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Full paper

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 polymer films, an output voltage up to 500 V, a short circuit current density of 10.6 mA/m^2 and a maximum power density over 5 W/m^2 are achieved with a device dimension of 4 × 4 cm^2. Performance of the BD-TENGs using different material combinations under various test conditions are investigated and analyzed. The BD-TENGs show excellent mechanical stability and reliability upon cyclical contact for up to 15,000 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] 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 [6,7], vibration [8] 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 polymer material combinations, nanostructured surfaces, nanomaterials such as nanofibers [9], piezoelectric nanomaterials and composite dielectric materials such as $ZnSnO_3$ and polydimethylsiloxane [10], or charge injection [11] to increase the surface charge density [12]. A TENG that can work under extremely moist environment was reported by utilizing a novel laminated cellular electret film [13]. 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 materials are not disposable, they may harm and pollute the environment. TENGs have also shown great potential to power implant medical devices [14] 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

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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, which used poly lactic-*co*-glycolic acid (PLGA) as the encapsulation layer for the TENG [15]. A transparent paper-based electret nanogenerator was demonstrated by Gao et al., which could self-degrade in natural soil [16]; and a recyclable TENG made from polyvinyl and sodium alginate with lithium and aluminium as current collectors was reported by Liang et al. [17]. However, limited by the choices and nanostructures of the biodegradable materials, these BD-TENGs exhibited very lower power outputs compared to those with non-biodegradable triboelectric materials [8,18,19]. 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 × 4 cm^2, could generate an output voltage up to 900 V and a peak power density over 5 W/m^2, higher than or comparable to those made from non BD polymer materials [8,18,19], 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 [20], including PLA, poly lactic-*co*-glycolic acid, poly (vinyl alcohol) (PVA), gelatin etc., we found that gelatin and PLA polymers possess high negative and positive electronic 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 [21]. 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 [22], and is commonly used as a gelling agents in food, vitamin capsules and cosmetic manufacturing [23,24]. PLA is a bioactive thermoplastic aliphatic polyester, derived from renewable resources [25], and has been widely utilized in implant devices [26], biodegradable medical tools [27] and three-dimensional (3D) printed tissues [28,29] 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 relatively high or low electron affinity, thus they are suitable for the development of the biodegradable TENGs for remote sensor networks 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 [30,31]. 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 and characterization 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, roughening the surfaces of the dielectric materials 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 Refs. [32,33].

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 h 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 s to obtain gelatin films with various rough surfaces. Solvent in the gelatin films was vaporized naturally at room temperature (~25 °C) for 5 h. 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).

2.2. Fabrication of electrospin PLA nanofiber membranes

PLA is a material with positive electron affinity (show later) comparing to that of the gelatin material, 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 h 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 high DC voltage of 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 to 4.5 min. The PLA nanofiber membrane thickness, d, was found to be linearly correlated to the electrospin time, t, with a relationship 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 carryout out at room temperature.

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 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 the hard support layers for easy handling of the devices and uniform application of forces on the devices for tests as all the TENG materials were flexible. As the PET plates were screened off by the metal electrodes, they play no role in the electrical properties of the BD-TENG. The effective device size is 4 × 4 cm^2 for all the devices characterized unless specifically stated.

2.4. Characterization setup

The vertical contact-separation mode was chosen for our BD-TENGs. A dynamic fatigue tester (Popwil Model YPS-1) with a motional arm