Research paper

A graphene nanoplatelets-based high-performance, durable triboelectric nanogenerator for harvesting the energy of human motion

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ABSTRACT

Triboelectric nanogenerators (TENGs) have been widely investigated to harness mechanical energy that is driven by repetitive human motion. Conventional human motion-driven TENGs are mostly based on contact–separation (CS) mode, but their energy harvesting performance is limited due to the high crest factor (the ratio of the peak to the RMS value of output voltage). Here, we demonstrate a new rolling type triboelectric nanogenerator (RL-TENG), exhibiting the lower crest factor than CS mode TENGs, using a metal layer and graphene nanoplatelets-doped PDMS. These additions helped improve the dielectric constant and the charge storage capacity of the TENG, which led to a high electrical output while minimizing surface damage. As compared to a pristine TENG, our device, a RL-TENG, generated an open-circuit peak voltage of 75.2 V, which was almost 15 times higher than that of the pristine device, and a short-circuit peak current of 7.36 \(\mu\)A, which was 12 times higher. With a dual-side double-belt TENG (DB-TENG), these values were improved to 164 V and 10 \(\mu\)A. Lastly, our device was used in a real-life application, to harvest mechanical energy from the movement of the human elbow while walking, and was able to produce a high voltage output of up to 821 V. These results show that the DB-TENG can be used for high-efficiency harvesting of energy from human motion.

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1. Introduction

The development of portable nanogenerators (NGs) offers a possible solution to the problem of the increasing power consumption of electronic devices (Cheng et al., 2019; Kim et al., 2017a; Liu et al., 2019; Shi et al., 2019; Yoon et al., 2018). Light, compact, and durable NGs using a variety of self-powered sensors can further improve the usability of portable electronic devices and significantly influence the expansion of Internet-of-Things technology (Shi et al., 2017; Shih et al., 2010; Wang et al., 2013; Zhang et al., 2020). Amongst several competitive candidates, the power generation efficiencies of triboelectric NGs (TENGs), based on their advantages of diversity in material selection and simple structure, have undergone rapid development in a very short time (Harnchana et al., 2018; Stanford et al., 2019; Wu et al., 2017; Xia et al., 2017b). Moreover, they are actively being studied not only as power sources but also as sensors to measure or detect various physical quantities (Meng et al., 2017; Shabbir et al., 2021; Wang et al., 2019, 2020b; Yoon et al., 2021). TENGs can harvest energy from various types of repetitive motions by using inter-surface interactions between two contact surfaces to produce a charge in the TENG, allowing it to generate a current. However, because the use of such a device is repetitive, the surfaces of the device may be damaged and the device’s stability and output may be decreased. Recently, research has focused has been on device-structure-oriented applications; however, still more work regarding materials is needed if a high electrical yield is to be ensured while keeping the device structure intact (He et al., 2018; Sun et al., 2020; Wang et al., 2018a,b). Thus, highly durable materials for use in TENGs as human-motion-driven sensors and energy generating materials in a compact area with a light structure need to be developed.

Although TENGs work in four modes, they can be categorized into two operational modes: the contact–separation (CS) mode
Graphene nanoplatelets (GNPs) are remarkable nanofillers and can be used to fabricate a stiff material with low interface resistance because of their great mechanical, electrical, and thermal properties (Wang et al., 2015). Being a commercially available, cheap, conducting nanofiller with excellent electrical properties, GNPs increase the dielectric constant (or relative permittivity) of the material in which they are placed (Shivakumar et al., 2019), which eventually augments the triboelectric output (Kim et al., 2021). Additionally, PDMS, being a sticky material, can be used to avoid slippage between contacting surfaces. Similarly, high output performance can be achieved using intriguing structural modifications such as origami (Wang et al., 2020a), gratings (Zhu et al., 2013), and physical spacers (Yoon and Kim, 2020). Moreover, a simple addition of a back metal layer can also increase the overall electrical capabilities of the system.

Taking advantage of the good filling properties of GNPs in a PDMS matrix, the stickiness of the PDMS surface, and the great mechanical properties of the GNPs fillers along with the addition of a back metal layer, we developed a graphene-nanoparticle (GNP)-filled PDMS (PDMS:GNP) matrix that could be used in a rolling-mode TENG (RL-TENG) to generate a high triboelectric output while minimizing surface abrasion. GNPs were added to increase and optimize the electrical output by improving the dielectric constant of the PDMS friction layer. The effective permittivity was also enhanced by using a back metal layer in addition to the typical TENG structure. Both of these novel strategies have worked well to improve the tribo-electric output of the device. We fabricated a rolling belt by using PDMS with its good tribo-negative characteristics, but sticky surface, to improve the output voltage of the RL-TENG. We also fabricated a dual-belt-type TENG (DB-TENG) to confirm the possibility of expanding the RL-TENG concept and we confirmed that such a device could be used to harvest energy from the motion of the human body.

