility and stretchability under the stimuli of external force. The bottom contact layer is an Al foil attached on the surface of hydrogel

substrate. The Al foil with anodized nanostructure plays dual roles as triboelectric contact material and electrode, and its morphology is shown in **Figure 1b**. As mentioned in literatures,[19] the nanostructures on the surface of Al foil could enhance the performance of TENGs by increasing the effective contact area.

The operation mechanism of the Hydrogel-TENG is schematically illustrated in **Figure 1c-1f**. When a pressure force is applied to Hydrogel-TENG, the PDMS film and Al foil are adequately contacted due to the elastic expansion of the hydrogel and PDMS film, wherein the maximum contact area (A_{max}) between PDMS film and nano-patterned Al electrode is achieved (**Figure 1c**). Since the surface electron affinity of PDMS is higher than Al,[35] electrons will be transferred at the interface between Al foil and PDMS, leaving positive triboelectric charges on the Al foil surface and corresponding negative triboelectric charges on the PDMS surface. By releasing the external force (**Figure 1d**), PDMS film and nano-patterned Al electrode could be separated due to the elastic contraction of the expanded hydrogel and PDMS film, which leads to the decrement of contact area. Accompanying with the electrostatic induction between PDMS and Ni electrode, the separation of charged contact surfaces creates the electric potential difference between Ni and Al electrodes, which drives electrons flow from the Ni electrode to the Al electrode until the external force is fully released (**Figure 1f**), where the minimum contact area (A_{min}) is reached. When the Hydrogel-TENG is compressed again (**Figure 1e**), an opposite electric potential difference will be formed, which causes the electrons flow back to the Ni electrode from the Al electrode until the A_{max} is achieved again (**Figure 1c**). Therefore, the AC electricity can be continuously generated by periodical contact-separation between PDMS film and Al electrode. The electric output amplitude depends on the change of contact area (LIA), which equals to $A_{max} - A_{min.}$

In order to characterize the electric output of Hydrogel-TENG, a standard device with the bottom contact layer of 8 cm x 8 cm was fabricated by fixing the frozen time of PVA (5.5 hours), the concentration of PVA aqueous solution (25 %) and the diameter of hemisphere hydrogel (4

cm). As shown in **Figure 2a-2b,** the open-circuit voltage and short-circuit current of standard device could achieve up to 200 V and 22.5 μA, respectively. Besides, the short-circuit transfer charge (Qsc) of the device is also shown in **Figure S1a**. For further evaluating performance of the Hydrogel-TENG, the resistance dependence of the output voltage and current is investigated as illustrated in **Figure 2c.** The results reveal that the voltage increases with increment of loading resistance, while the current shows a reverse trend. Correspondingly, the maximum electric power could reach up to 2 mW at a load resistance of around 10 Mn as shown in **Figure S2**. The as-prepared TENG can light up 20 commercial white LEDs simultaneously as displayed in **Figure 2d.**

As aforementioned, the AC triboelectricity is generated by periodical change of the contact area between PDMS film and Al foil, which is caused by elastic deformation of the hydrogel. It means that the elasticity of hydrogel has an effect on the performance of the Hydrogel-TENG. Herein, there are two parameters which can affect the elasticity of PVA hydrogel, i.e. frozen time and concentration of PVA. **Figure 3a** and **3b** show the relationship between the frozen time and the performance of Hydrogel-TENG. The results indicate that the maximum open-circuit voltage of 200 V and the maximum short-circuit of 22.5 μA are achieved at the frozen time of 5.5 hrs. Further elongating and shorting the frozen time leads to the decrement of open-circuit voltage and short-circuit current. This is mainly attributed to the elasticity change of hydrogel under different fabrication conditions. The elasticity of utilized hydrogel originates from the formation of micro-crystallites among PVA molecular chains. These micro-crystallites can serve as physical crosslinkers and provides the hydrogel with 3D crosslinking network structure and the tunable elasticity.[36-38] When extending the frozen time for 5.5 hrs, the size and amount of micro-crystallites increase and the expansibility of PVA hydrogel thus decreases, which leads to the reduced *LIA*. Therefore, the open-circuit voltage and short-circuit current decrease to about 165 V and 18 μA, respectively at the frozen time of 7.5 hrs. However, when the frozen time is less than 5.5 hrs, the amount of micro-crystallites existed in PVA hydrogel is

