https://doi.org/10.1016/j.nanoen.2017.08.045

Fully Self-healing and Shape-tailorable Triboelectric Nanogenerators Based on Healable Polymer and Magnetic-assisted Electrode

*Wei Xu, Long-Biao Huang, Jianhua Hao**

W. Xu, Dr. L.-B. Huang, Prof. J. H. Hao,

Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, P. R. China

E-mail: jh.hao@polyu.edu.hk

Abstract

Triboelectric nanogenerator (TENG) as a promising mechanical energy harvester has been rapidly developed recently. However, its robustness and endurance are seriously challenged by frequent and inevitable mechanical impacts during operation. Herein, we demonstrate, for the first time, a fully self-healing TENG possessing the ability to recover its performance after damage by introducing healable polymer materials and electrodes consisting of small magnets into the device. Our works imply that high-performance self-healing TENG can be readily realized attributed to not only the excellent mechanical-healing capability of the employed healable polymer but also the quick electric-healing capability of the novel magnetic-assisted electrodes designed for the TENG. The measurements indicate that both the output voltage and current of the healed device can reach up to above 95 % of their original values even

after the 5th breakage-healing cycle. Additionally, the presented TENG also shows shape-tailorability and object-adaptability. This maximizes the effective contact area of device and further increases the electric output performance to benefit energy harvesting and self-powered sensing of versatile mechanical motions. This research will offer feasible strategies for developing novel mechanical energy harvesting devices and self-powered sensors with recoverability, robustness and adaption.

Keywords: triboelectric nanogenerators, self-healing, energy harvesting, shape-tailorable

1. Introduction

Alongside the continued growth in consumption of limited fossil energy, developing sustainable power technology has become urgent to meet the human energy requirement in modern society.[1-4] As abundant and renewable energy, the ambient mechanical energy has been attracting increased attentions due to the extensive availability of target resource and low cost in engineering.[5-7] Accordingly, a variety of mechanical energy harvesters have been developed to convert the ambient energy into usable power such as electricity.[8-11] Among them, triboelectric nanogenerator (TENG), as an emerging technology based on the triboelectric and electrostatic induction, has recently achieved rapid progress from both fundamentals and applications due to its many advantages, including simple fabrication process, expected size and flexible constituent materials choice, and therefore presents great potential as future sustainable power source.[12-16]

However, during the harvesting process of mechanical energy, TENGs must be constantly and long-termly exposed to mechanical impacts, originated from not only the external mechanical stimuli but also the internal mechanical friction between contact materials of the device itself.[11,17-18] These mechanical impacts will inevitably lead to the material fracture and eventually TENG failure, generating a series of problems, such as degradation of device performance, reduction of reliability, lack of function, generation of waste, even the serious safety hazards. In order to overcome these obstacles, it is greatly desired to develop a TENG with self-healing feature to restore configuration and property's integrity once the mechanical damage is occurred.

The healable polymer, one kind of smart material allowing to repair fracture to the original state through external stimulus, such as temperature or light, [19-24] could be an ideal material to realize self-healing TENG. Given its unique recoverability, the healable polymer has been considered in various functional devices with added self-healing property, such as battery, supercapacitor and electronic skin.[25-28] Compared with these attempted devices, TENGs require far more direct and frequent contact with mechanical stimuli as aforementioned. Therefore, it will be interesting and more realistically significant to conceive healable polymers as the constituent material of TENGs. Unfortunately, few attempts have been made for realizing recoverability of TENGs using such a direct and feasible approach to achieve the self-healing TENG. Besides healable polymers, fully self-healing TENG requires healable electrodes as well for electric generation. At present, most electrodes utilized in self-healing devices are formed based on the connection of conductive fillers, such as Ni particle, carbon nanotube and Ag nanowire.[25-29] Due to the lack of interaction among these conductive fillers themselves, the healing of the broken electrode can only be achieved by means of the simple contact of conductive fillers around fracture surfaces. This results in the limited healing capability of the electrode and the reduced reliability of the healed device. In this regard, developing healable electrodes with intrinsic healing property is highly recommended in addition to introducing the self-healable polymers into TENG.

Herein, we present a fully self-healing TENG for the first time, which is fabricated by combining both the healable polymer material based on Polydimethylsiloxane-polyurethane (PDMS-PU) and the novel healable electrode

consisting of small magnets. When the damage of TENG is occurred, the mechanical property of PDMS-PU and the electric property of magnetic-assisted electrodes can be self-recovered by simply connecting the broken ends. As a result, an excellent self-healing capability of TENG is realized, and the output performance of the self-healed device can be restored to above 95 % of their original value after the 5th cutting-healing cycle. Taking advantages of self-healing features, the device is shape-tailorable and object-adaptive to match with applied mechanical stimuli. This can maximize the effective contact area of device, and furthermore increase the performance of device in energy harvesting and self-powered sensing of versatile mechanical motions.

2. Experimental

2.1. Preparation of the healable PDMS-PU: Trifunctional Poly(propylene glycol) (PPG) (Mn = 6000) was purchased from Bayer Materials Science. Hydroxyl-terminated PDMS (Mn = 2000) was purchased from Dow Corning. Isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTDL), bis(4-aminophenyl) disulde (AFD) and tetrahydrofurane (THF) were purchased from Aladdin-reagent Co., Shanghai, and used without further purification. 25 g trifunctional PPG and 25g hydroxyl-terminated PDMS were firstly mixed in a 100 ml glass reactor. Then the mixture was heated at 120 ℃ for 2 hr under vacuum and magnetic stirring for water removal. After cooling to 70 ℃, 8.38 g IPDI and 0.3 ml catalysis of DBTDL were added

to conduct the sealed reaction with the mixture for 20 min at the stirring rate of 120 r/min. Then, the reaction was further evolved at constant temperature of 95 ℃ for 3.5 hr to form the isocyanate terminated prepolymer. The prepolymer was stored in a tightly closed glass bottle for further use after vacuum removal of residual monomers for 5 min. To obtain a healable PDMS-PU layer, 10 g prepolymer was firstly dissolved in 7 mL THF, Then, 1 ml solution of AFD in THF (0.6 g/ml) was added and adequately mixed with prepolymer. The mixture was poured in a Polytetrafluoroethylene (PTFE) dish to allow the curing process at 55 ℃ for 48 hr. At last, the healable polymer elastomer was obtained, which can be used to fabricate insulating layer and substrate of self-healing TENG.