2. Experimental section

2.1. Preparation of PDMS:GNP solutions

The fabrication process for a PDMS:GNP belt is shown in Fig. 2a. GNPs dispersed in a tetrahydrofuran (THF) solvent were sonicated for 2 h to prepare a PDMS:GNP solution. Then, the solution was blended with Sylgard A (purchased from Sigma Aldrich), after which it was stirred for 30 min, and then heated in a fume hood at 60 °C to evaporate the THF solvent. The solution was evaporated for more than 12 h to remove the residual THF completely.

2.2. Fabrication of PDMS:GNP films

The already prepared GNP-doped Sylgard A solution was mixed with Sylgard B in a weight ratio of 10:1. The mixture was placed in a vacuum chamber for 30 min to remove bubbles. Then, the bubble-free mixed solution was bar-coated on a UV/O3 treated aluminum (Al)/polyethylene (PE) film by using a Meyer bar #10. Later, it was placed in the atmosphere for 10 min to remove the fine bubbles on the surface and was then treated thermally on a hot plate at 100 °C for 1 h. After the PDMS:GNP layer had been coated on the PE substrate, an UV/O3 treatment was performed for 6 h to improve adhesion to the PDMS surface. Then, an intrinsic PDMS layer was bar-coated on the PDMS:GNP layer and treated thermally at 100 °C for 1 h.
2.3. Measurements of electrical characteristics

The voltage generated in the fabricated TENG was measured using an oscilloscope (TDS 2024C, Tektronix). The current was converted into a voltage by using a voltage–current conversion amplifier (DLPCA-200, Femto) and then measured by using the oscilloscope. An Arduino-based measurement unit composed of a step motor, a driving belt, and a control circuit was fabricated to investigate the repetitive driving characteristics of the TENGs. Scanning electron microscopy (SEM) (NOVANANOSEM 450, FEI) images were taken before and after repeated cycles of the RL-TENG to investigate the change in the surface of the friction layer. The TENG output was rectified and connected to an electrolytic condenser, and an electrometer (DMM7510, Keithley) was used to measure the voltage change to investigate the charge generation and capacitor-charging characteristics of the TENG.

2.4. Material characterization

The crystallinity of the material was measured using a high-resolution X-ray diffractometer (Bruker D8 ADVANCE). Scanning parameters were 40 kV, 40 mA, and CuK$\alpha$ radiation at 0.154060 nm. Samples were scanned at a scan speed time of 0.35 s per step over a 2θ range from 10 to 50 degrees with a step size of 0.02 degrees. The relative permittivity of PDMS:GNP was measured by capacitance–voltage (C–V) curves using an LCR meter (Keysight E4980A).

3. Results and discussion

PDMS:GNP was synthesized by doping pristine PDMS with two-dimensional GNPs. (Fig. A1) Fig. 2b shows the molecular structure of PDMS:GNP. The repetitive and layered structure of GNP helps improve the overall crystallinity of the material. An XRD analysis of both materials showed that the GNPs had a significant effect (Fig. 1c). The addition of the GNPs to the PDMS increased the intensities of two PDMS peaks at 12 and 26 degrees, which demonstrated that the crystallinity of the doped PDMS had increased in those specific planes. In a previous work, we established that the electrical performances of triboelectric generators were enhanced by the introduction of a dielectric material with high crystallinity (Kim et al., 2017c).

The basic schematic for a multi-layered RL-TENG that can harness an input mechanical energy is illustrated in Fig. 3a. The structure consists of three components: (1) a tribo-negative layer made of conjoined thin films, (2) an aluminum (Al) thin film used as electrodes which also doubles as a tribo-positive layer, and (3) an acrylonitrile butadiene styrene (ABS) substrate to support the overall structure. In this design, a rollable tribo-negative layer moves over the Al electrodes with a rolling frequency of 2 Hz to produce a continuous electrical output based on a repetitive mechanical energy input driven by a horizontal oscillator. This motion resembles to the rolling movement of a car’s tires over a road. The Al electrodes were electrically connected via a load resistance to measure the voltage and the current generated by the device while operating. An actual RL-TENG is shown in Fig. 3b. In the RL-TENG device, width of tribo-negative layer is 30 mm which provides total surface contact area as 7.8 cm$^2$. AFM is used to measure surface roughness of Al electrode (65.40 nm) and PDMS layer (1.15 nm), as shown in the Fig. A2.