limited with low crosslinking density in 3D crosslinking network. Accordingly, the hydrogel cannot provide sufficient resilience force to separate the charged contact surfaces completely after the external force is released. Hence, the electric output is decreased. **Figure 3c** and **3d** present the performance of Hydrogel-TENG fabricated with PVA aqueous solution at different concentration. When the concentration of PVA changes from 25 % to 17.5 %, the open-circuit voltage and short-circuit current decrease from 200 V to 171 V and from 22.5 μA to 20.7 μA, respectively. At the low PVA concentration, the reduced amount of PVA molecules will limit the formation of micro-crystallites, which leads to the lower resilience of the hydrogel. As a result, the charged contact surfaces cannot be separated effectively and results in the reduced electric output of Hydrogel-TENG. Further reducing the concentration of PVA, the hydrogel has not enough micro-crystallites to remain hemispheric structure even at the original state. We further investigate the dependence of electric output on the diameter of hemisphere-shaped hydrogel as shown in **Figure 3e** and **3f**. The results indicate that the open-circuit voltage increases obviously from 105 V to 236 V when the diameter of hydrogel increases from 2 cm to 5 cm. The electric output of Hydrogel-TENGs mainly originates from the change of contact area (*LIA*) between triboelectric materials, which is related to the change of the average separation distance between contact layers (*LId)*. According to earlier model[39, 40, 41] as illustrated in supporting information, the open-circuit voltage of TENGs could be approximately calculated as

$$V_{oc} = \frac{at1d}{E_0}$$

where V_{oe} is the open-circuit voltage, c_O is the permittivity of vacuum, a is the average surface charge density of contact materials, *LId* is the change of the average separation distance between the top contact layer and the bottom contact layer. Under a certain external force, increasing the diameter of hydrogel could cause the increase of *LId*, thereby leading to the increment of *LIA* and electric output. When the diameter of hydrogel arrives at 5 cm, the saturation of the electric

output is occurred. The possible reason behind the observation is that *LIA* already reaches the maximum value based on the certain applied external force and the electric output will not enhance when increasing the diameters. For further comparing the quality of devices with different parameters, their Qsc and performance Figure-of-merit (FOMp) [41] are shown in Figure S1b-d and **Table S1**, respectively.

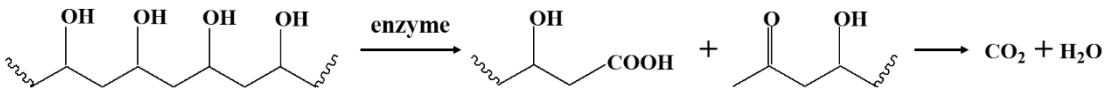
For harvesting mechanical energy from various human motions, a Hydrogel-TENG with tube-shaped structure is designed by combining several standard devices as shown in **Figure 4a.** The system includes six series connected hemisphere-shaped top contact layers with the diameter of 2.5 cm, and a tube-shaped bottom contact layer (8 cm x 10 cm). Under the external force, the tube-shaped Hydrogel-TENG can deform and cause the volume compress. This leads to the change of the contact area between PDMS and nano-patterned Al electrode, and therefore results in the generation of triboelectricity. Due to the high deformation and flexibility of hydrogel, the tube-shaped Hydrogel-TENG shows great flexibility and is able to deform following various human motions as demonstrated in **Figure S3**. The open-circuit voltages of tube-shaped Hydrogel-TENG generated from bending, twisting and stretching motion are shown in **Figure 4b**, **4c** and **4d,** respectively. The results indicate that the Hydrogel-TENG could harvest mechanical energy from different human motions and the open-circuit voltage can reach up to about 40 V when the bending angle and twisting angle are 150°. Additionally, it is also observed that the open-circuit voltage of Hydrogel-TENG is enhanced with the increment of bending angle, twisting angle and tensile stain as shown in **Figure 4b**, **4c** and **4d**. That is contributed to the larger *LIA* with the increased deformation of the TENGs, which leads to the improved electric output.

Based on above results, the as-prepared Hydrogel-TENG could generate distinctive voltage signals triggered by various motions, which indicates its potential applications as a self-powered sensor to monitor the human motion in real time. **Fig Sa-Sd** exhibit the application of the Hydrogel-TENG as a self-powered elbow-joint motion sensor, which is a tube-shaped

