Fully biodegradable triboelectric nanogenerators based on electrospun polylactic acid and nanostructured gelatin films

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Abstract: Here, we present a fully biodegradable triboelectric nanogenerator (BD-TENG) based on gelatin film and electrospun polylactic acid nanofiber membrane. By optimizing the material properties of the gelatin and PLA films through processing, an output voltage up to 500 V, a short circuit current density of 10.6 mA/m\textsuperscript{2} and a maximum power density over 5 W/m\textsuperscript{2} are achieved with a device dimension of 4x4 cm\textsuperscript{2}. Performance of the BD-TENGs under various material and test conditions are investigated and analyzed. The BD-TENGs show excellent mechanical stability and reliability upon cyclical contact for 15000 times. Biodegradation experiments show that all the materials of the TENG could be degraded completely into water in about 40 days. The BD-TENGs provide a promising green micro-power source for environment monitoring, biomedical implants through harvesting energy from wind, heart motion et al, yet they can dissolve with no adverse effect to environment or human body.
1. Introduction

Green energy is playing more and more important role in today’s ordinary life and industries as one of the measures for protecting environment and sustainable development. A great deal of research efforts has been devoted to obtain green energy such as those from solar radiation, wind, ocean waves and so on in large scales. With the rapid progress of microfabrication and microelectronics, micro-scale energy sources are highly demanded and desirable for various applications, particularly for these modern electronic devices and microsystems, such as remote sensor networks, implant devices and portable electronics etc. Small scale energy harvesting technologies such as piezoelectric [1], electrostatic [2] and triboelectric [3] nanogenerators have been developed to provide energy for these types of applications. Among them, the triboelectric nanogenerators (TENGs) have attracted particular attentions as they can convert waste mechanical energy into electricity with high output power and efficiency, yet they have very simple device structures and utilize low cost materials. TENGs produce charges (electricity) through the electrification and electrostatic effects occurring between two contact surfaces of materials with dissimilar electron affinities when they are in contact and separation. TENGs are particularly attractive for powering remote sensing networks in remote and not-easily accessible areas as they can harvest mechanical energy locally from wind [4, 5], waves, vibration [6] etc with high power and conversion efficiency, as self-powered autonomous systems.

Intensive researches are undertaken to develop high performance TENGs by utilizing either the better material combinations, nanostructured surfaces and nanomaterials such as nanofibers [7] and piezoelectric nanomaterials, or charge injection [8] to increase the surface charge density [9]. However, so far, most materials used to fabricate TENGs are non-biodegradable, thus they may become an electronic waste at the end of their service time. As majority of these are not disposable, they may harm and pollute the environment. TENGs have also shown great potential to power implant medical devices [10] such as monitoring of wound healing and operation temporally. It would be very attractive and useful if the TENGs and electronics could be degraded in the environment, leaving no pollution and impact to the surroundings; or resorbed by human body at the end of implant application. Biodegradable (BD) and biocompatible materials are natural or synthetic materials that do not harm and pollute the environment, or can be resorbed by living systems without adverse effects when they are considered for implant application. To date, only few energy harvesting devices were made from partial biodegradable materials. Zheng et al presented a biodegradable
triboelectric nanogenerator as a power source for transitional medical devices [11]. A transparent paper-based electret nanogenerator was demonstrated by Gao et al, which could self-degrade in natural soil [12]; and a recyclable TENG made from polyvinyl and sodium alginate with lithium and aluminium as current collectors was reported by Liang et al [13]. However, limited by the choice and nanostructure of the biodegradable materials, these BD-TENGs exhibited very lower power outputs compared to those with non-biodegradable triboelectric materials [6, 14, 15]. To develop usable BD-TENGs and improve their performance, more work need to be done, such as develop suitable BD materials, fabrication methods, novel device structures. Here we report a high power density triboelectric nanogenerator using biodegradable materials: electrospun poly(lactic) acid (PLA), nanostructured gelatin films as the tribo-materials of the TENG and transitional metal as the electrodes. The BD-TENG, with an area of 4 x 4 cm², could generate an output voltage up to 900 V and a peak power density over 5 W/m², higher than or comparable to those made from non BD polymer materials [6, 14, 15], yet the devices can be dissolved in natural water completely in about 40 days with no trace remaining.