2.2. Fabrication of the self-healing TENG: The top and bottom electrodes were first prepared by the array of magnetic balls with diameter of 3mm and magnetic cubes with side length of 3mm, respectively. The utilized magnetic balls and cubes with nickel plating were purchased from Shenzhen Youci Industrial Co., Ltd., China, and Xinhongchang Magnetic Industrial Co., Ltd., China, respectively. Then the mixture of prepolymer and AFD was poured and cured on the top electrode to form a PDMS-PU film, which encapsulates the top electrode inside. A pattern was formed on the surface PDMS-PU as a gap by curing prepolymer with template. The diameter of each circular hole in the pattern is 8 mm, and the thickness of the gap is about 1.5 mm. The self-healing TENG was achieved by assembling the top electrode encapsulated by PDMS-PU film and the bottom electrode attached on another PDMS-PU film as substrate.

2.3. Measurement of the device: The open-circuit voltage and short-circuit current were characterized by LeCroy WaveRunner Oscilloscope (44MXI) with the probe resistance value of 10 MΩ and low noise current amplifier (Stanford Research Systems, SR570), respectively. During the measurement of output voltage, the top and bottom electrodes were directly connected with the both ends of probe of oscilloscope. The noise filter and the coupling of the oscilloscope were 1 bits and AC 1MΩ, respectively. For the measurement of output current, SR570 was connected between the device and the oscilloscope on the basis of the voltage measurement. The tensile property of healable polymer was measured by INSTRON 3344 according to ASTM D638. The current-voltage (*I-V*) curves were measured by Keithley 2400.

3. Results and Discussion

In order to present the concept of self-healing TENG, a device composed of healable polymers and magnetic-assisted electrodes was fabricated as a prototype. As shown in Fig. 1a and 1b, the structure of self-healing TENG mainly consists of three parts, namely insulating layer, top electrode and bottom electrode. The insulating layer is made from healable polymer film based on Polydimethylsiloxane-polyurethane (PDMS-PU) copolymers with a pattern on the undersurface as a gap, as shown in the inset of Fig. 1b. The top electrode encapsulated into insulating layer is composed of neodymium magnetic balls with nickel (Ni) plating on the surface. The Ni plating serves as protective coating and provides high conductivity for magnetic balls. Because of their strong magnetism, magnetic balls

can firmly contact with each other, forming the useable electrode for the device. Similarly, the bottom electrode is fabricated by magnetic cubes and attached on the surface of a healable polymer substrate, as shown in the inset of Fig. 1b. The bottom electrode plays dual roles of both triboelectric contact material and electrode in the self-healing TENG. It is observed that the top electrode consisting of magnetic balls could be partly flexible and deformable under the applied force. While the usage of magnetic cubes in the bottom electrode benefits the form of the gap between the insulating layer and the bottom electrode for the generation of electricity.

The operation principle of self-healing TENG is schematically illustrated in Fig. 1c-1f. When a mechanical force is applied to the self-healing TENG, the insulating layer and the bottom electrode are adequately contacted (Fig. 1c). Since the healable polymer material has a higher surface electron affinity compared to Ni plating on the surface of bottom electrode, [30] electrons at the interface will be redistributed to generate positive charges on the bottom electrode surface and corresponding negative charges on the insulating layer surface. When the charged contact surfaces start to be separated by releasing the external force (Fig. 1d), the electric potential difference will be created between the top and bottom electrodes accompanying with the electrostatic induction between insulating layer and top electrode. Correspondingly, electrons are driven to flow from the top electrode to the bottom one until the external force is fully released (Fig. 1f). When the TENG sustains mechanical force again (Fig. 1e), an opposite electric potential difference is formed, which causes electrons flowing back to the top electrode from the bottom electrode. Therefore, the AC

electricity can be continuously generated by the periodical contact-separation between insulating layer and bottom electrode.

For characterizing the performance of as-prepared prototype of self-healing TENG, the electric output of a standard device with the size of 4 cm × 6 cm was measured as shown in Fig. 2a and 2b. It is observed that the open-circuit voltage (*Voc*) and the short-circuit current (*Isc*) of self-healing TENG are about 20 V and 1.9 μA, respectively. The corresponding electric performance of device under different applied force and contact frequency is shown in Fig. S1 and S2. Besides, the resistance dependence of the output voltage and current is also investigated as illustrated in Fig. 2c. The results reveal the increase of voltage and the decrease of current with increment of loading resistance. Consequently, the maximum electric power density of about 6 mW/m^2 can be arrived at a load resistance of 10 MΩ, as shown in Fig. 2d.

As aforementioned, the self-healing TENG is composed of healable polymer materials and healable magnetic-assisted electrodes. In this regard, the utilized healable PDMS-PU polymer, serving as the insulating layer and the substrate in self-healing TENG, plays an important role in establishing self-healing property of device. To demonstrate the self-healing behavior of employed polymers, the PDMS-PU film with the dimension of 1 cm × 3 cm × 0.1 cm was firstly prepared. Then the film was cut into two pieces using conventional scissor. After rejoining the cut ends for treatment under 65 ℃ for 2 hr, the wound was successfully healed without a scar left on the surface (Fig. 3a and 3b). Specifically, the healing process of the

broken polymer film was conducted as following steps: (1) The breakage ends of polymer were contacted. (2) The surface of the sample was covered by a PTFE film. (3) A glass slide and a mass of 7 g were successively put on the sample to provide a pressure. (4) This sample was treated in an oven for healing. For further quantifying the mechanical healing property of PDMS-PU, stress-strain curves of the dumbbell-shaped specimens at original state and healed state under different conditions were systematically investigated. As shown in Fig. 3d, the original specimen exhibits a tensile strength of 0.87 MPa and an elongation of 2745 % at breaking point. After healing the broken specimen for 2 hr at 65 ℃, the stress and strain of healed specimen can recover to about 0.85 MPa and 2680 %, respectively. This means that the recovery percentage in strain, which is defined as the proportion of restored strain relative to the original strain, can reach up to 97 % at this stage. It is also found that the healing percentage decreases with reducing healing time and healing temperature. Nevertheless, a recovery percentage of 57 % can still be arrived when the healing temperature is decreased to room temperature (20 ℃), as shown in Fig. 3d and 3e. Meanwhile, the room-temperature healed specimen could be stretched without breaking as displayed in Fig. 3c. For the sample with top electrode inside, it is found that both the tensile strength and the elongation at breaking point will obviously decrease, as shown in Fig. S3. This may be attributed to the defects and stress weak spots in the sample originated from the introduction of magnetic balls. Even though the decrease in healing capability is observed after encapsulating the magnetic balls into the polymer, the recovery percentage of the sample at 65 ℃ still remains 90 %,

indicating the excellent self-healing and mechanical properties of the employed PDMS-PU to meet functional requirements of self-healing TENG. Besides, the cyclic stress–strain curves of the polymer are also shown in Fig. S4.