Hydrogel-TENG with the diameter of 1 cm and the length of 18 cm. The device is fixed over the straighten elbow joint at the original state. After changing the bending angle periodically, including 30 °, 90 ° and 120 °, the different output voltages of 3.5 V, 13 V and 16 V are generated, respectively (**Figure Sa**). Correspondingly, the relationship between open-circuit voltage and the bending angle is shown in **Figure Sc**. The results presents that the bending angle is proportional to the open-circuit voltage of the Hydrogel-TENG at the bending rate of 1.5 times/s. Hence, the change of bending angle in the elbow joint motion can be monitored through the change of open-circuit voltage. Moreover, the Hydrogel-TENG is also capable of distinguishing elbow motions with different bending rate by monitoring the peak interval and peak amplitude of open-circuit voltage. As shown in **Figure Sb**, when the bending rate of elbow joint is increased from 0.6 times/s to 2 times/s, the peak interval is shortened from 1.67 s to 0.5 s with the increased voltage amplitude from 3.7 V to 17.5 V. **Figure Sd** shows the dependence of peak interval and open-circuit voltage on the bending rate with the bending angle of 90 °. It is observed that the peak interval between adjacent voltage signals is inversely proportional to the bending rate, while the open-circuit voltage is linearly associated with the bending rate, which indicates the advantages of hydrogel-TENGs as a bending rate sensor. By adjusting the dimension of device, the Hydrogel-TENG could also be utilized to detect human motion in other human body parts. **Figure S4** presents a finger-joint motion sensor based on a small size of tube-shaped Hydrogel-TENG with the diameter of 1 cm and length of 8 cm. It shows that the difference in bending angle of finger joint could also be recognized by measuring the open-circuit voltage. Improving bending angle from 30^{o} to 120^{o} leads to the similar increment in open-circuit voltage from 2.7 V to 5.1 V. Therefore, the as-prepared Hydrogel-TENG may identity different human motions by analyzing the peak amplitude and peak interval of voltage signals. In general, electronics which directly contact with human body has some specific requirements, such as non-toxicity, high comfortability, biocompatibility or biodegradability. In this context, the Hydrogel-TENG as a human motion sensor presents great advantages

compared with other flexible TENGs due to its high safety, biocompatibility and flexibility, which might indicate its potential in diverse applications, such as artificial skin, health care, wearable electronics and criminal investigation.

With the rapid development of modern electronics, the relevant environmental issues have been raised due to the electronic wastes pollution. As a kind of environmentally friendly material, the PVA shows promising potential in the fabrication of green electronics with biodegradability and biocompatibility to solve above problems. [42, 43] The biodegradable reaction of PVA in the environment is shown below:[42, 43]



It should be mentioned that the final degradation products of PVA are carbon dioxide and water, which are highly safe for environment. Besides, other materials utilized in Hydrogel-TENG also present environmental compatibility. Briefly, PDMS is known polymer routinely utilized as a biomedical implant material and for cellular studies, while Al and Ni show abundant applications in various fields, such as metal implants and biomaterials.[44, 45]

Therefore, the Hydrogel-TENG fabricated with PVA possesses excellent environmental friendliness. Additionally, the formation of micro-crystallites in the PVA hydrogel presents reversibility,[36-38] which means that the 3D crosslinking network structure among PVA molecular chains could disappear with the melting of micro-crystallites at high temperature and rebuild with the regeneration of micro-crystallites under the frozen treatment. Based on this process, the PVA hydrogel utilized in the Hydrogel-TENG can be fully recycled for the refabrication of device without environmental contamination. To provide further evidence, the optical images in **Figure 6a** show the recycling process of PVA hydrogel. The pristine hemisphere-shaped hydrogel with the diameter of 4cm is firstly prepared by freezing 25% PVA aqueous solution at - 20 ℃ for 5.5 hrs, where the micro-crystallites among PVA molecular chains are generated **(i)**. Then the hydrogel is cut into pieces **(ii)**. After heating the

hydrogel pieces for 1 hr at 95 °C, a PVA aqueous solution is achieved due to the disappearance of micro-crystallites at high temperature **(iii)**. By means of the frozen-thawed process of PVA aqueous solution at - 20 ℃ for 5.5 hrs,[36-37] the 3D crosslinking network structure can be re-built with the regeneration of micro-crystallites, which leads to the formation of hemisphere-shaped hydrogel **(iv)** for the refabrication of Hydrogel-TENG. **Figure 6b** and **6c** show the open-circuit voltages of the pristine Hydrogel-TENG and the refabricated Hydrogel-TENG, respectively. Compared with the voltage of 200 V generated by the pristine device (**Figure 6b)**, the voltage of the refabricated device can arrive at about 185 V (**Figure 6c)**, which is about 92 % as high as that of the pristine one. This demonstrates the recyclability of the Hydrogel-TENG as a mechanical energy harvester, and also provides a feasible way for developing environmentally friendly and low-cost electronics.

3. Conclusion

In summary, a high-flexible, environmentally friendly and recyclable Hydrogel-TENG is demonstrated for harvesting ambient mechanical energy and serving as self-powered human motion sensors. The dependence of electric outputs on the frozen time, the concentration of PVA and the dimension of standard device has been systematically investigated. The standard device can generate an open-circuit voltage of 200 V and a short-circuit current of 22.5 μA with the peak power of approximately 2 mW at a load resistance of 10 Mn and therefore power 20 LEDs directly. The tube-shaped Hydrogel-TENG is capable of harvesting mechanical energies from various kind of motions, including bending, twisting and stretching. It can also serve as self-powered human motion sensor. Moreover, the utilized PVA hydrogel is recyclable for fabricating renewable Hydrogel-TENG. This study provides the feasibility of developing flexible, environmentally friendly and recyclable power generation devices as well as self-powered sensors based on the hydrogel.