2. Experiment section

To develop the biodegradable microscale power sources, all the materials used for this type of TENGs must be biodegradable, i.e. dissolvable in water, soil, or other natural environment or in human body without causing harmful effects to environment or body if they are used in implants. After initial investigation on a number of biodegradable tribo-materials [16], including PLA, poly lactic-co-glycolic acid (PLGA), poly(vinyl alcohol) (PVA), gelatin etc., we found that gelatin and PLA polymers possess high negative and positive affinities respectively in tribo-series. The polymers could be processes to form nanostructures on the surfaces that could enhance the output performance of the devices significantly [17]. Both the gelatin and PLA materials are abundant with low costs. Therefore, PLA and gelatin were chosen to be the positive and negative tribo-materials to fabricate the BD-TENGs and to investigate their performance and biodegradable characteristics.

Gelatin is a translucent, colourless, flavourless food derived from collagen obtained from various animal body parts [18], and is commonly used as a gelling agents in food, vitamin capsules and cosmetic manufacturing [19, 20]. PLA is a bioactive thermoplastic aliphatic polyester, derived from renewable resources [21], and has been widely utilized in implant
devices [22], biodegradable medical tools [23] and three-dimensional (3D) printed tissues [24, 25] because of its biocompatibility and biodegradable characteristics. Both the gelatin and PLA are well known for their biocompatibility and biodegradable properties, besides, they are also good insulators with relative higher or lower electron affinity, thus they are suitable for the development of the biodegradable TENGs for remote sensor network or implant applications.

Magnesium (Mg) has been proven to be a biocompatible metal with high electrical conductivity and high dissolvability for a number of transitional electronics with no side effect to environment and human body [26, 27]. Thus, Mg has been chosen to be the electrode metal for both sides of the BD-TENGs in this work. For simplicity, a 100 µm thick commercial Mg foil was used as the electrodes for the fabrication of TENGs.

2.1 Fabrication of nanostructured gelatin films

Initial investigation showed that smooth gelatin and PLA films do not produce high charge density. Based on the working principle of TENG, the insulator materials with rough surfaces could enhance the TENG performance significantly owing to the greatly increased effective surface areas. To increase the power density of the BD-TENGs, gelatin films with rough surfaces were used to fabricate the devices. Sandpapers with different grades (different particle sizes, MATADOR Co.) were used as the templates to obtain gelatin films with rough surfaces using the process similar to that reported in ref.[28].

Gelatin granules (WUXI ZHANWANG CHEMICAL Co., China) were dissolved in de-ionized (DI) water with a mass concentration of 10%. The gelatin solution was kept in an oven at 50 °C for 1 hr to obtain a fully dissolved and well-mixed solution. The gelatin solutions were spin coated on sand papers of various grades at a speed of 4000 rpm for 40 sec to obtain gelatin films with various rough surfaces. Solvent in the gelatin films was vaporized naturally at room temperature (~25 °C) for 5 hr. The films were glued to Mg foils using a soluble adhesive tape, and peeled off from the sandpapers with the rough surface exposed outside. The fabrication process of the gelatin films is shown in Fig. 1(a) and in .

