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RAPID COMMUNICATION

Base-treated polydimethylsiloxane surfaces as enhanced triboelectric nanogenerators

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Abstract
Due to its flexibility, transparency, easy fabrication, and high negative polarity, polydimethylsiloxane (PDMS) has been considered as one of the most appropriate materials for the use in triboelectric nanogenerator (TENG) applications. Here, we report the significantly enhanced triboelectric surface charge of PDMS simply by sprinkling of NaOH solution. Fresh PDMS-based TENGs generated an open-circuit voltage of 3.8 V and a closed-circuit current of 65 nA after the contact/separation from an indium tin oxide (ITO) electrode. After sprinkling the PDMS surface with 1 M NaOH, in contrast, the resulting TENG generated voltage of 10.4 V and current of 179 nA. Exposing the PDMS to ultraviolet-ozone prior to sprinkling with NaOH solution resulted in a triboelectric voltage and current of 49.3 V and 1.16 μA, respectively, which are almost 15-fold larger than those of fresh PDMS. The origin of the enhanced triboelectric charge is related with an increase of polar Si-O bonds at the expense of non-polar Si-CH_3 bonds in PDMS. This work demonstrates a cost-effective method for producing large-area and high-efficiency PDMS-based TENGs and helps clarify the triboelectric mechanism of PDMS.

Introduction

Among the various alternative environmental energy sources, motion-based mechanical energy is abundant, ubiquitous, and more accessible than solar and thermal energy [1,2]. While the amount of energy harvested from

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mechanical vibrations is relatively small, the greatly reduced power consumption of modern devices allows it to replace or at least supplement traditional batteries [3]. There have been numerous works to increase the conversion efficiency through prudent choice of appropriate one-dimensional nano-materials [4-7] and by optimizing existing device structures [8-11].

In 2012, Dr. Wang group at Georgia Institute of Technology invented a new means of converting mechanical energy into electricity based on triboelectrification and electrostatic induction [12]. Compared with piezoelectric nanogenerators, triboelectric nanogenerators (TENGs) are more cost-effective, generate more power, and are easier to fabricate [13-16]. Recently, Fan et al. reported a highly transparent and flexible TENG based on a polydimethylsiloxane (PDMS) polymer and an indium tin oxide (ITO) electrode [17]. This polymer-electrode TENG exhibited a significantly enhanced triboelectric charge than polymer-polymer TENGs. Especially, they reported that ultraviolet-ozone (UVO) treated PDMS films yielded full power output without a charging step, which suggests the modification of triboelectric surfaces. To enhance the triboelectric surface charge of PDMS for application, it is quite important to develop low-cost and large-area compatible techniques and understand the triboelectric mechanism of PDMS [18].

In this communication, we report a facile method to increase the triboelectric surface charge of PDMS. Using fresh PDMS film with a prolonged curing time, we obtained a low but stable triboelectric voltage and current from the beginning of contact/separation from ITO electrode. The triboelectric charge of fresh PDMS significantly increased upon irradiation of UVO. With the extended irradiation of UVO, however, the triboelectric charge started to decrease. We found that the triboelectric charge can be further enhanced by simply sprinkling the PDMS surface with a strong base solution like NaOH after the irradiation of UVO. The NaOH and UVO treated PDMS resulted in a 15-fold increase in triboelectric charge compared with fresh PDMS. Attenuated total internal reflection and X-ray photoemission spectroscopic measurements indicated significant changes in Si-OH vibrations, the atomic ratio of O/Si, and the oxidation state of Si. These changes can be explained by a modification of Si-CH_3 bonds to Si-O bonds after UVO and NaOH treatments. The simple process of sprinkling NaOH solution onto PDMS after UVO irradiation to enhance its triboelectric charge, without losing transparency as well as flexibility, should be quite suitable for large-area and low-cost PDMS-based TENG applications.

Experimental section

Fabrication of surface-treated PDMS-based TENGs

PDMS films were fabricated using conventional spin-coating and curing methods. The PDMS elastomer and cross-linker were thoroughly mixed at a weight ratio of 10:1 and then degassed under vacuum for 30 min. A small amount of the resulting PDMS mixture was spin-coated at 500 rpm for 1 min onto commercially available ITO-coated polyethylene terephthalate (PET) substrates and cured in an oven at 100 °C for 5 h. Fresh PDMS films were exposed to UVO at a power density of 28 mW/cm^2 (AH1700, AHTECH) and then sprinkled with a 1 M solution of NaOH. To fabricate the TENGs, another ITO-coated PET substrate was used as a top electrode. Surface-treated PDMS and ITO-coated PET were attached to acryl plates and assembled with springs in such a way as to enable contact and separation with a gap size of approximately 2 mm. The effective surface area of the PDMS was 2.5 cm $\times$ 2.5 cm and 300 μm in thickness.

Characterization of the TENG

The chemical bonds of PDMS were examined using attenuated total internal reflection (ATR) Fourier transform infrared (FT-IR) spectroscopy (VERTEX 80 V, Bruker) and micro-Raman scattering at a laser excitation of 532 nm (LabRAM HR Evolution, Jobin Yvon). For the ATR measurements, small pieces of the PDMS film were cut and attached to a ZnSe crystal supporting multiple reflections of infrared light. Chemical bonds were additionally characterized by X-ray photoemission spectroscopy (XPS) using Al Kα radiation (E=1486.5 eV) (PHI 5700, Physical Electronics). The optical transmittance and surface morphology of PDMS were characterized by grating spectrophotometry (Cary5, Varian) and field-emission scanning electron microscopy (SEM) (SU 8010, Hitachi), respectively.

TENG performance was characterized using a custom mechanical system in which a linear motor was used to periodically apply and release compressive forces to the device. The pushing amplitude and frequency were fixed at 10 N and 0.16 Hz, respectively, over the course of the measurement. The output voltage and current of the TENGs were recorded by a Keithley 6517A electrometer and an SR570 low noise current amplifier from Stanford Research Systems, respectively. All electrical measurements were conducted in a Faraday cage to minimize noise.

Results and discussion

Figure 1a-(i)-(iii) illustrates the surface treatment procedure used on the PDMS films. A small amount of PDMS solution was spin-coated onto ITO-coated PET substrates and then cured for a prolonged time. The fresh PDMS polymer was exposed to UVO in air and then sprinkled with a 1 M solution of NaOH. After drying in air, the surface-treated PDMS and ITO-coated PET were attached to acryl plates and assembled into a TENG (Figure 1a-(iv)). Four springs were used to restore initial positions after contact.

The surface morphology and optical transmittance of the resulting films are shown in Figure 1b and c, respectively. Discernable differences were not observed in the surface morphology and roughness of the fresh and surface-treated PDMS films. In the visible light region, the transmittance of all three PDMS films exceeded more than 90% with a small variation of within 3%. The flexibility of fresh PDMS film was also unchanged after the surface treatments. As evidenced in the inset of Figure 1c, all three PDMS films were easily foldable.

Figure 2 compares the triboelectric power generation of fresh, UVO irradiated, and NaOH-treated PDMS-based TENGs. To directly compare, we fixed pushing amplitude and frequency and used same TENGs except PDMS. During