To shed more light on the self-healing property of the utilized polymer materials, we further investigate the healing mechanism in terms of polymer structures. The self-healing ability of PU-PDMS is first ascribed to the introduction of disulfide links in polymer structure as shown in red rectangle of Fig. 4a. These disulfide groups can exert reversible exchange reaction at a moderate temperature, as depicted in Fig. 4b, leading to the renewal of crosslinking net across damaged surfaces. [20,31-32] Secondly, another structural element which assists the self-healing of PU-PDMS is the formation of multiple hydrogen bonds between the urea groups in polymer networks (blue rectangle in Fig. 4a). These hydrogen bonds are also reversible links and can be reconstructed to bridge the cleaved surface, as shown in Fig. 4c. [25,26,31] To explain the healing behavior of PU-PDMS insulating layer more clearly, the healing mechanism based on the reversible bond breakage and recovery in self-healing process is schematically demonstrated in Fig. 4d. It is considered that once the PU-PDMS sample is cut and separated, both the initial disulfide links and the hydrogen bonds are broken around the fracture surface, accompanying with the equilibrium shift of these reversible reactions. When the fragments are brought into contact, the damaged disulfide and hydrogen bonds can re-contact with their counterparts by means of chain mobility and diffusion, further reconstructing the polymer network by the reversible reaction. The re-establishment process may keep occurring until the renewal

equilibrium is achieved to around the initial state, where the cleaved surface is reconnected with the mechanical property recovery of as-prepared PDMS-PU film. Considering the reversible exchange reaction of disulfide links is prone to occur at higher temperature, the recovery percentage increases with the enhanced healing temperature. Additionally, higher temperature can also improve the mobility and diffusion of molecular chain along the cut surfaces, which leads to the intimate contact among reactive components with the enhancement of healing capability. According to its good mechanical healing property, the as-prepared PDMS-PU serves as the insulating layer and the substrate in our self-healing TENG.

Besides the insulating layer fabricated by healable polymers, another important component in self-healing TENG is the electrode, which functions for the electric healing of device. The electric healing capability for top electrode can be investigated by monitoring its conductive behaviour using a commercial light emitting diode (LED) bulb. As shown in Fig. 5a, when the top electrode formed by small magnetic balls was connected serially with a white LED, the bulb was successfully lit up at an input voltage of 2.5 V (i). After the electrode was cut with a scissor, the lighted LED bulb was extinguished because an open circuit state was formed at this stage (ii). Once the bifurcated electrodes were brought into contact, the LED would light up again immediately, indicating the potential of utilized electrodes in electric healing (iii). In addition, similar healing process of bottom electrode is displayed in Fig. 5b. For quantitatively characterizing the electric healing capability of electrodes, the current-voltage (*I-V*) characteristics of electrodes before damage and after healing

were compared. As shown in Fig. 5c and 5d, both *I-V* curves of top electrode and bottom electrode show linear behaviour with the initial top electrode residence of about 6.2 Ω and the initial bottom electrode residence of about 8 Ω. Meanwhile, for both top electrode and bottom electrode, the *I-V* curves of original and healed electrodes are almost identical with only slight resistance change, demonstrating their excellent performance as healable electrodes for self-healing TENG. Such outstanding electric recoverability should be resultant from the unique design of electrode structure, which is formed by the oriented arrangement of magnetic balls and cubes for top and bottom electrodes, respectively. When damaged electrodes were brought into contact, the magnetic balls or cubes can be immediately reconnected due to the magnetic attraction, leading to the recovery in electric conductivity. Compared with reported healable electrodes which need external pressure and time for healing,[25-29] the magnetic-assisted electrode utilized in this device can realize the instant recovery in conductivity, thus becoming an ideal candidate for self-healing TENGs.

Attributed to the cooperative self-healing functions of polymer materials and magnetic-assisted electrodes, the whole device is recoverable, which may restore its configuration integrity after damage. Most importantly, the excellent self-healing capability in output performance of as-prepared TENG is also observed. Fig. 6a and 6b illustrate the change of two primary parameters for evaluating TENG, including *Isc* and *Voc*, during the self-healing process of device. The results show that *Voc* of 21.5 V and *Isc* of 2 μA can be firstly generated by the original device. After the TENG is disconnected into two fragments, the *Voc* and *Isc* decrease to about 11 V and

1 μA, respectively. Once the broken ends are connected for self-healing, the *V*oc and *I*sc restore to about 21 V and 1.95 μA, respectively, which is similar to the initial performance and leads to the high healing efficiency of above 95 %. Such an obvious change in self-healing TENG's electric output may be considered as the result of the variation of effective contact area of the device before and after connection. According to earlier reports,[33] the transferred charge in TENGs under short circuit condition is approximately characterized by

$$Q_{SC} = \frac{S\sigma x(t)}{d_0 + x(t)} \quad (1)$$

where S is the effective contact area between triboelectric layers, σ is the average surface charge density of contact materials, x is the distance between the two triboelectric layers, varying under the agitation of mechanical force. d_0 is the effective thickness constant.

When the device is mechanically split, only the fragment connected with external circuit contributes to the generation of electricity, which means the decrement of *S*. Therefore, both *Voc* and *Isc* diminish with the reduced *S* and *Qsc*. After the broken ends are reconnected, both mechanical and electric property of device were recovered, thereby leading to the healing in *S* and output performance of device. To further evaluate the repeatability of healing process, we measured the electric output of TENG after 5 cutting-healing cycles. The results show that the healed device can still effectively work with negligible decrease in the performance, indicating the great recoverability of self-healing TENG for converting mechanical energy into electricity with enhanced lifespan, durability and robustness. As a mechanical energy harvester,

TENGs have to be long-termly and constantly operated under massive mechanical impacts, which causes the device breakdown and performance degradation. In this regard, the presented self-healing TENG possesses distinct advantage in the operation for practical application.