2.2 Fabrication of electrospin PLA nanofiber membranes

PLA is a material with positive electron affinity (show later) comparing to the gelatin, suitable to be the positive tribo-material for the TENG, i.e. it tends to donate electrons. PLA electrospun nanofibers were used to fabricate the membranes with high surface areas to
improve the device performance. After rigorous initial investigation, a receipt and process to fabricate proper PLA nanofiber films were obtained as follows. PLA powder (4032D, NatureWorks Co., USA) was dissolved in an acetone and chloroform mixed solution with a ratio of 0.7 g PLA:2 ml acetone:6 ml chloroform. The solution was stirred for 24 hr at room temperature to ensure uniformity of the solution. The PLA solution was then electrospun on a Mg foil which was placed on a polyethylene terephthalate (PET) support layer. A DC high voltage 15 kV was applied between the electrospin needle and the Mg foil which have a separation distance of 20 cm. The solution flow rate was kept at 25 μl/min for all the nanofiber membranes. The thickness of the PLA nanofiber membranes was controlled by varying the electrospin time from 0.5 min to 4.5 min. The PLA nanofiber membrane thickness, d, was found to be linearly correlated to the electrospin time, t, with a relation of d=20t (here d is the thickness in μm and t is the time in minute). The fabrication process of the nanofiber PLA films is shown in Fig. 1(b). All the electrospinning was carried out at room temperature.

![Fig. 1 Structure and fabrication process of the gelatin (a) and PLA (b) plates for a BD-TENG, respectively. A side view of the BD-TENG (c), and schematic working steps of the TENG (d).](image)

**2.3 TENG fabrication**

Once the nanostructured gelatin film and PLA nanofiber film were obtained, they were assembled into a TENG structure with two PET plates as the support. Fig. 1(c) is the three dimensional (3D) schematic structure of the BD-TENG. The Mg foil electrodes were further
glued to a 1 mm thickness PET plate for protecting the Mg electrodes and as support layers for easy handling and connecting electrical leads for tests. For this work, the effective device size is $4 \times 4 \text{ cm}^2$ for all the devices characterized unless specifically stated.

2.4 Characterisation setup

The vertical contact-separation mode was chosen for our BD-TENGs. A dynamic fatigue tester (Popwil Model YPS-1) with a motional arm that could control the contact force, impact frequency and distance between two plates was utilized to characterize the BD-TENGs. An oscilloscope (Tektronix MDO3022) and a picoammeter (Keysight B2981A) were used to measure the output voltage and current of the TENGs, respectively. Here, the open circuit (OC) voltage means the voltage obtained by the oscilloscope which has an internal load resistance of $100 \text{ M}\Omega$, and short circuit (SC) current means the current measured directly by the picoammeter. The electrode of the PLA side was connected to the (+) cable connected to the oscilloscope and the picoammeter in all the measurements, while the gelatin plate was connected to the (-) cable of both the equipment.

3. Results and discussion

3.1 Material characterization

As mentioned before, one effective way to enhance the performance of TENGs is to use nanostructured triboelectric films with high effective surface areas. In this work, for the gelatin films, the rough surfaces were obtained by spin coating the films on sandpapers; and the PLA were electrospun into nanofibers to form membranes which not only increases the effective surface area, but also speed up the biodegradable process [29] as shown later. Fig. 2(a) and (b) show typical SEM images of the nanostructured gelatin films and PLA nanofiber membrane, respectively.

As can be seen in Fig. 2(a), indented microstructures are formed in the gelatin film once it is peeled off the sandpaper, and majority of the microstructures deform or collapse due to the softness nature of the gelatin polymer. The microhole sizes are in the range of 15-20 µm determined by the grade of the sandpapers used for the films. Detailed investigation (show later) on the gelatin films coated on different grade sandpapers showed that the surface roughness increases with the decrease of the grade of the sandpapers. The grade P1000 sandpaper could produce 15~20 µm microholes and has the best performance for the TENG compared to gelatin films with other size nanostructures, hence it was selected to fabricate all
the TENGs studied here. The thickness of the gelatin films was found to be inversely proportional to the spin speed, and the optimal thickness of the gelatin films is in the range of 60 µm which could be produced by a spinning process of 1000 rpm for 40 sec on sandpaper which was then checked by a profilometer. The thickness and microstructures were confirmed and checked by profilometer and SEM respectively.

