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Full paper

Realizing the potential of polyethylene oxide as new positive tribo-material: Over 40 W/m^2 high power flat surface triboelectric nanogenerators

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ABSTRACT

The on-going research into the negative tribo-materials has led to significant improvements in the performance of triboelectric nanogenerators (TENGs), however, very little attention has been paid to the positive tribo-materials. This work reports on the use of poly(ethylene oxide) (PEO) as the positive tribo-material for the fabrication of TENGs and shows that PEO has much higher positive tribo-polarity than the existing choice of polyamide-6 (PA6). A 2 × 2 cm^2 TENG comprising of spin-coated flat PEO and polydimethylsiloxane (PDMS) films produces a voltage of up to 970 V, a current density of 85 mAm^{-2}, and a power of ~ 40 W m^{-2} under a 50 N contact force. Comparatively, the PA6/PDMS TENG only produces 630 V, 30 mAm^{-2}, and a power of ~ 18 W m^{-2}, showing the remarkable property of the PEO as the positive tribo-material. The results are further supported by the contact potential difference between PEO (1.26 V) and PA6 (0.87 V) obtained using Kelvin Probe Force Microscopy. Furthermore, the triboelectric behavior of PEO is explained in the context of the positively charged oxygen functional groups and the lower work function of PEO as compared to PA6. The work thus expands the current portfolio of materials used for triboelectric nanogenerators with great prospects.

1. Introduction

With the development of intelligent electronic devices, such as smart portable/wearable devices, wireless sensor networks and so on, renewable and sustainable power sources, that can be utilized to build battery-free systems, are becoming increasingly important. Since the power consumption of these electronic systems is of hundreds of microwatts to tens of milliwatt levels, it is possible to power these electronic systems by harvesting ubiquitous ambient small-scale waste mechanical energy. Microgenerators based on piezoelectric [1–3], electromagnetic [4] and pyroelectric [5] effects have been intensively studied and exploited for such applications. Triboelectric nanogenerators (TENGs), invented by Wang et al. in 2012 [6], can convert the available mechanical energy such as vibration [7], wind [8,9] and waves [10,11] into usable electrical energy, have gained great attention since then owing to their very high power output, excellent energy conversion efficiency and cost-effectiveness.

The TENGs have three basic operating modes: two electrode contact [12], single electrode contact [13] and sliding modes [14], with the first one being the preferred one owing to its simple architecture and high performance. The contact mode TENGs typically consist of two insulators with electric polarities far apart in the triboelectric series [15], *i.e.* upon contact and subsequent separation, one material has a high ability to donate electrons (hereafter called as the positive tribo-material), while the other material has a high ability to gain electrons (called as the negative tribo-material). Current efforts for the development of TENG technology mainly focus on the enhancement of the output power *via* an increase in the surface charge density. To this effect, the recent approaches have relied on: (i) judicious selection of triboelectric materials, (ii) modification of tribo-materials, for instance, surface patterning with micro-/nano-structures [16], chemical surface functionalization [17], and nanoparticles-filled or pore-formed polymers [18–20], (iii) charge injection [21] or use of polarized piezoelectric nanomaterials [22], and (iv) use of hybrid structures, such as piezoelectric/triboelectric structures [23], solar cell/triboelectric structure [24], and electromagnetic/triboelectric structures [25]. Of all the above mentioned methods, except for the judicious use of materials, the rest of the methods rely on time-consuming, complicated processes

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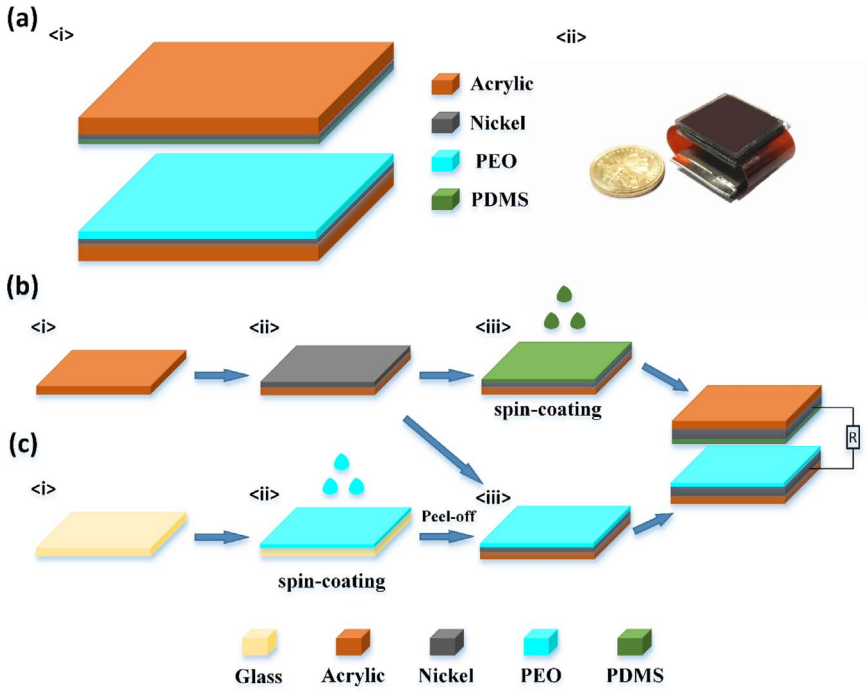