During harvesting process of mechanical energy, TENGs usually sustain complex mechanical stimuli with different shapes, which proposes challenge to regular TENGs with fixed shape and dimension. In contrast, another obvious advantage of our self-healing TENG over regular TENGs is its shape-tailorability originated from the healing capability. This means that the shape of self-healing device can be re-shaped or re-designed according to the variation of applied mechanical stimuli, offering an alternative solution to overcome the above problems. As an example of demonstration, Fig. 7a shows a re-shaping process of self-healing TENG from square shape to strip shape. The device (i) was firstly disconnected in the middle to form two fragments with similar shape (ii). After slightly peeling the bottom side of fragments, the two bottom sides were contacted (iii) to heal and finally form a strip-shaped device (iv). Taking advantage of the self-healing capability of device, the re-shaped device can operate successfully to convert mechanical energy into electricity. Most importantly, the shape-tailorability of device offers a facile strategy to realize shape match between device and mechanical stimuli, which maximizes the effective contact area of device and further increases the energy harvesting efficiency of device. Fig. 7b shows the *Isc* generated by original square-shaped TENG (4.5 cm × 4 cm) and re-shaped strip-shaped TENG (9 cm × 2

cm) under the action of different mechanical stimuli with two shapes, including square and strip shape. It is observed that the *Isc* of 0.5 μA can be achieved when the mechanical force is applied on the original device by a square-shaped active surface with the dimension of 4.5 cm × 4 cm. Once the shape of mechanical stimuli becomes strip shape, the *Isc* decreases to 0.25 μA even though both the applied impulse and the device dimension remain unchanged. The decrement of *Isc* may result from the reduced active area of mechanical force (4.5 cm × 2 cm) caused by the unmatched shape between the strip-shaped mechanical stimuli and square-shaped device at this state. By re-shaping the TENG into strip shape, the device can match well with the mechanical stimuli, leading to a larger effective contact area of about 9 cm × 2 cm and the increased *Isc* of 0.45 μA. Given the shape-tailorability, the self-healing TENG shows the potential to adapt complex mechanical stimuli when serving as energy harvester and self-powered sensor of various motions, such as human motion. Fig. 7d shows the *Voc* generated by energy harvesting from running motion based on a square-shaped self-healing device with dimension of 7.2 cm × 6.9 cm. After re-shaping the device into the hand shape (Fig. 7c), the re-shaped device can adapt to the motion of hand and successfully harvest mechanical energy from hand flap as shown in Fig. 7e. The results indicate the self-healing and shape-tailorable properties of as-prepared TENG, which therefore make it a promising energy harvester for further application. In future studies, we will further develop the healable TENG with higher flexibility and shape-adaption. [34-35]

4. Conclusions

In summary, self-healing TENGs have been fabricated by integrating healable PDMS-PU polymer with magnetic-assisted healable electrodes. After breakage, the mechanical property of healable polymer and the electric property of magnetic-assisted electrodes can be well restored. Correspondingly, the integrated TENG exhibits an excellent self-healing performance, and the *Voc* and *Isc* of healed device can reach up to above 95 % of their original value even after the 5th cutting-healing cycle. Additionally, the self-healing TENG is shape-tailorable and object-adaptive to benefit efficient and versatile mechanical energy harvesting or complex mechanical stimuli sensing. This study provides the feasibility of developing self-powered energy devices with improved lifespan, robustness and adaption.

Acknowledgements

The research was partly supported by the grants from Research Grants Council of Hong Kong (GRF No. PolyU 5005/13P) and PolyU Internal Grant (1-ZVGH).

References

[1] D. M. Kammen and D. A. Sunter, Science 352 (2016) 922-928.
[2] M. S. Dresselhaus and I. L. Thomas, Nature 414 (2001) 332-337.
[3] S. M. Niu, X. Wang, F. Yi, Y. S. Zhou and Z. L. Wang, Nat. Commun. 6 (2015) 8975.
[4] Z. L. Wang, J. Chen and L. Lin, Energ. Environ. Sci. 8 (2015) 2250-2282.
[5] G. Zhu, B. Peng, J. Chen, Q. Jing and Z. L. Wang, Nano Energy, 14 (2015) 126-138.

[6] G. Zhu, Y. S. Zhou, P. Bai, X. S. Meng, Q. Jing, J. Chen and Z. L. Wang, Adv. Mater. 26, (2014) 3788-3796.
[7] G Zhu, J Chen, T. Zhang, Q. Jing and Z. L. Wang, Nat. Commun. 5 (2014) 3426.
[8] B. Meng, W. Tang, Z. Too, X. Zhang, M. Han, W. Liu and H. Zhang, Energ. Environ. Sci. 6 (2013) 3235-3240.
[9] Z. L. Wang and J. H. Song, Science 312 (2006) 242-246.
[10] S. D. Moss, J. E. McLeod, I. G. Powlesland and S. C. Galea, Sensor. Actuat. A Phys. 175 (2012) 165-168.
[11] L. B. Huang, G. Bai, M. C. Wong, Z. Yang, W. Xu and J. Hao, Adv. Mater. 28 (2016) 2744-2751.
[12] Y. L. Zi, S. M. Niu, J. Wang, Z. Wen, W. Tang and Z. L. Wang, Nat. Commun. 6 (2015) 8376.
[13] W. Xu, L. B. Huang, M. C. Wong, L. Chen, G. X. Bai and J. Hao, Adv. Energy Mater. 7 (2017) 1601529.
[14] A. Li, Y. Zi, H. Guo, Z. L. Wang and F. M. Fernández, Nature Nanotech. 12 (2017) 481-487.
[15] C. Zhang, W. Tang, C. Han, F. Fan and Z. L. Wang, Adv. Mater. 26 (2014) 3580-3591.
[16] L. B. Huang, W. Xu, G. Bai, M. C. Wong, Z. B. Yang and J. Hao, Nano Energy 30 (2016) 36-42.
[17] J. Chen, J. Yang, H. Guo, Z. Li, L. Zheng, Y. Su, Z. Wen, X. Fan and Z. L. Wang, ACS Nano 9 (2015) 12334-12343.
[18] J. H. Lee, R. Hinchet, S. K. Kim, S. Kim and S. W. Kim, Energ. Environ. Sci. 8 (2015) 3605-3613.
[19] M. D. Hager, P. Greil, C. Leyens, S. van der Zwaag and U. S. Schubert, Adv. Mater. 22 (2010) 5424-5430.
[20] Y. Yang and M. W. Urban, Chem. Soc. Rev. 42 (2013) 7446-7467.
[21] B. J. Blaiszik, S. L. B. Kramer, M. E. Grady, D. A. McIlroy, J. S. Moore, N. R. Sottos and S. R. White, Adv. Mater. 24 (2012) 398-401.
[22] C. Wang, N. Liu, R. Allen, J. B.-H. Tok, Y. P. Wu, F. Zhang, Y. S. Chen and Z. Bao, Adv. Mater. 25 (2013) 5785-5790.
[23] D. Habault, H. Zhang and Y. Zhao, Chem. Soc. Rev. 42 (2013) 7244-7256.
[24] Y. Huang, Y. Huang, M. Zhu, W. Meng, Z. Pei, C. Liu, H. Hu and C. Zhi, ACS Nano 9 (2015) 6242-6251.
[25] H. Wang, B. Zhu, W. Jiang, Y. Yang, W. R. Leow, H. Wang and X. Chen, Adv. Mater. 26 (2014) 3638-3643.
[26] Y. Zhao, Y. Zhang, H. Sun, X. Dong, J. Cao, L. Wang, Y. Xu, J. Ren, Y. Hwang, I. H. Son, X. Huang, Y. Wang and H. Peng, Angew. Chem.-Int. Edit. 55 (2016) 14384-14388.
[27] S. Wang, N. Liu, J. Su, L, Li, F. Long, Z. Zou, X. Jiang, Y. Gao, ACS Nano 11 (2017) 2066-2074.
[28] B. C. Tee, C. Wang, R. Allen and Z. Bao, Nature Nanotech. 7 (2012) 825-832.