![Fig. 2 SEM images of the surface of a gelatin film obtained by coating on a sand paper (a), and surface and cross section of an electrospun PLA nanofiber membrane with a thickness of 60 µm (b). Other SEM images of different thickness of PLA nanofiber membranes can be seen in Figure SI1.](image)

The morphology and properties of PLA nanofibers were affected by multiple factors such as the concentration, viscosity and flow rate of the solution, the applied voltage, distance between the needle and holder etc. Careful optimization is required to obtain the solution conditions and suitable process. The optimized electrospin conditions are as follow: A Mg foil was used to collect nanofibers and was placed 20 cm away from the syringe needle tip. A voltage of 15 kV was applied between the collecting target and syringe tip. The flow rate of the solution was fixed at 25 μl/min. Under these conditions, PLA nanofibers with diameters in the range of 900-1800 nm can be obtained at a relatively fast speed, and the nanofibers will not coagulate together which makes the nanofibers collapse into a film. The thickness of the PLA nanofiber films has a linear relationship with the electrospin time. The optimal thickness is also about 60 µm, determined by the device performance as shown later. The SEM images of the PLA membranes with different electrospin times are shown in Fig. SI1 in Supplement Information (SI) for clarification, clearly showing the thickness of nanofiber membranes increases with electrospin time.

### 3.2 Performance of BD-TENGs

Fig. 3 shows the effect of nanostructured surface of polymers on the open voltage and short circuit current of the BD-TENGs. All the results were obtained at a 50 N contact force,
a 5 Hz frequency and a 4 mm separation distance between the two plates. Both smooth and rough PLA membranes and gelatin films were used for comparison. The smooth films of gelatin and PLA were spin coated, while the rough surface films were made by moulding on a sandpaper (degrade P1000) for gelatin and by electrospinning for PLA membrane. Both have a similar thickness of 60 µm. Device (1), labelled as (1) in Fig. 3(a) and (b) has a smooth gelatin film and a smooth PLA film. The open voltage for Device (1) is only about 16 V, and increases to about 33 V when the smooth gelatin was replaced by a rough gelatin film (labelled (2) in Fig. 3(a)). The rough surface of the gelatin film increases the OC voltage by a factor of 2, not significant possibly due to the low porosity of the film. For Device (3) (labelled as (3) in Fig. 3) with a PLA nanofiber film and a smooth gelatin, the open voltage increases to about 175 V, more than ten times larger than that of Device (1), implying the significance of the nanofiber structure. The open voltage reaches about 500 V for the TENG with a rough gelatin film and a PLA nanofiber membrane (labelled as (4)). Fig. 3(b) are the corresponding short circuit current density which is about 0.3 mA/m², 0.6 mA/m², 4.2 mA/m² and 10 mA/m² for Devices (1), (2), (3) and (4) respectively, clearly indicating the significant effect of the microstructured surface on the performance of the TENGs. Nanostructured surfaces could drastically increase the effective surface areas of the two insulator films, thus more electric charges can be induced by contact-electrification, dramatically enhancing the output performance of the BD-TENGs.

Fig. 3 Schematics of the PLA and gelatin membranes and the TENGs with different material structure combinations. The OC voltage (a) and SC current density (b) of the TENG devices with different structure combinations accordingly.
Fig. 4(a) shows the OC voltage as a function of PLA film thickness, obtained at a contact force of 50 N, a contacting frequency of 5 Hz and a separation distance of 4 mm, respectively. The output voltage of the TENGs increases from 95 to 535 V when the thickness of PLA membrane increases from 10 to 60 µm, but it fluctuates round or decreases slightly when the thickness is more than 60 µm. The SC current density exhibits a similar trend to the output voltage when the thickness of PLA membrane is varied. For these tests, the gelatin film thickness was fixed at 60 µm.

Fig. 4 OC voltage (a) and SC current (b) of the BD-TENGs with various thicknesses of PLA membranes; (c) output power of the TENGs as a function of load resistance with different PLA thickness; (d) and PLA thickness dependence of the power density. All the tests were under 50 N force, 5 Hz frequency and 4 mm separation with a 60 µm thickness gelatin film.

