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PAPER

Shape memory polymer-based self-healing triboelectric nanogenerator

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Recently, triboelectric nanogenerators (TENGs) have received an increasing interest due to their high potential for mechanical energy harvesting. Important progresses have been achieved to increase the output power and efficiency while new structures emerged. Especially, their robustness and endurance have increased, but it still remains some critical concerns about the degradation and lifetime of TENGs. How TENGs will age under intensive use in our daily life? To address this issue, we propose in this paper to use shape memory polymer (SMP) to extend TENG's lifetime and guaranty their performances. For this purpose we introduced a new smart SMP-based self-healing TENG which has the capacity to be healed and to recover good performances after degradation of its triboelectric layer. We studied the degradation and the healing process of SMP-TENG, improving their endurance, life time and thus demonstrating the huge potential of self-healing SMP-TENGs.

Broader context

Recently smart systems met a large success. At the origin of the internet of things, they are a key driving force for the development of wireless, sustainable and independent autonomous smart systems. In this context, the autonomy is critical and despite all the progresses in low power electronics and battery, energy harvesters are becoming increasingly important. Thus harvesting mechanical energy is essential as it is widespread and abundant in our daily life environment. Among harvesters, triboelectric nanogenerators exhibit good performances and are easy to integrate which make them the perfect candidates for many applications, and therefore crucial to develop. Furthermore, in the actual environmental context, harvesting green and renewable energy is a necessity. Therefore energy harvesters have to be as much ecological and cheap as possible, which can be adressed by using polymers and by increasing their lifetime. For this purpose we introduced a new smart shape memory polymer triboelectric nanogenerator which has the ability to be healed and to recover good performances after degradation. Thus, we improved its durability and lifetime, making it more efficient and profitable while decreasing the wastes and the environmental impacts.

Introduction

Recently, triboelectric nanogenerators (TENGs) have received an increasing interest due to their high potential for mechanical energy harvesting. Important progresses have been achieved to increase the output power and efficiency while new structures emerged, improving their integration capabilities and going toward flexible and transparent TENGs among others. Especially, their robustness and endurance have increased, but it still remains some concerns about the degradation and lifetime of TENGs. How TENGs will age under realistic conditions and intensive use in our daily life, which imply strong and repetitive mechanical pulses and exposition to various environments potentially damaging for polymers over the time, because of the humidity and light for example. One solution would be to repair the polymer structures used or, even better, to heal them. For this purpose, shape memory polymer (SMP) is all indicated to be the perfect material as it is a smart material which has the ability to return from a deformed state (degraded polymer in TENG) to its original shape, this behaviour being triggered by an external stimulus such as temperature or light change. To test this concept we chose to use polyurethane (PU) because it is easy to use and it has a rather low healing temperature of 55 °C, named glass transition temperature (T_g), allowing to heal TENG without damaging its other components. In this paper we studied the degradation and the healing process of TENG using SMP. We

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improved their endurance, life time and demonstrated the huge potential of self-healing SMP-based TENGs.

TENG concept

TENGs have been developed on the basis of the coupling between contact electrification (triboelectrification) and electrostatic induction effects. The triboelectrification is the fact that the surface of a material becomes electrically charged after it gets into contact with another material.[1–4] The triboelectric charges generated on a dielectric surface can be preserved for a long time, which thus serve as an electrostatic induction source for the TENG electricity generation process. TENGs present numerous advantages: high output voltage, high versatility and their fabrication is rather simple and low cost. It exist different structures of TENG using different movements and leading to various working modes.[5–8] The most common structure of TENG used is the vertical contact-separation structure. Its working principle is rather simple: Two different triboelectric dielectric layers are parallel with electrodes deposited on the exterior. When under external forces, a physical contact is initiated between the two dielectric films, it generates triboelectric opposite charges at their interfaces. Once the external forces are released and the two surfaces are separated by a gap, a potential difference appears because of the triboelectric charge separation. By connecting the two electrodes, free electrons in one electrode will flow to the other electrode to balance this triboelectric potential difference and creating a current pulse. When the gap is closed again due to external forces, the triboelectric potential difference disappears and the free electrons flow back in the circuit, creating an opposite current pulse. In this way, mechanical movements are converted into electricity. A popular variant of this structure only use one triboelectric layer which exchanges triboelectric charges with the opposite electrode.

Different strategies have been experimented to increase the voltage output which is rather high in TENGs. Recent research has been done to select the best triboelectric dielectric materials using triboelectric series[5] in order to maximize the triboelectric charge generated. Another way to improve the output performances of TENG is to increase the roughness of the triboelectric layer in order to increase their contact surface and their friction,[9] which will increase the total amount of triboelectric charges generated and strength the electrostatic induction process. This can be realized by patterning the triboelectric layers with micro and nanostructures like pyramid,[10] cube,[10] or half sphere[11] for example. It can also be achieved by using a randomly generated nano-scale roughness[12,13] created by various process.[8] It is interesting to note that in this case the output signal will be more dependent on the force applied because a higher force will deform more the pattern and increase the contact surface. Like that it is possible to greatly improve the overall performance of TENGs. Indeed it has been demonstrated that the use of a patterned triboelectric layer can increase by more than 25% the output power.[10] This improvement is very important to boost TENGs, but this increased contact and friction between the triboelectric layers pose the questions of the wear and tear of TENGs. Indeed, if this enhancement is at the expense of the life time of TENGs, it could be a big inconvenience. Until now, no paper has been investigated on the aging of TENG and the evolution of their performances over their lifetime. Few papers mentioned that the compression and friction of the triboelectric layers could degrade the overall performances of TENG after a long operation time, but no deep study has been conducted. In high friction TENGs this problem has been approached by using PTFE nanoparticles to decrease the friction issue[14] but nothing more.