[29] H. Sun, X. You, Y. Jiang, G. Guan, X. Fang, J. Deng, P. Chen, Y. Luo and H. Peng, Angew. Chem.-Int. Edit. 53 (2014) 9526-9531.
[30] Z. L. Wang, ACS Nano 7 (2013) 9533-9557.
[31] A. Rekondo, R. Martin, A. R. de Luzuriaga, G. Cabañero, H. J. Grande and I. Odriozola, Mater. Horiz. 1 (2014) 237-240.
[32] R. Martin R, A. Rekondo, A. R. de Luzuriaga, G. Cabañero, H. J. Grande and I. Odriozola, J. Mater. Chem. A 2 (2014) 5710-5715.
[33] S. Niu, S. Wang, L. Lin, Y. Liu, Y. S. Zhou, Y. Hu and Z. L. Wang, Energ. Environ. Sci. 6 (2013) 3576-3583.
[34] X. He, Y. Zi, H. Guo, H. Zheng, Y. Xi, C. Wu, J. Wang, W. Zhang, C. Lu and Z. L. Wang, Adv. Funct. Mater. 27 (2017) 1604378.
[35] X. He, Y. Zi, H. Yu, S. L. Zhang, J. Wang, W. Ding, H. Zou, W. Zhang, C. Lu and Z. L. Wang, Nano Energy 39 (2017) 328-336.

FIGURE CAPTIONS:

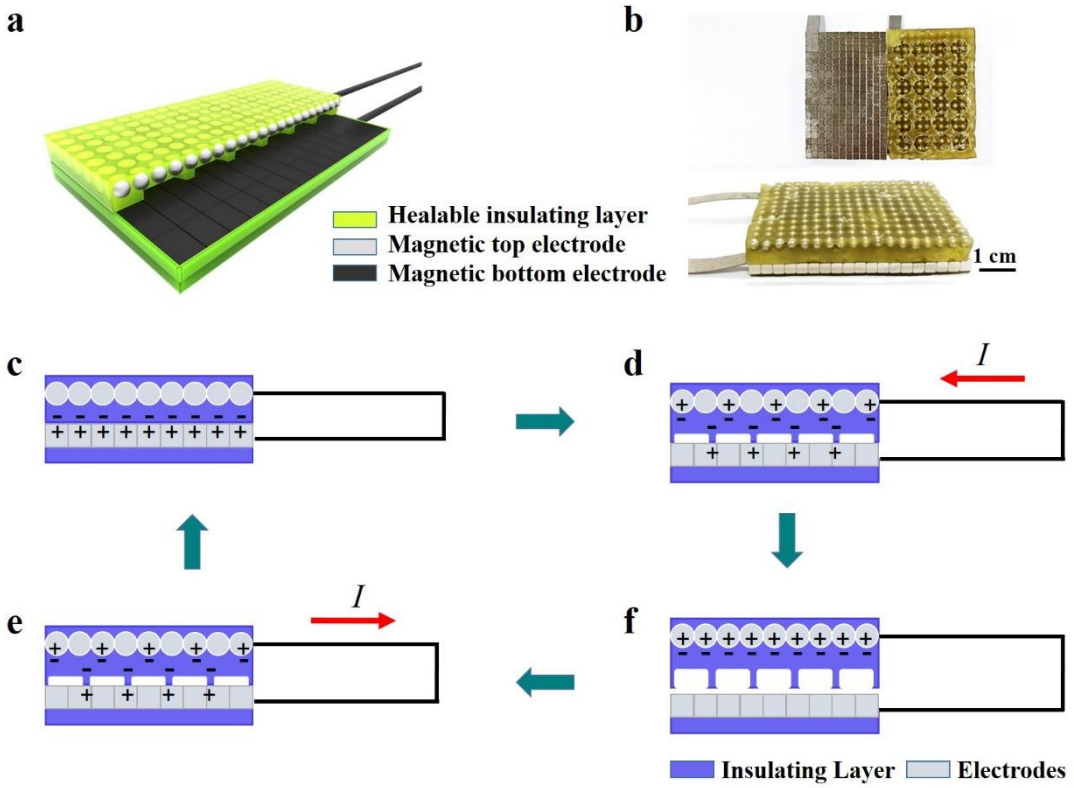

Fig. 1. (a) Schematic of the self-healing triboelectric generator (TENG). (b) Optical images of self-healing TENG (4 cm × 6 cm) with bottom electrode (left) and pattern on undersurface of insulating layer (right) illustrated in the inset. (c)-(f) Schematic illustration of operation principle of self-healing TENG. (c) Contact state (d) Separating state. (e) Contacting state. (f) Separation state.

