

Full paper

Reduced graphene-oxide acting as electron-trapping sites in the friction layer for giant triboelectric enhancement

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ARTICLE INFO

Keywords:

Reduced graphene oxide
Triboelectric nanogenerators
Triboelectric enhancement
Electron-trapping
Nanocomposites

ABSTRACT

The continuously seeking of approaches for enhancing the output of triboelectric nanogenerators (TENGs) has always been the goal of researchers attempting to harvest mechanical energy efficiently. Here a novel methodology for enhancing the output performance of the TENG by introducing electron traps into the common friction layer has been firstly developed. For this purpose, reduced graphene oxide (rGO) embedded in the friction layer has been used as electron traps. Because the triboelectric electrons generated on the surface of a polyimide layer can be efficiently captured and stored in rGO sheets due to the interaction between the rGO sheets and the polyimide layer, the loss of triboelectric electrons can be suppressed. The maximum output power density of a vertical contact-separation mode TENG containing rGO sheets reached 6.3 W/m^2 , which was 30 times larger than that of a device without rGO sheets. We also showed that the output performance of the lateral sliding-mode TENG, which is the other fundamental working mode of the TENG, can be enhanced due to the advantage of additional electron trapping in the friction layer, indicating that the concept demonstrated in this work holds potential for providing significant enhancements in next-generation triboelectric devices.

1. Introduction

Recently, triboelectric nanogenerators (TENGs), which can directly translate mechanical energy into electrical energy, have been extensively developed due to their high energy-conversion efficiency, low cost, simple structure, flexibility, and abundant choices of materials [1–3]. Energy harvesting from broadband mechanical energy sources, such as body motions, vibrations, wind flows, and ocean waves, by using TENGs has been demonstrated [4–12]. However, the performances of TENGs, including the output performance and the endurance, must be significantly improved through a rational design before the TENGs can act as practical, green power sources for large-scale application [13–15].

The output performances of TENGs rely highly on the efficiencies of the processes for triboelectric charge generation and for separating positive and negative charges. On the basis of the working principle, two routes can be typically considered for enhancing the outputs of TENGs. Appropriate friction materials with markedly different polarities can be used to increase the density of charge generated during the friction process [16–18]. The building of friction layers with a surface micro-/nano-structure and a nanoscale surface modification can also greatly increase the triboelectric charge density [19–24]. Furthermore,

the surface charge density can be enhanced by injecting ionized air [25]. Moreover, multi-layer integrations can increase the total number of electrons and simultaneously maximize the instantaneous output power [26,27]. As for the second route, effective separation of positive and negative charges is dominantly attributed to the design of the device's structure. Thus, novel structures, such as the linear grating structure, the rolling structure, and the planar structure, have been demonstrated to enhance the performances of the TENGs [28–30]. Even though various efforts have been committed, methods for integrating mature, robust technologies and cutting edge designs so as to enhance the performances of TENGs are still needed if these devices are to have future, large-scale applications.

Note that the electrons in the friction layer serve as an electrostatic induction source for the TENG's electricity generation process. Actually, once the triboelectric electrons are generated, the electron density on the surface of the friction layer will decrease gradually [31]. Thus, the loss of triboelectric electrons could decrease the potential difference between the two electrodes of the TENG. Here, we propose a superior methodology for enhancing the output performance of the TENG by introducing electron traps into the common friction layer. For that purpose, as electron traps we use reduced graphene oxide (rGO) embedded in the friction layer. A derivative of graphene, rGO consists

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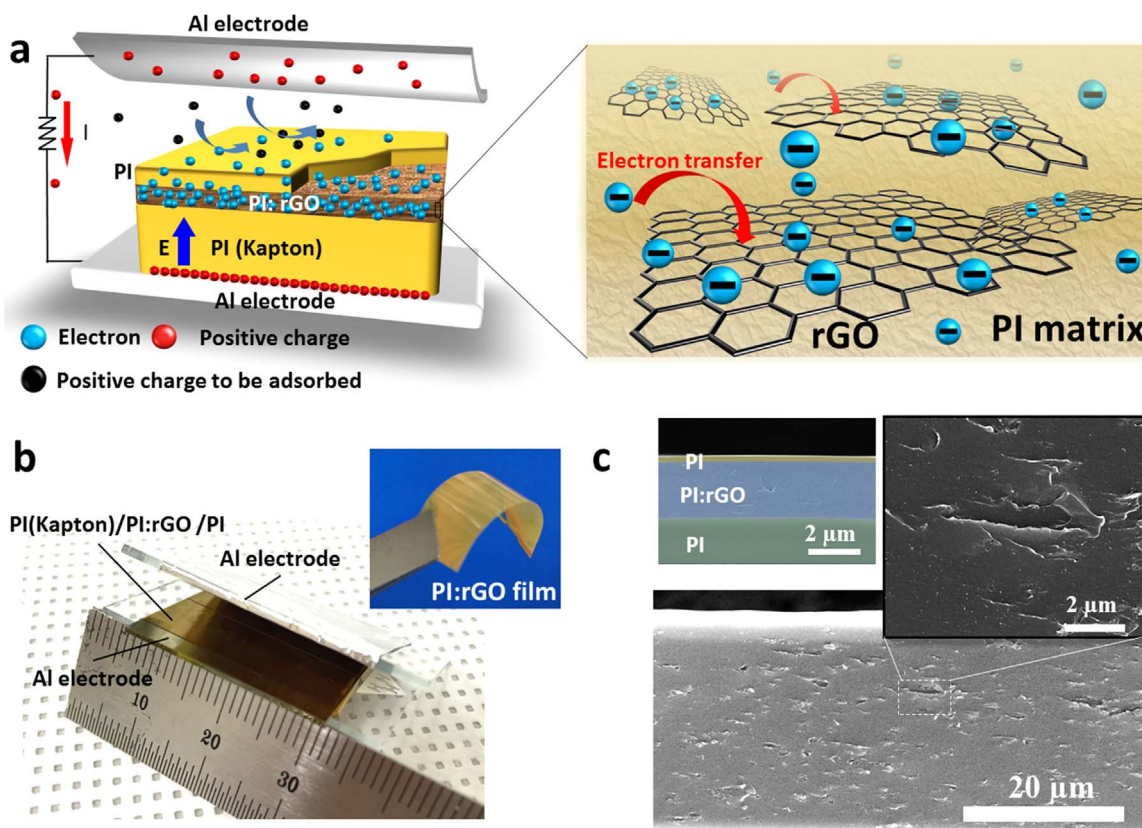