4. Experimental Section

Fabrieation of the standard Hydrogel-TENG: (1) Fabrication of the top contact layer: To achieve a hemisphere-structured PVA hydrogel, the PVA 1799 aqueous solution with the concentration of 17.5 %, 20 % and 25 % were firstly poured into a hemispheric PMMA vessel under 80 C, a circular nickle fabric was inserted into the PVA aqueous solution as electrode. Then the whole set was frozen at - 20 C for 3.5 - 7.5 hrs, and thawed consequently for 2 hrs to form the hemisphere-structured hydrogel. Then, the hydrogel was encapsulated by PDMS thin film which was fabricated by curing the mixture of PDMS and cross-linker (Sylgard 184, Dow Corning) at 80 °C for 1 hr in an oven. The ratio of PDMS to crosslinker is 30:1. (2) Fabrication of the bottom contact layer: The nanoporous structure on the aluminium surface was fabricated as following steps: An Al foil was used as anode and put into 3 % (mass fraction) oxalic acid ($H_2C_2O_4$) electrolyte for anodization of 5 hrs under a bias voltage of 30 V, with a platinum plate as the cathode. Then, the obtained Al layer was etched away in a chromic acid solution (20 g L^{-1}) at 60 °C for 2 hrs. Finally, the nanopatterned Al foil was attached on the surface of hydrogel substrate (8 cm x 8 cm). (3) The standard Hydrogel-TENG thus was achieved by assembling the top contact layer with the bottom contact layer. The optical image of the standard hydrogel-TENG is shown in **Figure SS** (supporting information).

Fabrieation of the tube-shaped Hydrogel-TENG: Six hemisphere-shaped top contact layers with the diameter of 2.5 cm are in series connection firstly. Then, the connected top contact layers are wrapped by a bottom contact layer (8 cm x 10 cm) to form the tube-shaped Hydrogel-TENG.

Measurement of the deviee: The open-circuit voltage and short-circuit current were measured by LeCroy WaveRunner Oscilloscope (44MXI) with the probe resistance value of 10 Mn and low noise current amplifier (Stanford Research Systems, SR570), respectively. An external force was applied by a linear mechanical motor. The surface morphology of the aluminum foil was characterized by a Hitachi SU-8010.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure lists