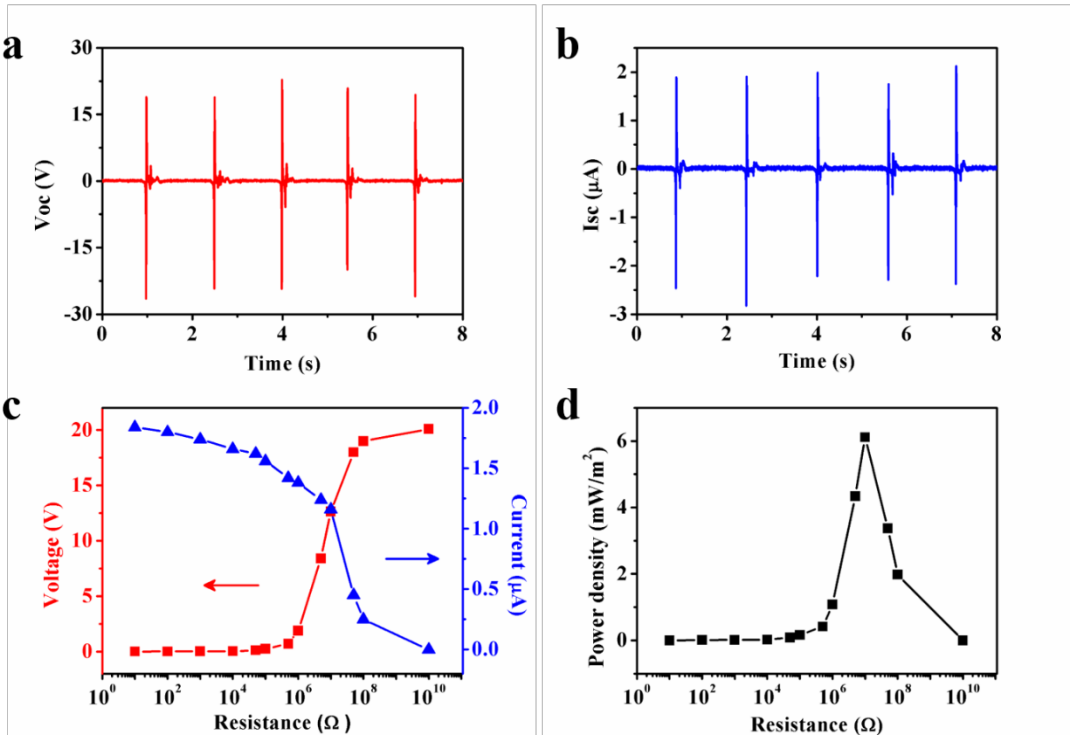

Fig. 2. (a) Open-circuit voltages and (b) short-circuit current of the standard self-healing TENG. (c) Output voltage and current versus the resistance of external loads. (d) Output power density versus the resistance of external loads. The applied force on the device is measured to be about 6.25 N.

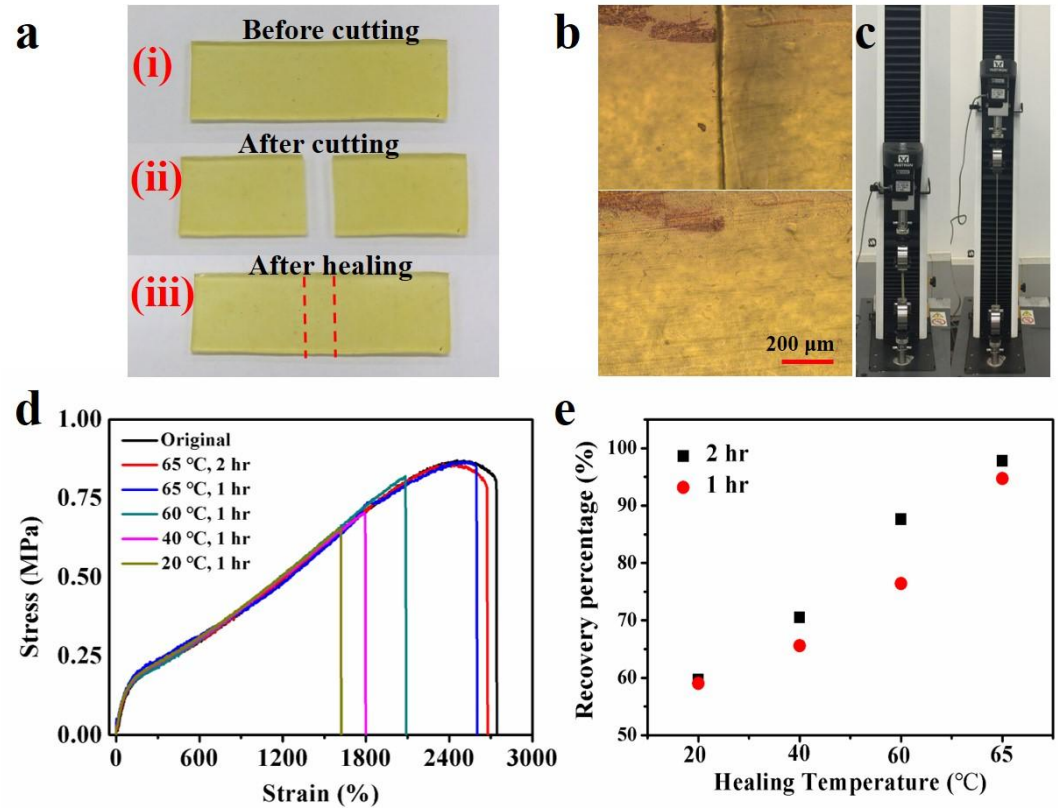

Fig. 3. (a) The self-healing process of PDMS-PU: (i) original PDMS-PU. (ii) after being cut. (iii) after healing at 65 ℃. (b) Optical microscope images of damaged sample (top) and healed sample (bottom). (c) Photographs of a healed sample before and after stretching. (d) Stress–strain curves of original and healed samples under different healing times and temperatures. (e) The strain recovery percentage of PU-PDMS film under different healing temperatures and times.