Our study shows that over the life time of TENG the micropatterns degrade and can be destroyed. As a result the performances in terms of voltage and current decrease and therefore the output power is drastically reduced. To solve this problem and enhance the lifetime of TENGs, we propose in this paper to use SMP to repair micropatterns and heal TENG. Indeed SMP has the ability to recover its shape after degradation thanks to an external stimulus, allowing reconstituting the micropattern and retrieving good performances after many usage cycles.

Results

TENG structure and operation

Following the above-mentioned concept, we built a TENG, integrating PU as a micropatterned triboelectric layer. The prototype is a vertical contact-separation mode TENG (Figure 1a). The bottom part is made of a thin acrylic plate substrate (1 mm thickness) onto which we deposited an Al electrode and a thin triboelectric layer of PU with a micro pyramid pattern (10 µm width) (Figure 1b). PU is a polymer with a moderate negative triboelectric effect. Its Kelvin probe force microscope (KPFM) characterization (Supporting Information S1) showed that it has an average negative triboelectric property between polyethylene terephthalate (PET) and polytetrafluoroethylene (PTFE). The top part is made of a thin acrylic plate substrate (1 mm thickness) onto which we deposited an Al electrode. Both parts are separated by a 2 mm gap held by foam spacers, which enable the contact-separation of the two TENG parts under external compression forces.

Its operation is simple: When the Al top electrode contacts the PU triboelectric layer during compressions, it generates negative charges on the PU surface and an opposite positive charge density on the top Al electrode. Once the force is released, the Al top electrode separates from the PU layer which generates a difference of potential between the electrodes and drive electrons to the top electrode to balance the separated charges' electric field, creating a current pulse. When the gap is closed, the reverse occurs. To show the importance of the micro-pyramid pattern we first characterized a basic TENG, using a flat PU layer as triboelectric layer.

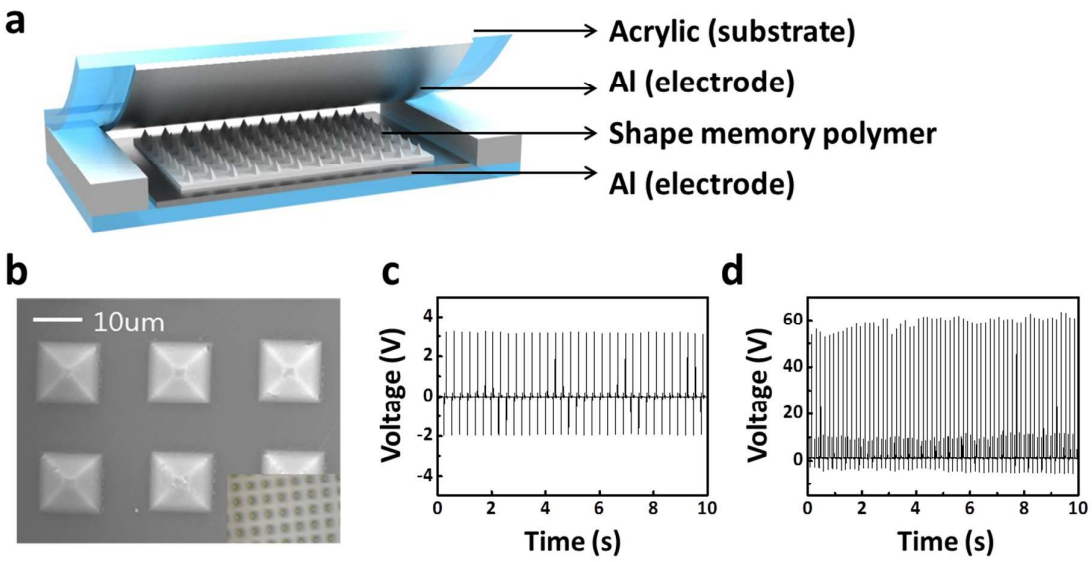

Figure 1 Structure and output voltage of the PU-TENG. a) Schematic of the PU-TENG structure. b) PU pyramid pattern on the PU triboelectric layer. c-d) Open circuit voltage of a PU flat triboelectric layer TENG and a PU pyramid patterned triboelectric layer TENG compressed by a force of 10 kgf, respectively.

The output open circuit voltage reached only 3 V (Figure 1c). Then, using a pyramid patterned PU layer (10 um width and height) as a triboelectric layer, the output voltage attained 60 V (Figure 1d) which constitutes a huge 20 times boost in the PU-TENG performance. This illustrates how significant the improvement of the PU-TENG output voltage can be when using micropatterning and that is why it is most of the time utilized.