When the PLA film is thin, e.g. ~10 µm, only small part of the electrode surface is covered by the PLA nanofibers as can be seen in Figure SI1(c) in SI. The effective contact area of the PLA film is very small, so that few charges could be induced and transferred between the two plates. As a result, the OC voltage and SC current density are small. With the increase of the nanofibers deposited on the Mg electrode, the effective contact area increases, and the OC voltage and SC current density become larger correspondingly. The output power density under different load resistances for these TENGs was also investigated with the results shown in Fig. 4(c). The output power density strongly depends on load resistance, and all the TENGs with different PLA thicknesses show the maximum power density at a load resistance of about 80 MΩ. Fig. 4(d) illustrates dependence of the peak
power density of TENGs on PLA film thickness. It increases rapidly with the PLA film thickness with a maximum value at \(~60 \mu m\) thickness, and the decreases with further increase of the PLA film thickness. This is because the membrane less than \(60 \mu m\) thick can not completely cover the Mg electrode surface (detail is shown in SI1) which makes the effective surface area not reach the maximum. Similar characterization has been conducted for the TENGs with different gelatin film thicknesses, and the results showed that the optimal thickness for the gelatin to achieve the best TENG performance is round \(60 \mu m\), similar to that of the PLA film.

Output performance of a contact-separation mode TENG is highly dependent on the contact speed and the imposed force. Fig. 5(a) and (b) are the OC voltage and SC current density of BD-TENGs as a function of contact frequency, tested with the contact force and separation distance fixed at 50 N and 4 mm, respectively. The thickness of both the PLA nanofiber and gelatin films is about \(60 \mu m\). The output voltage increases from 328 V to 496 V when the contact frequency rises from 1 to 5 Hz, and saturates at \(~496 V\) when the frequency is higher than 5 Hz. However, the SC current density increases continuously from 4.9 mA/m² to 10.1 mA/m² when the contact frequency rises from 1 Hz to 7 Hz. The increase of the SC current density and OC voltage is attributed to the fast induction and transferring of charges under fast contacting. Fig. 5(c) and (d) are the OC voltage and SC current of the TENG with the separation distance as a variable, exhibiting similar characteristics to those with varying contact frequency. The OC voltage increases slowly and saturates, while the SC current increases continuously with the increase of separation distance.

The OC voltage and SC current of the same BD-TENGs with different contact forces are shown in Fig. 5(e) and (f), with the contact frequency and separation distance fixed at 5 Hz and 4 mm, respectively. It can be clearly observed that both the OC voltage and SC current density increase with the rise of contact force. The maximum OC voltage reaches 560 V at a 70 N contact force (a pressure of 4.375 N/cm²), more than two times of 256 V at a 10 N contact force. The SC current density also increases more than double, from 5 mA/m² at 10 N contact force to 11 mA/m² at 70 N. The significant improvement of the outputs is attributed to the increased contacting area under larger forces. At a lower contact force, the surfaces of the PLA nanofibers and gelatin film are partially contacted, leaving some areas untouched, hence less charge are produced. Under larger forces, PLA and gelatin films can deform to fill more space and holes due to their elastic nature, resulting in larger contact area, hence more charges are induced. Consequently, the electrical output increases with the contact force.
Fig. 5 (a) and (b) are the OC voltage and SC current density of the BD-TENGs working at different frequencies, the contact force and separation distance were fixed at 50 N and 4 mm, respectively; (c) and (d) are the OC voltage and SC current density of the BD-TENGs working at different separation distances, with the movement frequency and contact force fixed at 5 Hz and 50 N, respectively; (e) and (f) are the OC voltage and SC current of the BD-TENGs working under different contact forces, the working frequency and separation distance were kept at 5 Hz and 4 mm; the summarized output voltage, current (g) and output power density (h) under various load resistance of the BD-TENGs.

Fig. 5(g) and (h) are the dependence of the OC voltage, and SC current and power density of the same BD-TENGs with different load resistances. The OC voltage increases initially and then saturates at a load resistance of about 120 MΩ, while the SC current decreases in a similar way. The power density was calculated by $P_s = I^2R/S$ (S the device area).
directly using the values shown in Fig. 5(g), exhibiting a maximum value of 5 W/m² at a load resistance near 80 MΩ at 50 N contact force, comparable to or higher than most of TENGs reported with non-biocompatible polymers.