Various combinations of films can be used in the tribo-negative layer to produce an electrical output, as shown in Fig. 3c. 100 $\mu$m Polyethylene (PE) is selected as a substrate for the tribo-negative layer. Initially, the PE layer coated with 80 $\mu$m PDMS produced peak-to-peak voltage and current values of 4.88 V and 0.59 $\mu$A, respectively, but the addition of a 50 $\mu$m Al back metal layer between the PDMS and the PE increased those output values to 50.4 V and 5.68 $\mu$A. The back metal layer provided a structure...

Fig. 3. (a) Schematic of the RL-TENG. (b) Actual image of the RL-TENG. (c) Various compositions of the tribo-negative layer in the RL-TENG and their corresponding open-circuit voltage and short-circuit current outputs. (d) FEM simulation results showing the electric potential distribution for various compositions of the tribo-negative layer in the RL-TENG.

capable of indirectly enhancing the permittivity by increasing the polarization of the electric field inside the dielectric material, as shown in Fig. A3. The addition of a metal layer into PDMS and PE also creates a laminated polymer/metal composite material with a high dielectric constant and a low dielectric loss (Feng et al., 2018) that eventually improves the charge storage capacity and the triboelectric output. The capacitance of the RL-TENG can be calculated using the following equation (Niu and Wang, 2014):

$$ C_{RL} = \frac{\varepsilon_0 \varepsilon_r l}{d} \left( 1 - x \right), \quad (1) $$

where $\varepsilon_0$, $w$, $l$, $x$, and $d$ are the vacuum permittivity, vertical separation distance, length of the dielectric, lateral separation distance, and thickness of the dielectric film, respectively. Adding a metal back layer increases the overall permittivity of the structure due to the infinite permittivity of Al. Eq. (1) clearly shows that this rise in permittivity leads to enhanced charge storage in the dielectric material, which improves the performance of the TENG.

The electrical output is further increased when the 0.1 wt% PDMS (PDMS:GNP) is placed between Al back layer and the PDMS, as shown by the 75.2 V voltage and 7.36 µA current. When compared with original PE/PDMS structure, this final highly efficient structure produces a factor of 15 increase in the voltage and a factor of 12 increase in current due to the combined effect of GNP doping and the metal back layer. When the number of GNPs contained in the PDMS layer was increased, the effective permittivity of the PDMS layer increased, and more charges were induced in the Al layer. If the conducting nanoparticles, GNPs, are assumed to be perfect spheres when added to a dielectric film, PDMS, the equivalent capacitance can be calculated using the following equation (Xia et al., 2017a):

$$ C_{eq} = \frac{\varepsilon_0 \varepsilon_r S d}{2} + \varepsilon_0 \varepsilon_r m \pi (a/2)^2 \left( \frac{1}{d - na} - \frac{1}{d} \right), \quad (2) $$

where $\varepsilon_0$, $\varepsilon_r$, $S$, and $d$ are the vacuum permittivity, relative permittivity, electrode surface area, and thickness of the dielectric film, respectively. The terms $m$ and $n$ represent the number of GNPs in a single layer and the number of GNP layers in the dielectric film, respectively. The diameter of the GNPs is denoted by $a$. It is evident from Eq. (2) that increasing the number of GNPs will improve the capacitance of the device by simply increasing the energy storage capacity to generate a high electrical output.

The RL-TENG device is equipped with two ABS rollers, as shown in an exaggerated view in Fig. A4. Due to the triboelectric difference between the two materials ABS ($\alpha: -0.96 \mu C/m^2$) and PE ($\alpha: -0.63 \mu C/m^2$) (Zou et al., 2019), surface charge will be generated once the two materials come into contact with each other. However, we added a back metal layer (red-colored in fig. A4) that produces an electrostatic shielding effect (Celozzi et al., 2008) to prevent electrical interference between the ABS/PE interface and the PDMS/Al electrode interface.

We used FEM (Finite Element Method) simulations to observe the electrical potential effect of the tribo-negative layers with various compositions (Fig. 3d). We used 50 µm thick Al layers, 80 µm thick PDMS layers, and 10 mm wide PDMS:GNP layers. Furthermore, we used Al electrodes with the same thickness of 50 µm and relative permittivity values of 1.00 (Cable and Anderson, 2019) and 2.54 (Mark, 1999), for Al and PDMS, respectively. Relativity permittivity of PDMS:GNP has been measured.
as 8.00 using C–V curves. The voltage outputs from RL-TENG experimental data displayed in Fig. 3c are exploited as simulation boundary conditions for contact surfaces.