Micro-pattern improvement

To investigate the micro-pattern effect on the PU-TENG performances, we first calculated analytical equations and then performed finite element method (FEM) simulations of the flat PU-TENG. According to theoretical studies[15] the voltage generated is defined by the following equation:

$$V = -\frac{Q}{S.\varepsilon_0}\left(\frac{d_{PU}}{\varepsilon_{rPU}} + x(t)\right)\frac{\sigma.x(t)}{\varepsilon_0} \qquad (1)$$

where V is the difference of potential between the electrodes, Q the charge in the bottom electrode, S the surface of the electrode, ε the permittivity, d the thickness, σ the surface charge density and x(t) the gap between the electrodes at the instant time t. In open circuit conditions, the voltage equation (1) can be simplified. Thus the voltage generated is proportional to the surface charge density σ:

$$V = \frac{\sigma.x(t)}{\varepsilon_0} \qquad (2)$$

Following this we calculated that to generate 3 V our TENG need a surface electron density of σ_e=8.3×10^{10} m^{-2} on the PU film. Then, we simulated the flat PU-TENG structure (Figure 2a). Generally full simulation of the TENG operation is very challenging due to the problematic simulation of the triboelectric and friction phenomenon, which are critical in calculating the output performances and pose a real challenge. Nevertheless, we approached and found the same triboelectric surface electron density (σ_{e_sim}=8.3×10^{10} m^{-2}) necessary to obtain the output voltage measured in the experiment without pattern (Figure 2b). Then, keeping the same value of σ_e, we simulated the PU-TENG having the 10 µm pyramid pattern and considering the entire PU surface contacted and therefore electrically charged. We found an output potential generated of 3.92 V corresponding to an increase of +30.7%. This increase is proportional to the increase of the surface of the PU layer induced by the micro-pyramid pattern which is logical. At constant triboelectric surface electron density σ_e, the increase of the PU micro-surface area increases proportionally the total quantity of charge distributed in the TENG having the same size.

However, in this case, the potential experimentally measured was 60 V, corresponding to a PU triboelectric surface electron density of σ_e=1.27×10^{12} m^{-2}, which is about 15 times higher than expected. This huge improvement cannot be only attributed to the surface effect but is certainly mostly caused by another phenomenon such as the friction effect probably. Indeed, increasing the friction between triboelectric layers greatly increase the generation of triboelectric charges which leads to the big increase the generated potential. Usually the improvement of the triboelectric potential by micropatterning is usually around 25%,[10] but in our case we observed an increase of 20 times which is surprising and outstanding. This performance is probably mostly due to the increased friction of the PU, but the origin of this exceptional increase remains to be further investigated.

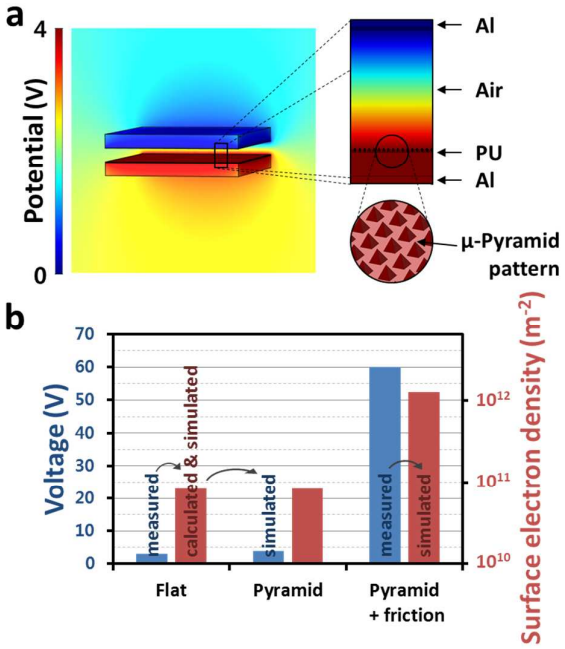

Figure 2 FEM simulation of the potential generated by the PU-TENGs. a) FEM simulation of the potential distribution generated by a PU-TENG with a micro-pyramid pattern. b) Graphic of the voltage and surface charge density depending on the PU-TENG structure. These values have been calculated using the measured voltage value and the performed FEM simulation.