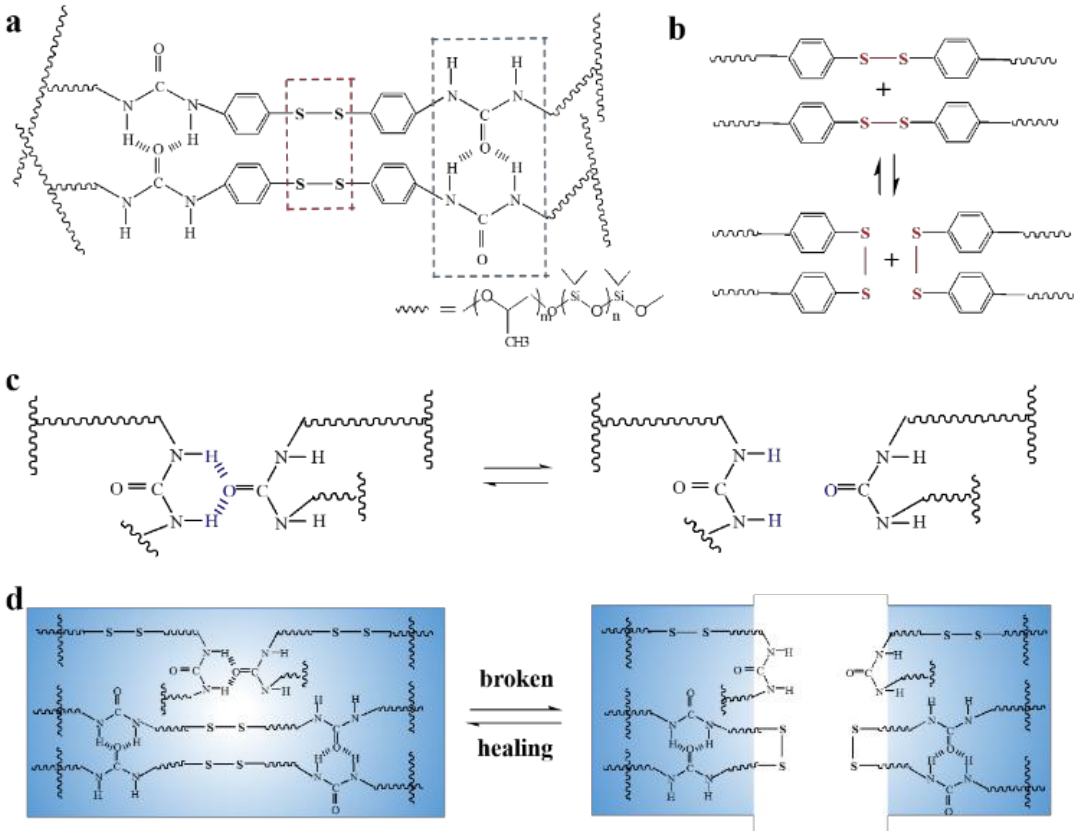

Fig. 4. Schematic illustration of (a) self-healing polymer structure, (b) reversible exchange reaction of disulfide links, (c) reversible hydrogen bond links, and (d) proposed healing mechanism of as-prepared PDMS-PU film.

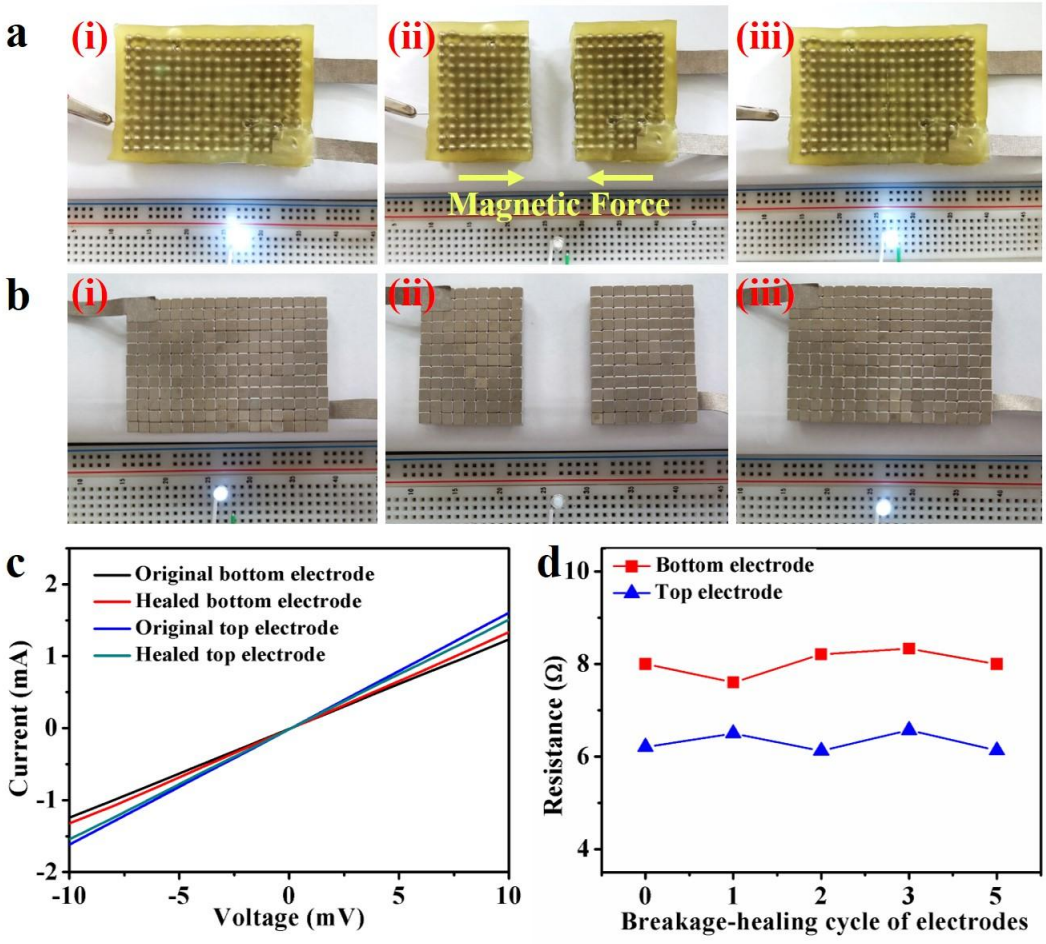

Fig. 5. Optical images of the electric healing process of (a) the top electrode and (b) the bottom electrode connected with a tandem circuit containing a LED bulb: (i) The original, (ii) after cutting, (iii) after healing. (c) *I-V* curve of electrodes before damage and after healing. (d) Resistance change of top and bottom electrodes after different breakage-healing cycles.