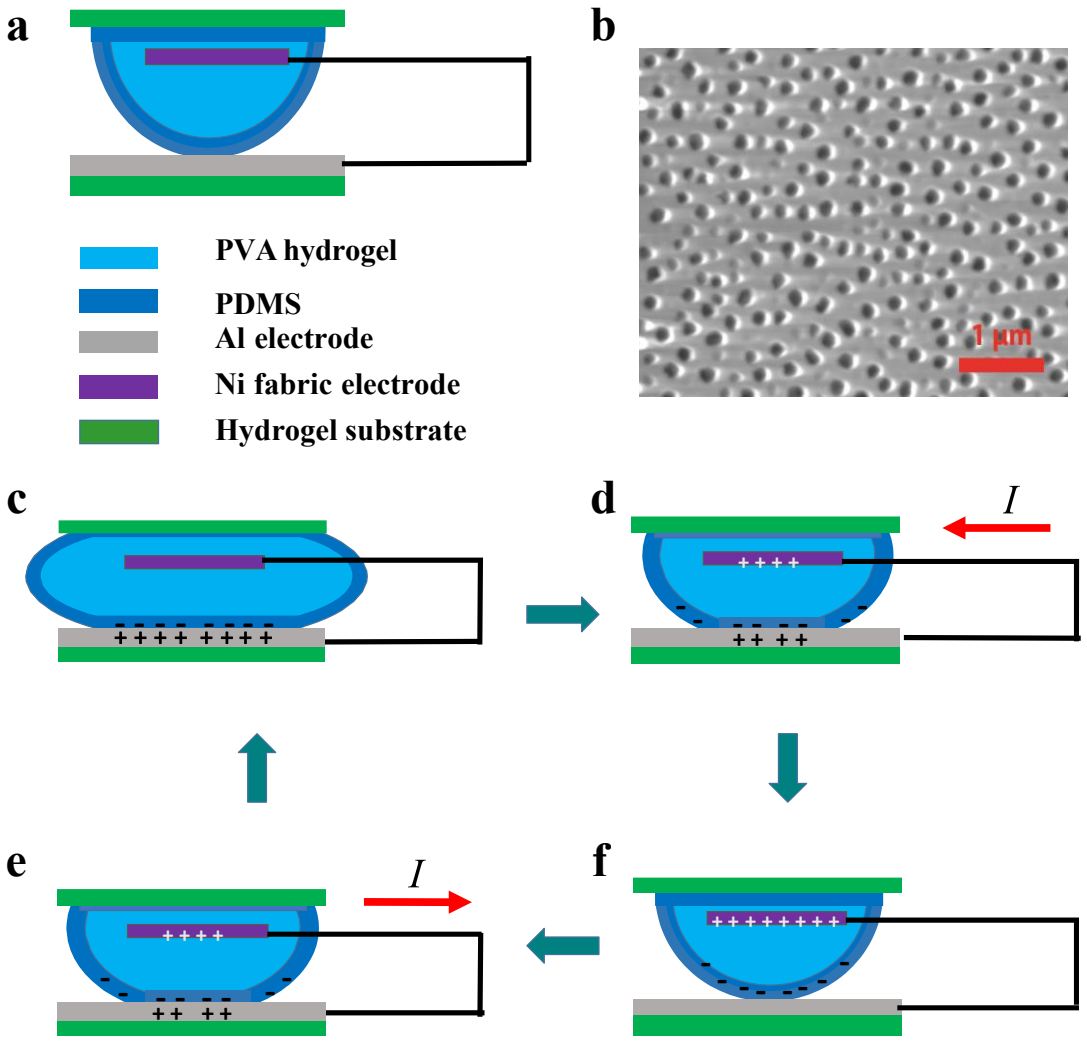

Figure 1. a) Schematic of the standard hydrogel-based triboelectric generator; b) SEM image of Al foil. (c)-(f) Schematic illustration of working mechanism of Hydrogel-TENG. (c) Expanded state (d) Releasing state. (f) Released state. (e). Expanding state.

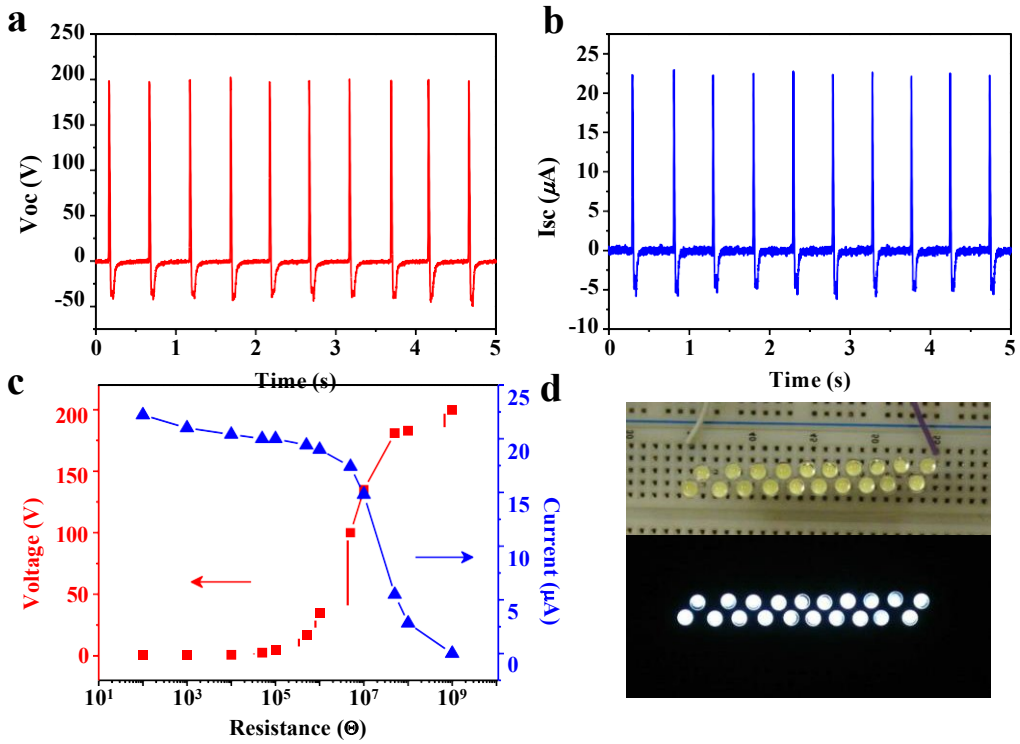

Figure 2. (a) Open-circuit voltages and (b) short-circuit current of the standard Hydrogel-TENG under a frequency of 2 Hz. (c) output voltage and current versus the resistance of the external loads. (d) The optical image of 20 LEDs powered by the standard Hydrogel-TENG.