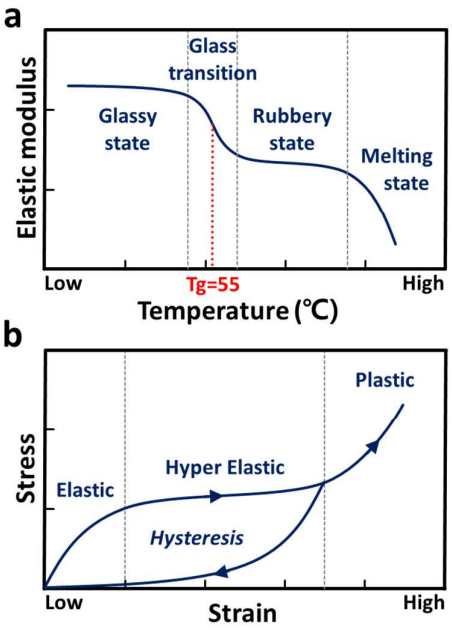

Figure 3 Diagram of the mechanical properties and behaviour of PU. a) Typical thermomechanical diagram of PU. PU can have three states: a glassy state, a rubbery state and a melting state. The glass transition temperature (T_g) between the glassy and rubbery state is T_g = 55 °C for our PU. b) Typical stress-strain diagram of our PU. The deformation of PU follows three phases: the elastic, hyper elastic and plastic deformation mode. When the load is released, the strain decreases by following a hysteresis cycle.

The approach of the constitutive mechanical equation of this material is based on the potential function form ψ which is the elastic potential energy density or the strain energy density.[16,17] In addition, for more realistic behavior, the equation also has to take into account the fading memory of the polymer[18] which represent the long-term memory contributions. Thus the fundamental stress tensor equation of such a material has the following form:[16]

$$S = S_e\big(C(t)\big) + \int_0^t F\big(G(t-s), s; C(t)\big)ds \qquad (3)$$

where: S is the second Piola-Kirchhoff stress tensor, S_e the elastic second Piola-Kirchhoff stress tensor, C the Cauchy tensor, F a general tensor-valued function that depends on variables G (t-s) and s, where s represents the historical time variable and t the current time. To solve this equation there are many models that consider the mechanical deformation of hyper elastic materials like PU. Among them, the most used form of the hyper elastic potential functions ψ for modeling PU are the: Ogden[19], Neo-Hookean[20], Mooney-Rivlin[21] and Yeoh[22] forms. However, PU behavior usually follows a global trend described by a phases diagram (Figure 3a) and stress/strain diagram (Figure 3b) composed of three phases: elastic, hyper elastic and plastic. PU has the particularity of being a hyper elastic material, which makes it more robust and resistant to plastic deformations, damages and degradations.

Nevertheless, after many hysteresis compression cycles, some micro-scale damages can occur. PU may experience two classes of damages which are:[23] mechanical and functional damages. Mechanical damages occur during their operational conditions and under their service loads (fatigue cycle, impact and thermomechanical damages), due to molecular chain failures, degrading the mechanical properties such as the young modulus. Functional damages occur mainly during the thermomechanical cycles due to molecular chain rearrangement, inducing shape memory effect, shape recovery ratio and stress recovery ratio losses. All these defects lead to the degradation of PU properties .

Degradation of the micropattern

Naturally, over the life time of the PU-TENG, which include numerous contact-separation cycles, PU micro-pyramid pattern should be deformed, damaged or degraded, leading to the overall decrease of the output performances of the PU-TENG. In order to have a better understanding of this issue, we analyzed the performance of multiple PU-TENGs composed of a micro-pyramid patterned PU triboelectric layer. We analyzed the PU-TENGs structure and performances after 15 min of compression cycles at 12.5 Hz under different forces. First we controlled the shape of the pyramid micropattern. As observed on the Figure 4a, after 15 min under a force of 2 kgf, the pyramid shape was still intact. But, at a force of 4 kgf the top of the micro-pyramid pattern was flattened and when the force increased until 10 kgf the pyramid was more and more

