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Original article

Performance enhancement of triboelectric nanogenerator using iodine doped PVDF

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ABSTRACT Because of the rapid improvement of energy collecting technologies, unique mechanical devices have been created. As a result of the energy problems, however, researchers began to create new procedures and strategies for storing as much energy as feasible. Nanotechnology is unique, and it spurred the invention of Triboelectric Nanogenerators (TENGs), which are employed as a source of energy in wearables by transforming mechanical energy into electrical energy. This article discusses TENG, which is a triboelectric material made from Polyvinylidene fluoride (PVDF) and aluminium (Al). TENG may be made in two ways: with PVDF alone or with iodine doped PVDF, with Al staying the same in the both cases. Despite the fact that the materials are triboelectric, aluminium electrodes are utilised to attach to the materials, which are created on a plastic substrate using a thermal evaporator and taped together. The existence of PVDF was verified by the Fourier transform infrared spectroscopy (FTIR) examinations, which revealed high absorption peaks at 723 cm^{-1} and 849 cm^{-1}, respectively. The digital storage oscilloscope (DSO) and pico- ammeter (10–12 m) measurements of the TENG device's output voltage and current yielded results of 25V and 8 pA, respectively. Additionally, this study reveals the power density produced and the distinctiveness of this TENG device, both of which are critical to the efficiency and applicability of TENG in a new generation of electronics.

KEYWORDS doping, iodine, Polyvinylidene fluoride (PVDF), Polyethylene terephthalate (PET), Triboelectric Nanogenerator (TENG).

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1. Introduction

The development of technology throughout many spheres of existence has enhanced man's creativity in several ways. Despite the advancements, there are still some concerns, one of which is the energy crisis, which has led to several environmental issues. The topic of renewable energy is therefore the subject of many researches. One of the most prevalent and plentiful forms of energy, mechanical energy is employed in practically all activities. With a capacity of up to 500W/m^2, the Nano generator is a tool used to convert mechanical energy into electrical energy on a smaller scale. Fig. 1 demonstrates the block diagram of the triboelectric nanogenerator.

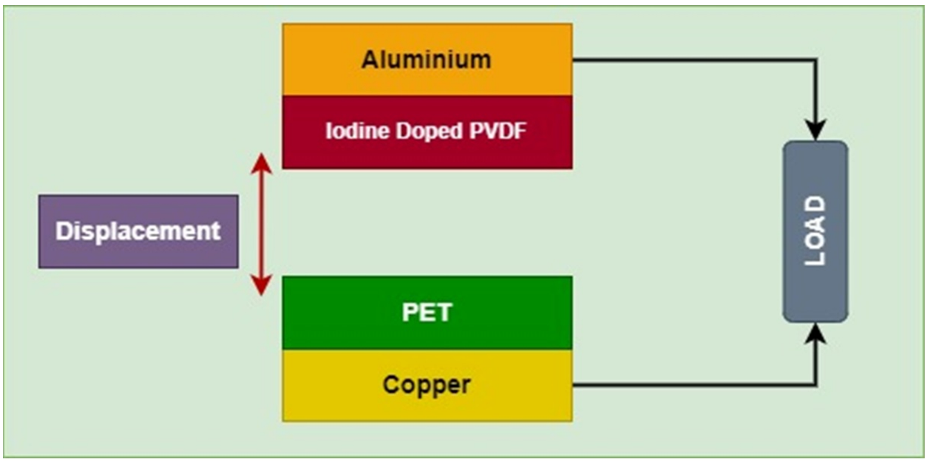

FIG. 1. Triboelectric nanogenerator setup with iodine doped PVDF and PET with aluminium and copper as electrodes