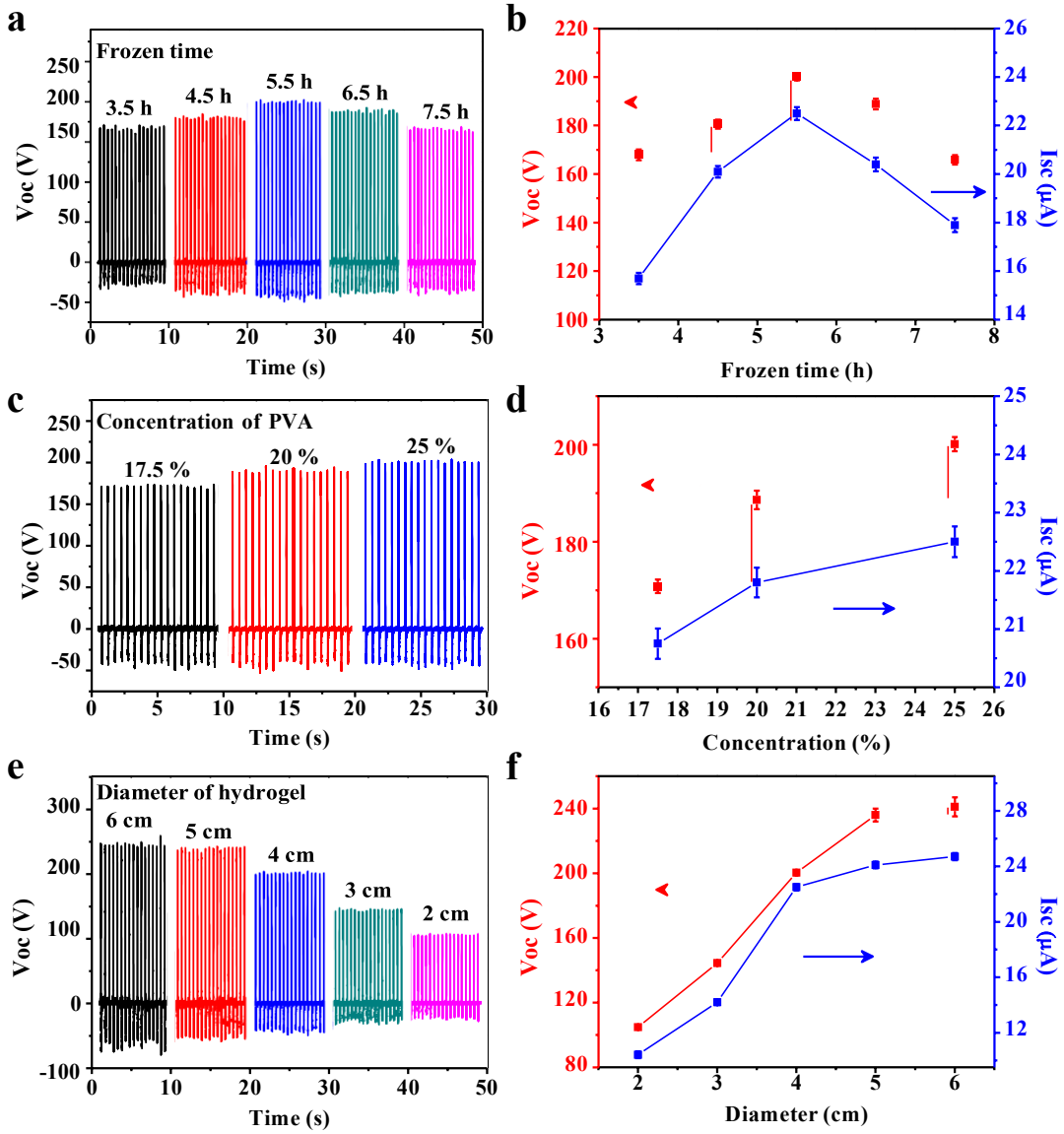

Figure 3. (a) The open-circuit voltage of standard Hydrogel-TENG at different frozen time. (b) The relation between the frozen time and the electric output. (c) The open-circuit voltage of standard Hydrogel-TENG fabricated with the different concentration of PVA. (d) The relation between the concentration of PVA and the electric output. (e) The open-circuit voltage of standard Hydrogel-TENG with the different diameter of hemispheric hydrogel. (f) The relation between the diameter of hydrogel and the electric output.