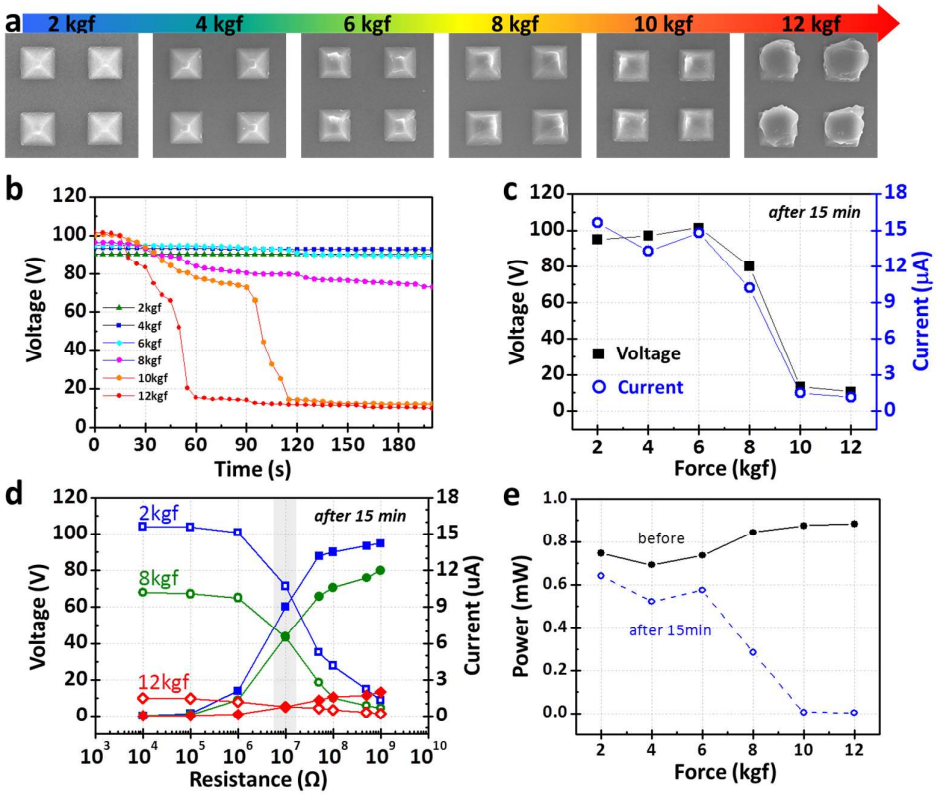

Figure 4 Structure and performances of the PU-TENG depending on the time and force applied. a) FE-SEM images of the SMPU micropattern after compressing the SMPU-TENG during 15 min at 12.5 Hz under different forces from 2 kgf to 12 kgf (1 kgf = 9.8 N). Depending on the force applied the SMPU pyramid pattern is deformed. b) Open circuit voltage as a function of the time and under different forces. Higher forces give higher initial voltage generated. After 60 s and 90 s the output voltage of the SMPU-TENG under 12 kgf and 10 kgf respectively start to drastically decrease. c) Open circuit voltage and short circuit current depending on the force after compressing the SMPU-TENG during 15 min. Lower forces give higher voltage. d) Voltage (filled) and current (hollow) outputs depending on the load resistance after 15 min of compression under various forces. The optimum resistance is around 10 MΩ. e) Maximum power of the SMPU-TENG depending on the forces applied before and after compression during 15 min. Under high forces, the power of the SMPU-TENG decrease a lot after 15 min.

flattened. Over a force of 10 kgf the pyramid pattern was highly deformed and lost its shape. Over time (Figure 4b) (Supporting Information S2), after only 1 min under a force of 12 kgf, the open circuit voltage droped from 100 V to 10 V because of the degradation of the micro-pyramid pattern. When under a force of 8 kgf the degradation took more time but is still noticeable. It is interesting to remark that the initial voltage is higher when applying stronger force, which is normal. But this advantage quickly reverse over time when applying too strong forces. Thus, after 15 min we observed that when increasing the compression force from 2 kgf to 8 kgf there is a small decrease of the output open circuit voltage and short circuit current of the PU-TENGs from 100 V to 80 V and from 15 μA to 10 μA respectively (Figure 4c). Howevere when the force applied was higher than 8 kgf the output open circuit voltage and short circuit current droped drastically to 10 V and 1 μA. Moreover, we characterized the voltage and current depending on the load resistance for different forces (Figure 4d) (Supporting Information S3) and we found an optimal impedance of 1 MΩ. But, because the performance decrease is similar for the voltage and the current, we noted only a negligeable shift of the optimal impedance toward the left. Finally, we calculated that the maximum power of the PU-TENG is around 0.8 mW (Figure 4e) and decreased by 13 % after 15 min of compression under a force of 2 kgf, but the power decreased by 99.6 % after 15 min under a force of 12 kgf. These results indicate that the pattern degradation of the triboelectric layer can significantly decrease the overall performance of TENGs by more than 90%, which constitutes a genuine issue for the commercial application of TENGs.

Healing the TENG using SMP

To address this problem, and enhance the performance of micro-patterned TENG over time, we propose to us SMP for the micropattern. Indeed, SMPs are smart materials which have the ability to return to their original shape from a deformed state (degraded polymer in TENG), this behaviour being triggered by an external stimulus such as a temperature change. Shape memory properties have been reported in a wide range of polymers including: PUs, epoxies, polyolefins and polyesters.[24–28] From those, we chose shape memory PU (SMPU) because it has numerous advantages like a light weight,

an ability to recover its shape from up to 400% of plastic strain, a wide range of T_g, a low recovery force, and it is low cost and easy to process. These last two attributes are especially important in developing TENGs that are high performing and cost effective. To evaluate this concept we fabricated and characterized SMPU-TENG composed of a SMPU micro-pyramid patterned triboelectric layer.

SMPU is a class of PU that has a segmented structure consisting of two different segments mixed together.[29] The hard segment is stiff whereas the soft one is elastic, making shape change and shape retention possible. The used SMPU is thermo-sensitive. Above T_g, SMPU has a rubbery elastic consistency, (Figure 3a) in which it can be easily deformed. When the material is cooled below its T_g, these deformations are fixed. The pre-deformation shape, molded under its molten state, can be easily recovered by reheating the material above T_g. To program and store the permanent shape of the PU, it has to go through a typical preparation process, which is as follows: first we mixed, under a vacuum at room temperature and at the appropriate weight ratio, the two monomers A (Di-isocyanate) 40% and B (Polyol) 60% constituting the PU polymer. Then, we put the mixture into a silicone mold and heated it up to 70 °C for 2 hours in an oven. During this step, the PU takes its original and permanent shape given by the mold. After that, we cooled down the PU at room temperature to below its glass transition temperature (more detail in the experimental part). Once the permanent shape of the polymer has been molded and memorized the SMP patterned layer is ready to be used as triboelectric material for TENGs operating at temperatures below T_g (55 °C). Then, if the micropattern is deformed or degraded, it only needs to rise the temperature above T_g to give back its original shape to the SMPU pattern and thus heal the SMPU-TENG.