### 3.3 Humidity effect and Reliability

Humidity is an important parameter affecting TENG performance significantly, and needs to be clarified before practical application. It was reported that the charge induction efficiency decreases when the humidity raises in other study [30]. The electric performance of the BD-TENGs under different humidity were investigated for the device with 60 μm thickness for both the PLA and gelatin films, at 50 N, 5 Hz and 4 mm spacer, respectively. As shown in Fig. 6(a) and (b), the current density and voltage are 12 mA/m² and 500 V at 40%RH humidity, and decrease to 8.6 mA/m² and 300 V when the humidity is 80%RH. Fig. 6(c) and (d) show the power density of the TENG versus load resistance under various humidity levels and dependence of the peak power on humidity. It is clear that the maximum power density is about 5.06 W/m² when the humidity is 40%RH, and it becomes almost quarter of the maximum power when the humidity is 80%RH. The decrease of output power indicates the surface charge density of the material decreases dramatically when humidity increases to a certain level, possibly due to the mobility of charge along the surface at high humidity levels. The results indicate it is better to avoid using TENGs in high humidity condition. To avoid the humidity effect on the performance of the BD-TENGs, methods such as tight sealing of package of TENGs should be taken.

TENGs are normally designed to harvest mechanical energy, i.e. they are subjected to rigorous mechanical impact or vibration, therefore mechanical reliability and stability of TENG devices are extremely important for applications. The stability of the TENGs has been investigated with the result shown in Fig. 7. The output voltage decreases slowly from the initial test of ~505 V to 468 V, showing 7.5% deterioration after 14000 cyclic contacts. Detailed investigation revealed that during the cyclic contacts, part of the PLA nanowires on edge were pulled off the PLA nanofiber membrane and connected to the gelatin film after the two plates being separated as shown in Fig. S123. The connection between the two plates would deteriorate the electrification effect, reducing the output performance of the TENGs. With the increase of cyclic contacts, the number of connecting nanofibers between two plates increases, deteriorating the performance of the BD-TENG continuously. To solve this problem, some degradable glue (gelatin solution) was added on the edge of the PLA plate to
increase the adhesion of the PLA nanofiber to the back of the Mg electrode. After this process, very few PLA nanofibers connecting the plates were formed, and the stability and repeatability of the BD-TENG has been improved.

Fig. 6 Output voltage (a), short circuit current (b), power at different loads (c) and the peak power of the BD-TENG under different humidity level, showing a rapid deterioration of the performance with the increase in humidity level.

Fig. 7 Stability of the BD-TENG, the OC voltage decreases slowly with the increase of cyclic contact.

3.4 Biodegradation of the TENGs

Our aim is to develop TENG devices that can degrade in natural environment or inside human body for implant application without harmful effects. Gelatin and PLA have been proven to be biodegradable and harmless materials by many researches under various environments [31]. Moreover, the dissolved gelatin can be absorbed by bacteria in the
environment as nutrition, without any harm effect or pollution to the environment. The degradation characteristics of the gelatin and PLA films are strongly related to the properties and structures of the films. Nanostructured film with large effective surface area could degrade much faster. Therefore, nanostructure of the gelatin film and nanofibers of the PLA membrane could not only improve the performance of the TENG as shown above, but also increase the degradation speed of the materials.

The degradation characteristics of the magnesium metal electrodes, gelatin and PLA membranes used for the BD-TENGs have been investigated using water from a natural spring with a pH of ~6.5. The water for the experiments was renewed every 12 hr and a magnetic rotor was used to stir the water very slowly to mimic water flow in the real environment. The properties of water in real environment will not change significantly by the degradation of materials as it either has a large volume or is refreshed continuously by the flowing water. The gelatin film and PLA nanofiber membranes attached on Mg foils used for a TENG were placed in the water in separated beakers at ~25 °C, and their degradation status with time was investigated. Fig. 8 presents the sequential photo images of the Mg foil, gelatin/Mg and PLA/Mg film degradation in water respectively, while the detailed SEM images of the corresponding degradation processes are shown in Fig. 9.