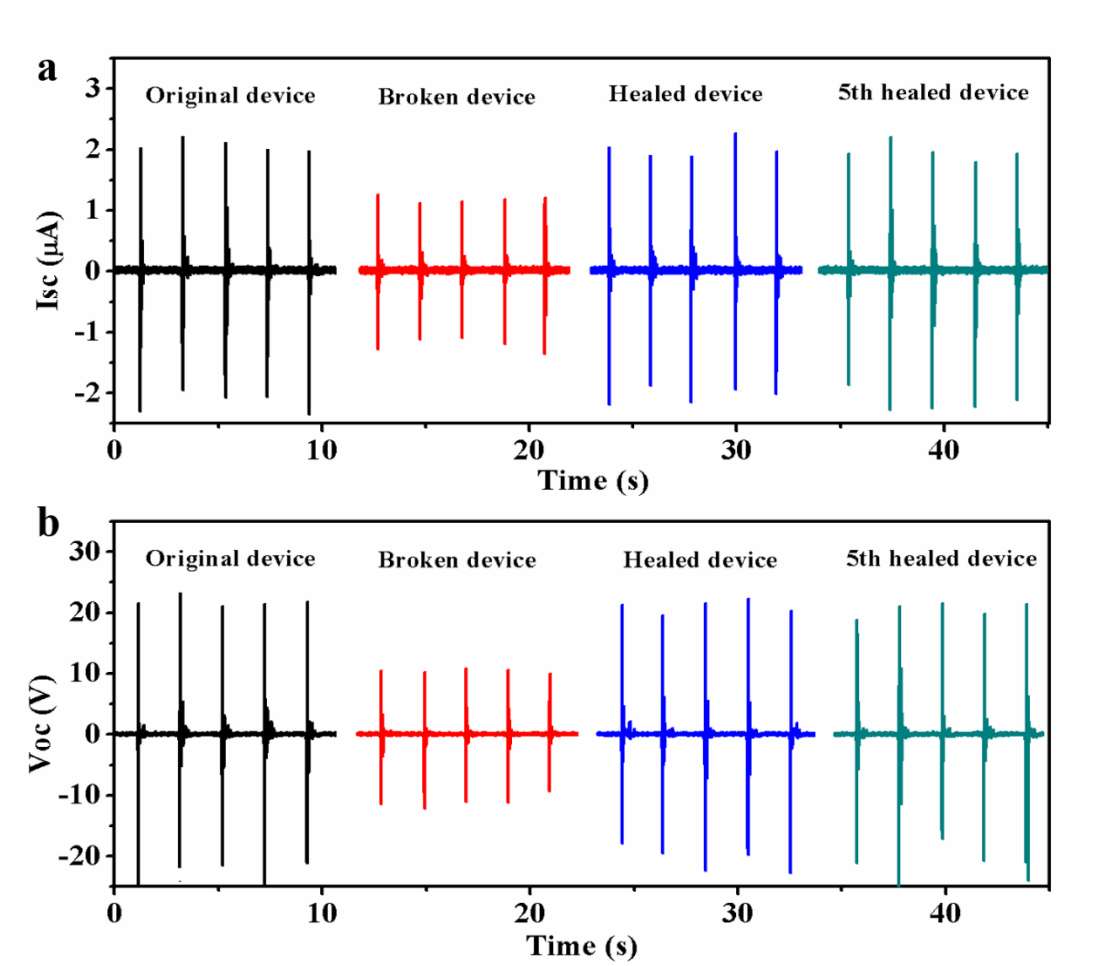

Fig. 6. Self-healing process in output performance of TENG: (a) short-circuit current and (b) open-circuit voltage of the as-prepared TENG at original, broken, and healed state.

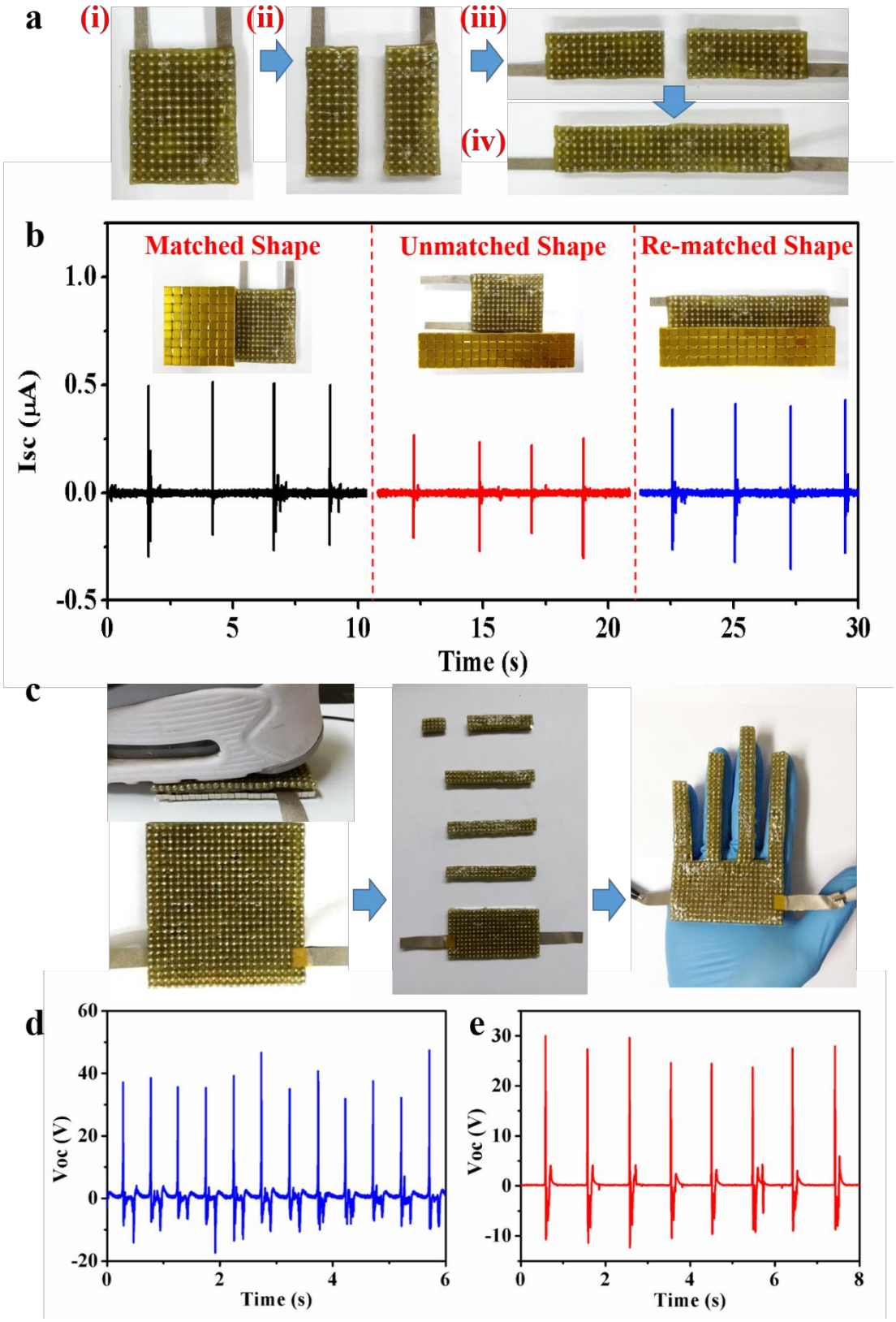

Fig. 7. (a) Optical images of re-shaping process of self-healing TENG from square shape to strip shape. (i) original device, (ii) after cutting, (iii) assembling fragments, (iv)

re-shaped device (b) The change in I_{SC} of devices generated under different shape match between devices and mechanical stimuli. (c) The re-shaping process of self-healing TENG from original square shape to hand shape. (d) *Voc* of original square-shape TENG generated by harvesting energy from foot motion. (e) *Voc* of re-shaped hand-shape TENG generated by harvesting energy from hand flap.

*Graphical Abstract

TOC Graphic:

We firstly demonstrate a fully self-healing triboelectric nanogenerator with high recoverability after damage, and the healing efficiency can reach up to above 95 %. The as-prepared device is shape-tailorable and object-adaptive to benefit efficient and versatile mechanical energy harvesting.