As demonstrated, the degradation of the micropattern can drastically reduce the performance of TENG. After compressing the SMPU-TENG during 15 min, under a force of 10 kgf at room temperature, the PU pyramid micropattern was heavily deformed and flattened (Figure 5a). As a consequence, the output open circuit voltage and the short circuit current decreased to 17 V and 0.5 µA respectively. To heal the device and recover higher performances, we raised the temperature of the device from 25 °C to 65 °C. For this purpose, the device was placed on a hot plate, and was heated in its entirety. As expected, when the temperature reached the glass transition temperature of T_g = 55 °C, the PU recovered its pyramid shape (Figure 5a iii). As a result, when characterizing the SMPU-TENG under an average compression force of 5 kgf, after healing the device at different temperatures, the output open circuit voltage and the short circuit current increased up to 83 V and 3 µA respectively when the healing temperature was 55 °C (Figure 5b). This shows that it is possible to heal a SMPU-TENG after its PU micro-pyramid patterns and performances were degraded, recovering its original micro-patterned structure and its mechanical energy harvesting capabilities. To check the stability and repeatability of this healing process, we performed 30 consecutive degradation and healing cycles on one SMPU-TENG. As shown on the Figure 5c, the healing still work perfectly after strong, rapid and intense degradation cycles.

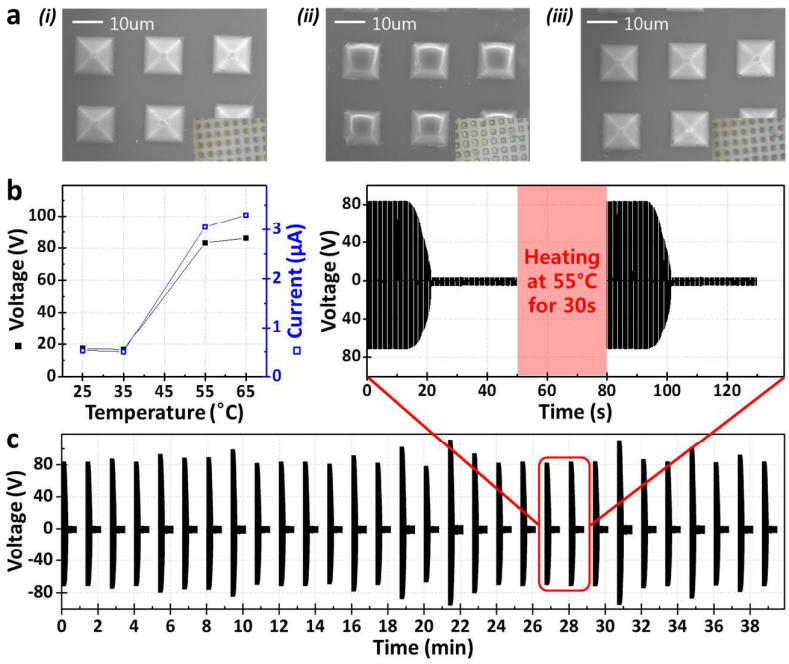

Figure 5 Structure and voltage of the SMP-TENG after healing. a) FE-SEM images of the SMP micro-pyramid pattern (i) before degradation by a high compression of 12 kgf of the SMP-TENG, (ii) after degradation and (iii) after the healing process applied to the SMP-TENG. b) Open circuit voltage and short circuit current of a healed SMP-TENG depending on the healing temperature. c) Open circuit voltage outputs from the SMP-TENG compressed by a strong force of 12 kgf and healed (30 times cycle).

Demonstration and advantages

To demonstrate the recovery potential of SMPU-TENG, we directly connected a light-emitting diode (LED) to a SMPU-TENG (Figure 6a) and we lit up the LED by compressing the SMPU-TENG with a high force of 10 kgf. As shown in Figure 6a, at the beginning the LED lit up when we compressed the SMPU-TENG and turned off when the force was released. As the time passed, the pyramid micropattern was deformed a little more with each compression, slowly decreasing the output power generated by the device. After 60 s, we started to note a decrease of the light intensity of the LED, indicating a significant enough decrease of the power generated that could barely keep the LED lit. After 90 s the micro-pyramid pattern degradation is such that the light generated is very small. As a result, we turned off the mechanical compression of the SMPU-TENG and we healed the SMPU-TENG by heating it at 55 °C for 10 s. Then, we turned the mechanical compression back on and we observed that the LED light intensity was back to its original state, demonstrating the recovery of the good initial power generation performance of the SMPU-TENG and therefore the healing of the SMPU micro-pyramid pattern. Thus, the old healed SMPU-TENG can be as efficient as when it was young.