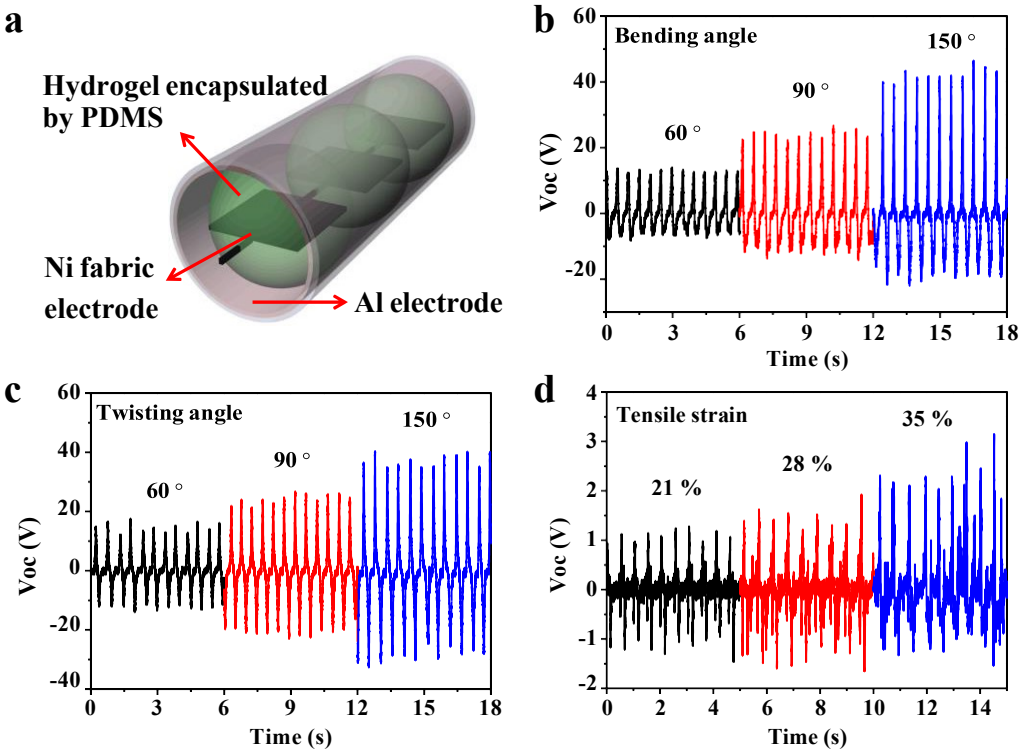

Figure 4. (a) The structural schematic of the tube-shaped Hydrogel-TENG. (b) The open-circuit voltage of tube-shaped Hydrogel-TENG under different bending angel (60°, 90°and 150°). (c) The open-circuit voltage of tube-shaped Hydrogel-TENG under different twisting angle (60°, 90°and 150°). (d) The open-circuit voltage of tube-shaped Hydrogel-TENG under different tensile strain (21 %, 28 % and 35 %).