Once the basic device structure had been confirmed, further material optimization was needed to get the best result from that structure. Fig. 4 presents the results for an optimal concentration of GNP’s doped into the belt-type TENG, as well as the variations in the output voltage and the surface state of the friction layer as functions of the number of cycles of repeated motion of the tribo-negative layer of RL-TENG. The variations in the output voltage and the output current are shown in Fig. 4a, for GNP concentrations in the PDMS belt of 0.0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 wt%. The maximum peak-to-peak output voltage and current were measured as 80.8 V and 5.9 µA, respectively, at a GNP concentration of 0.1 wt%. The output voltage decreased as the GNP concentration became larger or smaller than 0.1 wt%. The rise in electrical output due to increasing GNP wt% has already been discussed. However, GNPs added at concentrations above the optimum concentration agglomerated, leading to paths for leakage current and a decreased dielectric property of the PDMS:GNP layer, as described by percolation theory (Jin et al., 2020). Therefore, even though the GNP concentration was increased, at high concentrations, the output voltage decreased with increasing GNP concentration. The voltage and current outputs for repeated electrical measurements are also shown in the fig. A5 for various concentrations of GNPs in PDMS. Fig. 4b shows the output voltage as a function of the number of cycles of repeated motion of the RL-TENG, and Fig. 4f shows SEM images of the PDMS surface before and after 16,000 cycles of that repeated motion. Under repetitive input motion, contacting surfaces show signs of wear and tear and decreased performance with the usage (Long et al., 2021). However, due to the rolling movement of RL-TENG, contacting surfaces have shown minimal damage along with steady voltage output, as shown in Fig. 4(b). These SEM images in Fig. 4(f) indicate that the contact surface of RL-TENG remained free of any significant damage even after 16,000 cycles. The peak-to-peak voltage over 16,000 cycles was 75 V when the GNP concentration in the PDMS was 0.1 wt%, and that voltage was similar to the initial voltage. Additionally, even though the motion was vigorous, no observable surface change could be seen in the SEM image magnified 3000x. The voltage and current outputs for various electrical resistances were also measured, and the results are shown in Fig. 4c. Although the voltage continues increasing with increasing resistance, the current showed a downwards trend. The overall output power tended to peak at 40 MΩ, as shown in the inset. An array of 40 red LEDs was also illuminated using the output power from a RL-TENG, as shown in Fig. 4d. Lastly, 10 µF, 100 µF, and 1000 µF capacitors were charged for 100 s to check the charging capability of the devised structure (Fig. 4e). Because the electrical output of the RL-TENG was in an alternating current (AC), a rectifying circuit was devised to light the LEDs and to charge the capacitors.

For a real-life application, we devised a structure made with a dual-side DB-TENG that could be worn to measure the levels of human walking gestures: walking, jogging, and running. The basic structure of the device (70 × 80 × 78.5 mm³) was the same as that of the previously discussed device, the only difference being that this DB-TENG had metal electrodes and tribo-negative layers on both sides of the ABS substrate (Fig. 5a). This device was easily installed on a wearable backpack for the sake of energy harvesting and signal acquisition (Fig. 5b). The motion of the elbow was used as an input mechanical energy source, as shown in Fig. 5c. Initially, the current and the voltage were measured in a standing position with casual arm movements. The resulting voltage and current were measured as 164 V and 10 µA, respectively, when at an operating at a frequency of about 1 Hz. Various forms of human motion, such as walking, jogging and running could also be distinguished with this device. Fig. 5d shows that the voltage outputs of the DB-TENG are distinctively different for walking.
jogging and running. These kinds of motion involve different frequencies and forces, thereby resulting in electrical outputs with different characteristics. Walking, jogging, and running motions generates 207 V, 492 V, and 821 V, respectively. The DB-TENG was also used to charge 10 µF, 100 µF and 1000 µF capacitors for 100 s (Fig. A.6).

In the supplementary data in Table A1, we compare our work with various other existing triboelectric solutions to harvest elbow movement (Haque et al., 2017; Peng et al., 2020; Yang et al., 2021a,b; Zhu et al., 2018). Our device has a high output voltage, as well as an additional advantage of being detachable from human body.

4. Conclusion

In summary, a wearable, high-performance, durable, rolling-type TENG (RL-TENG) was developed and characterized. The results show that such a device can be used to harvest energy from human motion and to distinguish between the various features of human walking. The mechanism underlying the RL-TENG was used to incorporate the best characteristics of CS and SL-mode TENG by decreasing the crest factor. The addition of a metal layer and the GNP doping of PDMS significantly improved the overall electrical output of the device. A high voltage of 75.2 V and a current of 7.36 µA were generated, which are almost 15 times and 12 times larger than the values for an original PDMS TENG. While producing such great results, the RL-TENG maintained its stability and for up to 16,000 cycles of repeated motion and was able to light a set of 40 red LEDs using harvested energy. Using the concept of the RL-TENG, we developed a dual-side DB-TENG that when worn on a backpack was able to harvest energy of up to 821 V and to distinguish among human walking, jogging, and running. The result of this research indicates that such devices, RL- and DB-TENG, can be used for high-voltage but low crest factor applications in harsh working environments.

CRediT authorship contribution statement


Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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