Two triboelectric materials are used in this generator, and they are brought into contact via charge transfer between their two layers. Material selection is critical in triboelectric materials. The TENG in this gadget is made up of two materials. The first is a polar material, whereas the second is non-polar. PVDF is one such non-polar material that is used, and it is recognised as the best polymer in the energy yielding sector because to its strong piezoelectric response, remarkable flexibility, and superior mechanical and ferroelectric properties [1, 2]. Aluminium (Al) is another substance that is recyclable, colourless, semi-crystalline resin, flexible, and present in its natural state. This work demonstrates the fabrication of a triboelectric Nanogenerator using PVDF and PET as triboelectric layers. Second, the focus of this study is on the layer-by-layer manufacturing of PVDF doped with iodine and PET [3,4]. Because of its charge transfer capability, iodine doped PVDF contributes significantly to higher output power when compared to other doping materials. PVDF is a semi-crystalline, high thermoplastic fluropolymer that can withstand temperatures of up to 1500 °C and has strong mechanical, piezoelectric, and pyroelectric characteristics for increased processability. It is created by the synthesis of 1, 1-difluroethylene (CH_2-CF_2). This occurs in emulsion or suspension form at 10–1500 °C and 10–300 atm pressure. It is then converted into film sheets. PVDF has the property of being roughly 50% amorphous. The majority of PVDF units are connected head to tail, with only a small number of monomers attached head-to-head.

The phases α, β, γ and δ configurations are the four potential configurations. Because all of the dipoles are aligned in the same direction with regard to the PVDF phase, the carbon-fluorine bonds are polar and have large dipole moment. Although the melting point is low, the temperature under load during heat deflection is quite high. Low permeation is caused by the PVDF's high surface tension and high crystallinity. When exposed to heat or flame, PVDF does not burn or leak, demonstrating its excellent resistance to ultraviolet (UV) radiation. As previously said, another material is PET, thermoplastic polymer, which is well recognised for its superior mechanical, thermal, and chemical property combinations, also known as dimensional stability. PET is a widely recycled polymer. Recycled PET is transformed into fibre, textiles, and sheets for use in packaging and the production of vehicle parts. In its natural condition, it is a flexible, colourless, semi-crystalline resin with high dimensional stability, impact resistance, moistures, solvents, and alcohols. PET is employed because it promotes strength and is extremely strong and light in weight, which increases energy density. It is created from the condensation reaction of monomers acquired using any of the following techniques.

a) Esterification between terephthalic acid and ethylene glycol.

b) Trans-esterification between glycol and dimethyl terephthalate.

Kise et al. [5] experimented with dehydrofluorinating PVDF powder and films, and the results indicated that iodine doping increased electrical conductivity and even caused anisotropy to be seen. The linear slope may be seen in the conductivity temperature dependency. Increased iodine doping results in higher conductivities. As a dehydrofluorinated material, the doping of iodine on PVDF film doesn't show a significant improvement in conductivity [5]. Lee et al. [10] exhibited PVDF as a functional material in TENG that may also be utilised for deicing self-powered sensors. PVDF is a non-polar triboelectric material/polymer that functions as one of the layers of TENG [6]. Despite its numerous benefits, PVDF is notable for its high dipole mobility in its phase, strong formability, and flexibility. The dielectric constant increases as the charge density of the substance increases. Work functions and dielectric constants are kept as high as possible. The dielectric constant is high because PVDF belongs to the fluorine functional groups, which have a strong electron affinity, which boosts the charge accepting properties. When the TENG is pointing forward, the dipole movement increases. Garcia et al. [7] demonstrated TENG as a self-energizing impact sensor. TENG is used to transform mechanical energy from the surrounding environment into electrical energy via the triboelectric effect [7]. Because the electrical reaction from the TENG is precisely proportional to the mechanical motion, it is employed as a power activate sensor. TENG is made by sandwiching PVDF and PVP between copper electrodes, and PET is employed as the wrapping material. A drop ball test is used to measure the impact of electrical conductivity, which determined that the greater the drop height, the larger the sensor's velocity and impact energy. Madhuri et el. [8] exhibited the impacts of iodine on the structural morphology and physical characteristics of manganese phthalocyanine thin films, as the doping is done using Iodine and it is a halide group that includes ions and they are doped to modify the material's properties [8]. In terms of magnetic and electrical characteristics, semiconductor properties are changed. They alter the structure of molecular packing. Physical characteristics may also be connected. There is a shift in optical properties owing to iodine, indicating the creation of distinct polymorphs due to structural alterations. The structural characteristics of the film are also altered when the iodine doping concentration increases, resulting in a decrease in crystallinity and an increase in amorphous nature. Magnetic characteristics are also altered because they disrupt interchain reactions by reducing magnetic saturation, which disrupts molecular stack order. However, iodine improves electrical characteristics by increasing electrical conductivity.