To quantitatively illustrate the benefit of the healing of SMPU-TENG, we charged a capacitor of 10 µF using both a degraded SMPU-TENG and a healed SMPU-TENG (Figure 6b i). Because the output power of the healed SMPU-TENG is much higher than when it was deteriorated, the healed SMPU-TENG can charge this capacitor 5 times faster, (Figure 6b ii) which is an important advantage. Having a stable device performance is important for its overall operation. That is why this healing process is a determining factor in keeping good performance over time, and thereby extending the life-span of the device. In comparison to degraded TENGs, having the same initial performances as SMPU-TENGs, this healing process allows an increase in the quantity of energy harvested by SMPU-TENGs over their lifetime.

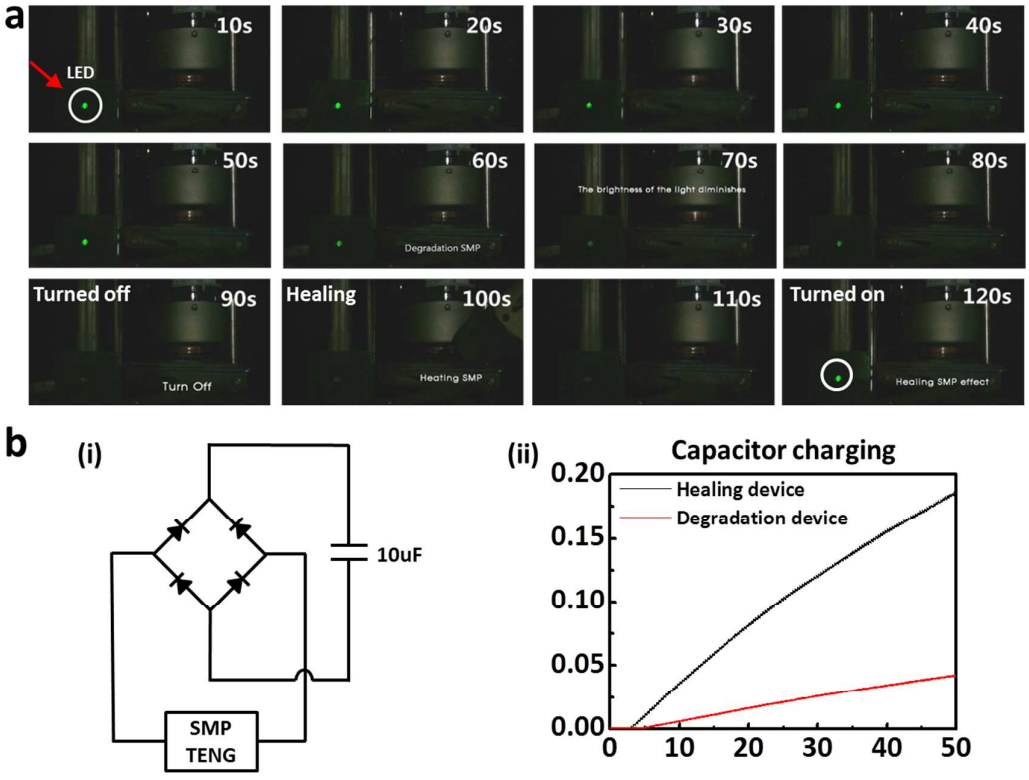

Figure 6 Demonstration of the healed SMPU-TENG for powering an LED and charging a capacitor. a) Video snapshots of the degradation and healing effect. b) (i) circuit for charging the capacitor and (ii) capacitor charging characteristics.

Discussion

The new concept of SMPU-TENG is important, as it allows TENG to keep good performance over the time and increase its life-span; this involves using an SMP material for fabricating the micropatterned layer. Usually, this layer serves as triboelectric layer for the triboelectric charge generation process. Because the efficiency of the device depends on the property of the material used, utilizing SMP material instead of a highly triboelectric material like PTFE can decrease the triboelectric charge generation process, which leads to lower performances of the SMPU-TENG compared to other optimized TENGs. Nevertheless, this issue can be addressed by coating the SMPU pattern with a thin highly triboelectric material. Another way to address this issue is to process the

surface of the SMPU pattern with a highly triboelectric element such as fluorine[30-31] which can significantly increase the triboelectric property of the SMPU layer and so the output performance of SMPU-TENGs.

Another concern is the healing process. In this article we used PU, which has a thermally induced shape-memory effect. The healing process is triggered by raising the temperature up to T_g = 55 °C in our case. For some devices sensitive to the temperature or for some applications in special conditions such as in the human body or in a cold environment, this trigger could be a problem. Nevertheless, most electronic technologies can support 55 °C and this T_g can be adapted, and different SMPs with different types of trigger stimuli exist. For example, light induced SMP can be used to trigger the healing process of a transparent TENG. It would be a natural and permanent healing mechanism, which would be very convenient.