For Mg degradation in water, there are many kinds of intermediate products according to the different ions in water. Basically during the reaction of Mg with water, Mg is oxidized and MgO is generated, and MgO reacts with H2O further to produce Mg(OH)2 [32, 33]. The main degradation process of magnesium is expressed by ionic chemical formula as follows [26],

$$2\text{Mg} + 2\text{H}^+ = \text{Mg}^{2+} + \text{H}_2 \uparrow$$

$$\text{Mg(OH)}_2 + 2\text{H}^+ = \text{Mg}^{2+} + 2\text{H}_2\text{O}.$$

In general, Mg dissolution in water is relatively fast. As mentioned above, we used a commercial Mg foil (not high purity) of 100 µm for the convenient fabrication of the BD-TENGs, which made the dissolution of Mg foil in water much longer time. If a thin Mg film, typically less than 1 µm for TENGs, is used, then the dissolution of Mg in water would be in a few hours. As it can be seen in Fig. 8, the dissolution of magnesium is taken place from all directions, but faster on the edges. Mg foil dissolves almost completely in water in about 18 days. This is a rather slow dissolving process, probably due to the low purity of the metal and grease on the surface of the foil. Detailed SEM investigation is shown in Fig. 9. As
it can be seen, there appear a lot of cracks in the film from day 3, and the density increases with time. The cracks are mostly from the scratches, bending, folding boundaries etc in the film, and dissolution occurs along the cracks first as they are weaker, making them larger and more, eventually the whole area dissolves in the water.

Fig. 8 Sequential photo images of the degrading gelatine/Mg, PLA/Mg films and Mg foil in natural water. Both the gelatin and PLA films have a thickness of about 60 µm, while that of Mg is 50 µm.

The general degradation process for gelatin film in water is well known and is as follows: the gelatin chains have hydrogen atoms attached to their sides, and the hydrogen branches can weakly bond with water molecules, resulting in disparity of gelatin molecules from the polymer and dissolution of polymer in water. It was found that mainly hydrolytic degradation process occurs due to solvation and depolymerisation of the polymeric chains [34]. The photo images surrounded by the blue dotted line in Fig. 8 represent the degradation of gelatin/Mg plate. It can be seen that dissolves in the natural water gradually, and the edge part dissolves first and approaches the middle part of the plate. The whole gelatin/Mg plate is dissolved almost completely in about 20 days, slightly longer than that of the Mg foil. The detailed study by SEM (the images surrounded by the blue dotted line in Fig. 9) shows that gelatin film degrades in water much faster than Mg foil, leaving Mg to continue the degradation in water. The slightly longer dissolving time for the gelatin/Mg plate than that of Mg is due to the coverage of gelatin film and residual of gelatin that slow down the degradation process. Once the gelatin is gone, the dissolution process for the gelatin/Mg plate is again dominated by the Mg foil. As it can be seen from the gelatin/Mg SEM images from Day 12 in Fig. 9, cracks appear in the substrate, very similar to those of Mg foil images from Day 3, implying the dominant degradation of Mg foil, and most of the gelatin film dissolves from Day 12.
Gelatin is commonly used as capsules for drug with much short dissolving capability. The gelatin used here has longer degradation time in water mainly due to the low temperature compared to that of body, and the different composition which was specifically selected for the fabrication of devices, not for intake.

For the degradation process of PLA in water, it is known to be related to the hydrolytic reaction process. Water molecules attack the ester bonds in the polymer chains and make the average length of chains shorter, resulting in fragments of chains with carboxyl end groups that become soluble in water \[^{[35]}\]. Bulk degradation is the dominant mechanism for polyesters such as PLA \[^{[36, 37]}\], the reaction occurs extensively through the chain break and polymer swollen due to water presence, resulting in erosion in the polymer. The degradation of PLA will ultimately lead to monomers (lactic acid in PLA), which can be metabolized into carbon dioxide and water or excreted \[^{[38]}\].