Fig. 1. Device structure. (a) Illustration of the vertical contact-separation mode TENG with a PI:rGO film. The right panel shows a schematic diagram of electron transfer from the PI layer to the rGO sheets. (b) Optical image of the vertical contact-separation mode TENG. The inset presents an optical image of the separated PI:GO layer. (c) SEM images of the PI:rGO layer. The inset presents an SEM image of the PI (Kapton)/PI:rGO/PI stacked layer.

of a hexagonal carbon network with both sp^2 - and sp^3 -hybridized carbon atoms bearing hydroxyl and epoxide functional groups on basal planes [32]. Tailoring the functional groups of rGO can modify extensively its electronic structural and chemical properties, enabling it to have various applications. Especially, we have illustrated in our previous work that rGO can efficiently capture external electrons with nonvolatile electron-trapping properties due to its unique electronic and morphologic properties [33–35]. In the case of a vertical contact-separation mode TENG with a polyimide (PI) flat film as a friction layer, by employing rGO as electron traps we showed that the maximum power density of the TENG with rGO reached 6.3 W/m^2 , which was 30 times larger than that of the device without rGO. In addition to rGO being applied in vertical contact-separation mode TENGs, we have shown that its introduction into the friction layer can enhance the performance of lateral sliding-mode TENGs, which proves that the strategy for enhancing the output performance of a TENG by introducing electron traps into the friction layer can be widely applied in the field of TENGs and triboelectric devices.

2. Experimental section

2.1. Preparation of the polyamide acid (PAA) and the PAA:GO solutions

The GO used in this experiment was prepared from purified natural graphite by using the modified Hummers method. PI, from a PAA precursor, was prepared by dissolving polyamic acid in dimethylformamide (DMF), which consisted of 287.5 mg of *p*-phenylenediamine (PDA) and 781.25 mg of biphenyltetracarboxylic dianhydride (BPDA) dissolved in 500 mL of DMF solvent. For the preparation of the PAA:GO mixture, GO sheets were added into the PAA precursor, followed by ultrasonication for 1 h. The GO sheets were uniformly dispersed in the PAA precursor.

2.2. Fabrication of TENG

To fabricate the negative friction layer of the TENG, an Al film, acting as an electrode, was deposited on the surface of a glass substrate by using thermal evaporation. The PAA:GO film was deposited on the surface of the PI (Kapton) film by using the spin-coating method and was baked at $135 \text{ }^\circ\text{C}$ for 30 min to evaporate the solvent. Then, another PAA layer was spin-coated onto the surface of the as-prepared PAA:GO layer. After the amination treatment at $400 \text{ }^\circ\text{C}$ for 2 h, the GO sheets were reduced to rGO sheets, and the PI:rGO hybrid layer was obtained. Then, the PI (Kapton)/PI:rGO/PI stacked layer adhered to the surface of the as-fabricated Al electrode. The positive friction layer was composed of a glass substrate with a piece of Al foil affixed to its surface. The positive friction layer was supported by a spring of 10 mm in thickness, which served as a spacer for the TENG. The active size of the TENG was $1.5 \text{ cm} \times 2.5 \text{ cm}$. For the lateral-sliding mode TENG, the positive and the negative parts were kept parallel to each other. The Al surface on the top plate and the surface of the friction layer on the bottom plate were in intimate contact.

2.3. Characterization and electrical measurement

Scanning electron microscopy (SEM, NOVA nanoSEM 450) was used to investigate the distribution of graphene-oxide sheets embedded in the PI layer. Fluorescence spectra of the PI and the PI:rGO films were obtained by using a HITACHI F-4600 fluorescence spectrophotometer. Fourier-transform infrared spectroscopy (FTIR) spectra of PI and PI:rGO were measured with a NICOLET 360 spectrophotometer. An oscilloscope (Tektronix TDS2024C) and a current meter (Keithley 2400) were used for measuring the output voltage and the current of the TENG. The capacitance-voltage (C - V) curves were measured by using a Keithley 4200SCS unit.

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