Zhu et al. investigated the performance of grapheme films steam doped with iodine for electrochemical capacitive energy storage [9]. This study showed that iodine is an efficient p-type dopant that increased the material's electrical conductivity while also exhibiting strong cyclic stability and favourable electrochemical stability. Lee et al. described a TENG device that could self-improve the charge density and charge accumulation speed [10]. The charge density was the measure used to describe performance in prior TENGs, however, it was limited due to air breakdown. Unlike the previous devices, this device attained a maximum charge density of 490 cm^{-2}, which is double that of a standard TENG operating in air environment. This device has higher effective charge density and improved output performance, resulting in faster charge accumulation. Bahrami et el. demonstrated the improved output of TENG in PVDF by coating printer ink. PVDF is utilised as one of the materials because of its well-known features such as ferroelectricity, piezoelectricity, and high crystallinity [11]. Since printer ink was utilised as nanofibers in PVDF by electron spin process of diverse growth rates to make PVDF PI NFs, phase is deemed to be the biggest and 88% is boosted and is noticed. These devices are well-known for being extremely efficient, self-powered gadget candidates.

Based on the research, it can be concluded that iodine doped PVDF is the most crucial factor in the device's manufacturing. Doping is a material modification technique in which one or more elements or compounds are doped with a substrate to achieve certain electrical or optical characteristics. Despite the fact that there are many different compounds, Iodine is chosen for doping because it offers few advantages in terms of ionic conductivity, charge transfer creation, high polymer charge-storing capacity, and good electrical and dielectrical characteristics.

2. Experimental

2.1. Materials and Methodology

Sigma-Aldrich provided the PVDF powder, DMF (N, N - Dimethylformamide), and acetone used to make the PVDF solution. Merck provides the PET film. Sigma-Aldrich supplies copper and aluminium adhesive tape. PVDF solution is made by dissolving PVDF power (10 wt% PVDF) in N.N Dimethylformide and acetone in a 3:2 volume ratio and stirring well. For Iodine doped PVDF solution, 6% (w/w) Iodine (I) is mixed in 3:2 volume ratios of N, N Dimethylformide and acetone, which is made and agitated until the solution is well disseminated, and then 10% PVDF powder is added.

Triboelectric Nano generators are made in two ways: PVDF without any doping and PVDF with iodine doping. Regardless of the triboelectric materials, aluminium and copper electrodes are required, with the aluminium electrode being manufactured on a plastic substrate using a thermal evaporator. This electrode is connected to PVDF, one of the TENG materials. The PVDF solution is used to spin coat the initial dielectric layer on aluminium. The second material is PET film, which serves as a second dielectric and is bonded to a copper electrode. A spacer separates the two dielectric layers. Copper wires are used to link the electrode at the receiver's end to the load. The only common feature between the first and second TENG devices is the doping of PVDF with Iodine. One triboelectric layer is Al, while the other is a PVDF layer doped with Iodine.

The fabricated nanogenerator is characterized using the Fourier transform infrared (FTIR) spectroscopy for functional bond analysis, and the output voltage of TENG devices is measured using a Digital Storage Oscilloscope (DSO), and the current output is measured using a pico-ammeter (10–12 m) and pushing tester at constant force of 33.8 N.