Fig. 1. Device structure, photo image and fabrication process of the TENG using PEO and PDMS films as the positive and negative tribo-materials, respectively. (a) Schematic diagram and a photo of the fabricated device, showing the structural design of the TENG, (b) and (c) fabrication flowchart for PDMS and PEO films, respectively.

or structures, and/or use expensive equipment, and thereby lead to an increase in the cost of the TENGs. For instance, the nano/micro-structured surfaces and injected charges tend to deteriorate with operation due to the damage to the microstructures and thus may not provide the required stability and reliability of the devices, whereas the hybrid structures have the potential for high conversion efficiency [26], but are yet to achieve satisfactory results. Consequently, the selection of the optimal materials with high electron affinity difference is the simplest and most effective way to improve the performance of TENGs, but is currently restricted by the limited choices of existing materials.

Vigorous investigations have shown that polydimethylsiloxane (PDMS), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) are among the best negative tribo-materials for high performance TENGs owing to their strong negative electron affinity [27–29]. On the contrary, not much attention has been paid to the selection of positive tribo-materials, even though they are equally important as the negative tribo-materials for enhancing the surface charge density and subsequent power density. It is clear from the triboelectric series, there are only very limited choices for positive insulator tribo-materials and mostly metals such as aluminum (Al) and copper (Cu) have been used as positive tribo-materials [30–32]. However, these metals do not rank high in triboelectric series in their ability to donate electrons. For example, flat surfaced Cu/PTFE TENG shown in the literature was shown to have a charge density of 40 μCm^{-2} only [33], much smaller than those of other reported TENGs. Several other positive triboelectric insulator materials have been employed to construct TENGs, such as silk [34], carbon nanotubes (CNTs) [35], glass [36] and polyamide-6 (PA6, Nylon) with varying degrees of success [37]. The silk/PET TENG obtained a maximum peak power density of only 10 $mW\,m^{-2}$, while the CNTs/PDMS TENG produced about 5 $W\,m^{-2}$ which was mainly attributed to the high surface area of CNT arrays [35]. Among the positive triboelectric insulator materials, PA6 is regarded as the best choice for developing high performance TENGs as it has a strong positive tribo-polarity in triboelectric series. Our earlier works utilizing PA6 as the positive tribo-material against poly(vinylidene fluoride), PVDF, was shown to perform excellently, providing an open-circuit voltage, V_{OC}, of 520 V, and a short-circuit current density, J_{SC}, of 2.7 mAm^{-2} [37]. Similarly, in this work, using PA6 against a PDMS counter-surface, the PA6/PDMS TENG was shown to provide a V_{OC} of 630 V and J_{SC} of 30 mAm^{-2} (corresponding a surface charge density of 110 μCm^{-2}), with an effective maximum peak power density of 18 $W\,m^{-2}$. It is apparent that the search for positive materials for TENGs is lagging far behind that of negative tribo-materials and thus warrants the question: is there any other low-cost material which possesses higher positive polarity for enhancing the power output and surface charge density of TENGs?

Polyethylene oxide (PEO) is a synthetic, low-cost commodity polymer which is also bio-compatible and water-soluble [38]. Here, we report for the first time on the use of pristine PEO films as the positive tribo-material to fabricate high performance TENGs in combination with PDMS. Relying on a simple spin-coating process without the added complication of micro/nano-fabrication process, we demonstrate PEO/PDMS TENGs with a peak-to-peak V_{OC} of 970 V, a J_{SC} of 85 mAm^{-2} (corresponding a charge density of 154 μCm^{-2}), and a peak power density of $\sim$ 40 $W\,m^{-2}$, significantly higher than those of CNTs/PDMS and PA6/PDMS TENGs, and is one of the best performances reported yet for TENGs comprising of pristine flat membrane structures. The higher positive electronic affinity of the PEO films as compared to that of PA6 is further verified by Kelvin probe force microscopy (KPFM), wherein the contact potential difference (CPD) values for PEO and PA6 are 1.26 V and 0.87 V, respectively. And the voltage and current density of the PEO/PDMS TENG increase with the increase in contact force, movement frequency and spacer distance. Considering the desirable properties of water solubility and bio-compatibility, we believe that the PEO based TENG devices have broad application prospects in implantable and bio-compatible electronic devices besides their use as high performance energy harvesters for conventional portable electronics.

2. Fabrication and experimental setup

2.1. Fabrication of triboelectric nanogenerators

The physical structure (i) and the photo image (ii) of the contact-mode TENG are shown in Fig. 1(a), with the fabrication processes for PEO and PDMS films described in Fig. 1(b) and (c), respectively. Two pieces of acrylic (2 cm × 2 cm × 0.1 cm) plates were used as the substrates onto which a conductive, adhesive nickel (Ni) tape was glued