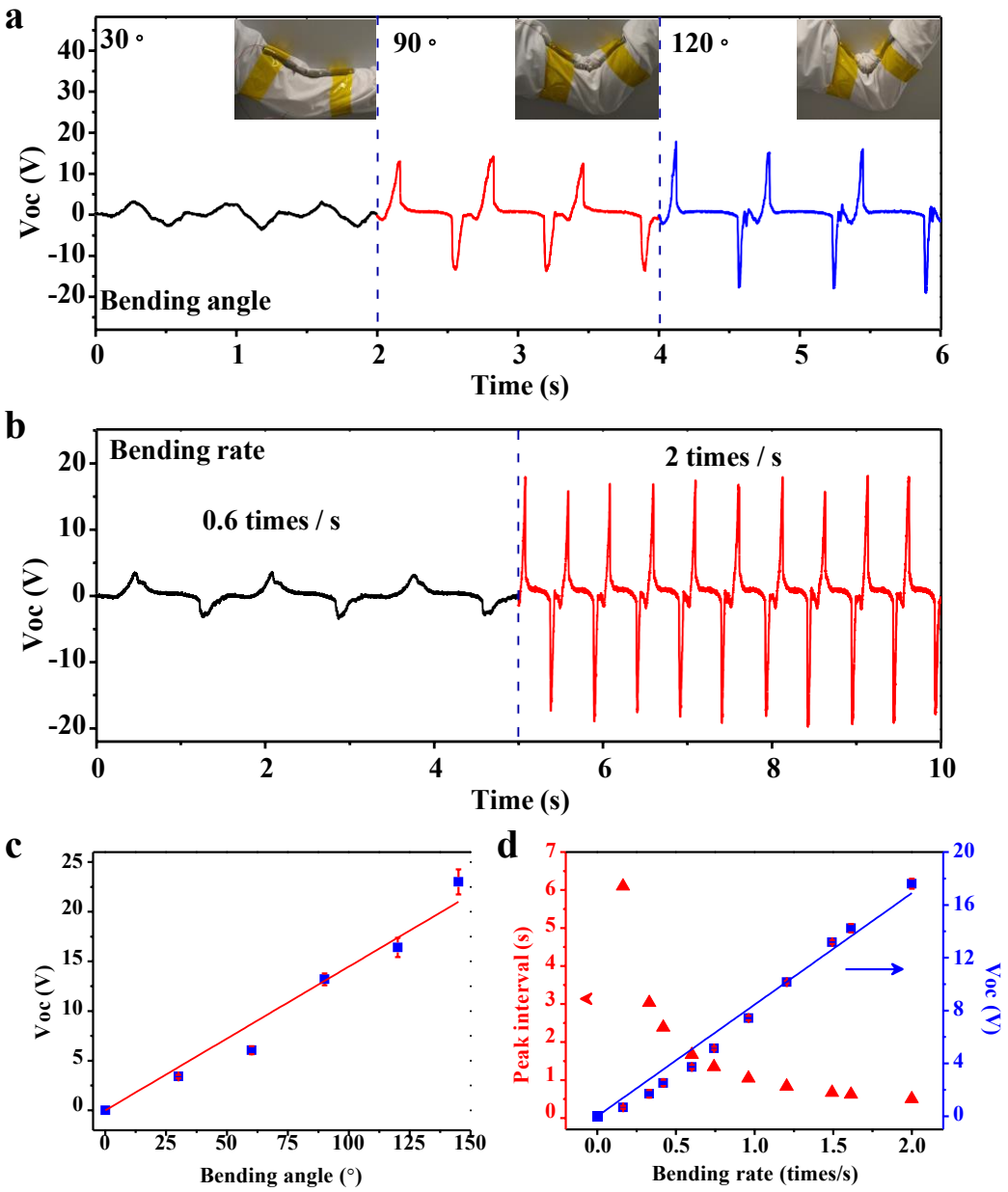

Figure S. Applications of the Hydrogel-TENG to detect joint motion. (a) optical images of the device as the elbow joint motion sensor and the open-circuit voltage responses when bending the elbow joint at different angles (30°, 90°and 120°) (b) open-circuit voltage responses when bending the elbow joint at different bending rates (0.6 times/s and 2 times/s). (c) relationship between open-circuit voltage and bending angle of the elbow joint motion at the bending rate of 1.5 times/s. (d) open-circuit voltage and peak interval versus the bending rate of the elbow joint motion at the bending angle of 90°.

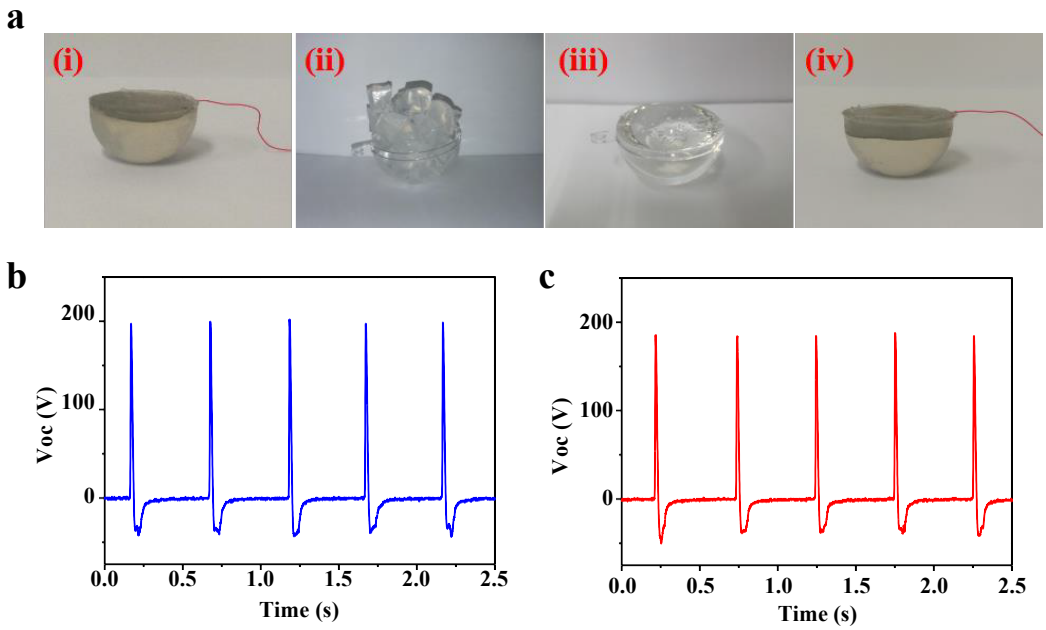

Figure 6. (a) The optical image of the recycling process of PVA hydrogel. (i) The optical image of pristine hemisphere-shaped hydrogel (ii) The optical image of hydrogel pieces. (iii) The optical image of PVA aqueous solution. (iv) The optical image of reshaped hemisphere-shaped hydrogel. (b) The open-circuit voltage of pristine device (c) The open-circuit voltage of reshaped device.

Table of Content:

We firstly demonstrate a hydrogel-based triboelectric nanogenerator with high flexibility, recyclability and environmental friendliness simultaneously for versatile energy harvesting and self-powered human motion sensor. The utilized Polyvinyl Alcohol (PVA) hydrogel is recyclable to benefit for fabricating the renewable TENG, and the Voc of renewed device can reach up to 92 % of the pristine performance.

Keyword

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Environmentally Friendly Hydrogel-based Triboelectric Nanogenerators for Versatile Energy Harvesting and Self-Powered Sensors

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