![Fig. 9 Sequential SEM images of the degrading Mg/PLA and Mg/Gelatin films and Mg foil.](image)

Normally, PLA films need a long time to degrade in water, and it was found that the PLA nanofiber membranes can dissolve in water much quicker owing to the much increased surface areas. The detailed degradation process of the PLA nanofiber membrane with time is shown in Figs. 8 and Fig. 9 in the areas surrounded by the red dotted lines. From Fig. 8, it can be seen that the PLA membrane/Mg plate dissolves almost completely in Day 20, almost same as that of gelatin/Mg plat, indicating the whole dissolution process is again dominated by the Mg foil with PLA nanofiber disappeared faster. PLA nanofiber membrane/PLA plate is different from the gelatin/Mg. The latter has the whole gelatin film covered the Mg foil, while the nanofiber membrane is not a dense film but a coarse membrane with large Mg foil
area not being covered as shown by the SEM image of Day 0. Dissolution of both the Mg foil and PLA nanofibers can take place even from the beginning. From Day 3, cracks appear in the substrate similar to that of Mg foil. Meanwhile, it can be seen that the PLA nanofibers break, swell, and decompose as those reported in refs [37] and [38]. The small nanofibers dissolve first, while the large ones takes much longer time. Since Mg underneath is dissolved as well, the PLA nanofiber membrane would eventually lift and float in water after 15-20 days in small pieces, leaving the remaining Mg foil only to be dissolved in water. Fig. SI 3 is the photo of small pieces of PLA floating in the water when they are partially dissolved and detached from the Mg foil. The time required to dissolve the floating small piece PLA nanofiber membranes completely is about 15-20 days, making the total dissolution time for PLA nanofibers about 40-45 days.

![Fig. 10 SEM image of the PLA nanofiber during its degradation process in protease K solution.](image)

Natural water may contain enzymes (for example, protease K) produced by fungi [29, 39] or bacteria [40, 41], and the temperature may rise over 30 °C that could speed up the degradation process of polymers significantly. To assess the degradation of PLA in a condition closer to natural environment, we have also conducted an experiment to degrade PLA nanofiber membrane in a protease K solution with a pH value of 9, a concentration of protease K of 0.5 mg/ml at 40 °C which are optimal conditions for enzyme [29]. The SEM images of the degradation progress are shown in Fig. 10 (note the PLA nanofiber was on a Al substrate for easy characterization. Al does not dissolve in the protease K solution). The degradation is much faster in the protease K solution than that in spring water. In about 2.5 hr, the PLA nanofibers have disappear almost completely, consistent with the observation in ref.[29]. The degradation process is slightly different from that in natural water at room
temperature, there is no break and swollen of the fibres as seen in Fig. 9, but the decomposition. This is probably because the fast decomposition process, leaving no time for swelling process. The weight loss is shown in Fig. 11 as a function of time for the PLA membrane, showing a linear relationship. The high degradation rate is mainly attributed to the high enzymatic reaction at high temperatures and the large surface-to-volume ratio of the PLA nanofibers, which increases the interaction area between the fibres and catalysis of the enzyme significantly [29]. The results show that the degradation rate of PLA would be between these two experiments.

![Graph showing weight loss as a function of time.](image)

**Fig. 11 PLA weight loss in a protease K solution as a function of time, showing a linear relationship.**

4. **Conclusions**

In summary, we have demonstrated a new fully biodegradable or transitional triboelectric nanogenerator based on contact-separation mode triboelectrification. By using nanostructured gelatin film and PLA nanofiber membrane, the output performance of the TENG was greatly enhanced with an output OC voltage of 500 V, SC current density of 10 mA/m² and power density over 5 W/cm². All the materials of the device could degrade in natural water completely in about 40 days, without introducing pollution to the environment or harmful effect to human body if they are used for implants, demonstrated its potential application as a green power source. Moreover, both gelatin and PLA are low-cost, easy to obtain and easy to process in large scale. The whole process for BD-TENG fabrication is simple, environmental friendly and facile, which is suitable for mass production.

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Appendix A. Supporting information
Supplementary data associated with this article can be found in the online version at doi:xxxxxxxxxxxxxxxxxx.

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