Finally, using SMP is an innovative method for healing TENG from the degradation caused by the application of extreme forces on the device. However, the ability of the SMP to recover its shape has a limit. We healed our SMPU-TENG more than 30 times consecutively after compression by a strong force of 12 kgf. Under excessive force, SMP could reach its limit and have such high degradation that it is no longer possible for it to recover. In addition, SMP has a finite lifetime, and can be slowly degraded over time. Therefore SMP-TENGs are not eternal, but the stress that they can bear is higher than most of the usual polymers used in TENGs. For comparison we faricated and characterized a PDMS-TENG having the same structure with the SMPU-TENG (Supporting Information S4). Although the voltage output of the PDMS-TENG gradually decreases as compared with that of the SMPU-TENG by applying a continuous force of 12 kgf, it is not possible to heal the PDMS-TENG. Consequently, the advantages provided by SMPU far outweigh the basic TENGs.

Experimental

Device fabrication

The photo resist (PR) was spin coated on SiO_2 and photolithography was performed using a checkboard shaped mask. Then, non-covered squares were etched out by a Buffered Oxide Etch solution. After removing the PR, a KOH solution of 1.24 M mixed with isopropyl alcohol (IPA) 18 mL was used to etch the Si along the (100) plane at 82 °C. Finally the sample was cleaned with acetone, methanol and DI water and dried. SMP was prepared by mixing A (Di-isocyanate) and B (Polyol) with a 4:5 ratio, and was stirred for 30 s. Air bubbles in the SMP were removed in a vacuum chamber under a 0.1 Torr pressure for 40 s. Then the SMP was spin coated on the Si mold, pressed by an Al/acryl template and dried at 70 °C for 2 hours. After that it was cooled down at room temperature. The top and bottom template were composed of an acryl substrate and an Al electrode. Their sizes were 4×2.5 cm and 2×2.5 cm. Top template was supported by a sponge of 2 mm thickness serving as spacer for the TENG.

Characterization

The micro pyramid pattern was observed using a field emission scanning electron microscope (FE-SEM). The images of the pyramid pattern while pushing it with high force was observed using an optical microscope (SAMWON XT-VISION-UM2). For measuring the output voltage and the current of the TENG, an oscilloscope (Tektronix DPO3052) and a current meter (Stanford Research Systems Inc SR570) were used. To compress the TENG, a pushing tester (Labworks Inc ET-126-4) was utilized, pushing the TENG at a speed of 100 mm/s and varying the force applied from 2 kgf to 12 kgf.

Conclusions

In summary we investigated the degradation of micro-patterned triboelectric layer commonly used in TENGs. We noted the degradation of this layer over the operation time and we observed a decrease of more than 90 % of the output performances of TENGs when applying high compression forces of 10 kgf on the device. Therefore, we developed and fabricated a TENG composed of a SMPU triboelectric layer which has the ability to be healed. We showed that by rising up the temperature to T_g = 55 °C to trigger the healing process, the SMPU micro-pyramid pattern recovers its initial shape. The characterization of the healed device show that its performances increase back to its original state at around 80 V and 3 μA. Thus, after degradation of the SMPU-TENG and its output performances because of the application of too strong forces, we were able to heal the structure of this device and to observe the recovery of its mechanical energy harvesting capability. To illustrate this ability we shown the degradation and the healing process of a SMPU-TENG lighting up one LED. In addition we measured the charging time of a capacitor depending on the condition of the SMPU-TENG, emphasizing the advantage of having a healthy SMPU-TENG by charging 5 times faster a capacitance of 10 μF.

We proposed an innovative improvement of the patterned triboelectric layer commonly used in TENGs to extend their good performance over the time. For this purpose, using SMP, we introduced a new smart SMP-TENG structure enabling to heal its structure, allowing it to recover good performances after the degradation of the triboelectric layer and enhancing the lifetime of TENGs. This improvement is important as extending the good performances lifetime is determinant for the democratization of TENGs in the actual context of energy harvesters where harvesting green and renewable energy should be done using small devices as much ecological and cheap as possible. Thus, using SMP, TENGs could be more efficient and profitable over the time while decreasing the maintenance and wastes because of their extended lifetime.

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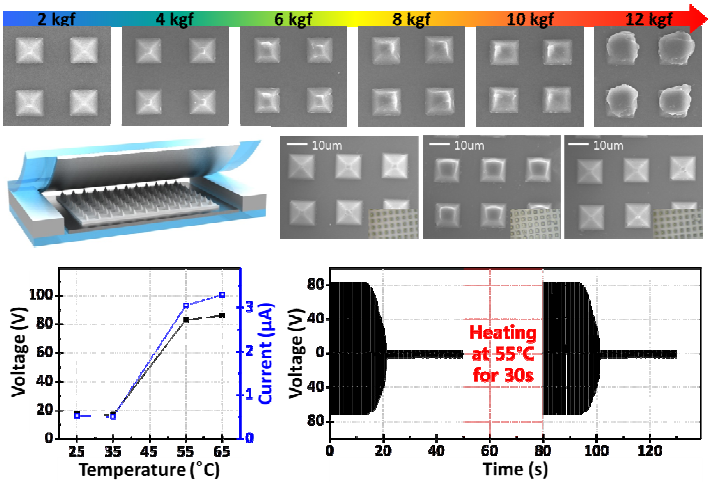

We introduce a new smart SMP-TENG structure and study the degradation, healing process of SMP-TENG. It improves their endurance, life time and thus demonstrating the huge potential of self-healing SMP-TENGs.