3. Results and discussions

Figure 2 depicts the Fourier transform infrared spectroscopy analysis on the fabricated TENG. The absorption peaks identified at 724 cm^{-1} and 849.833 cm^{-1} correspond to α crystal and β crystal shapes of PVDF, respectively. C–H stretching vibrational bonds were observed at 1021 cm^{-1}. Furthermore, the peaks observed at 1095 cm^{-1} and 1244 cm^{-1} show amorphous phase of PVDF and stretching frequency of C–F bond.

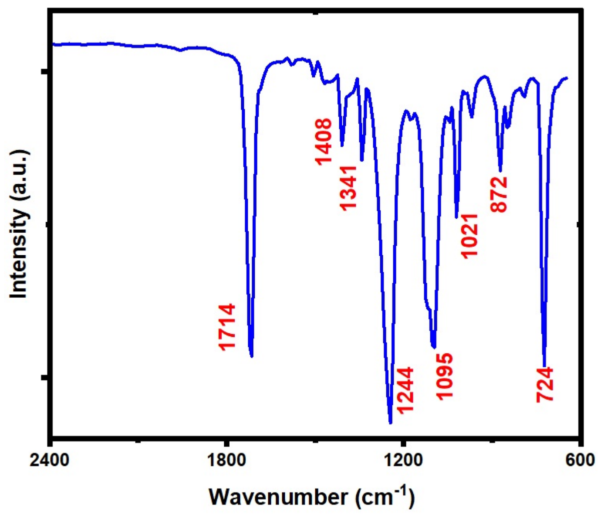

FIG. 2. FTIR spectra of the Iodine doped PVDF

A plot between resistivity and temperature of iodine doped PVDF is shown in Fig. 3a,b. The figure clearly shows that the resistivity of the constructed TENG reduces with increasing temperature with dramatical drop at 37 °C. hence, the below Fig. 3b between resistivity and temperature also suggests that the conductivity of a PVDF-based nanogenerator increases with device temperature.

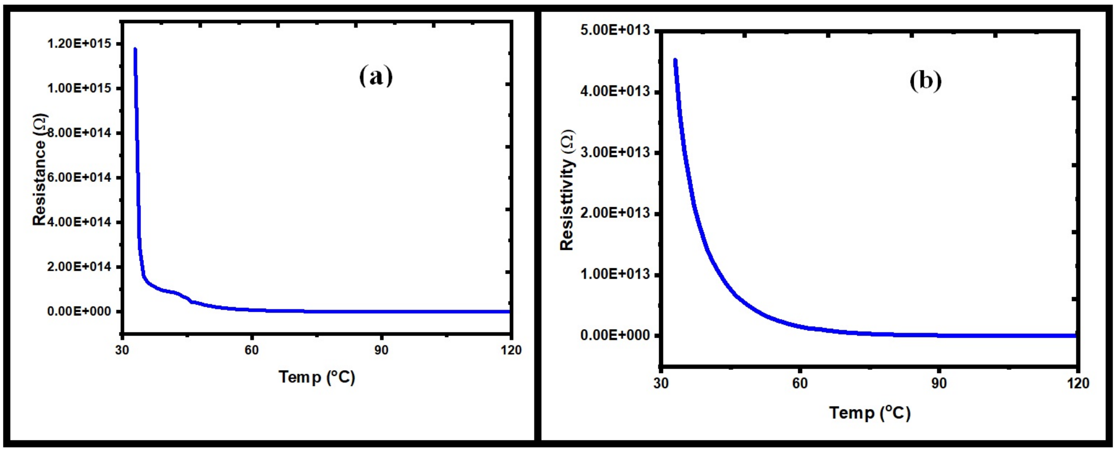

FIG. 3. The resistance (a) and resistivity (b) dependence on temperature

In this scenario, one of the triboelectric materials or layers is PVDF or iodine doped with PVDF layer, while another layer is PET. When the two layers come into contact, charges are generated on their surfaces, and when the surface separates, an electric potential is produced on the aluminium and copper electrodes. These copper and aluminium electrodes are connected to an external load. The passage of current will occur between them, resulting in a screen out of the electric field with charged surfaces created on them. A pushing tester is used to tap the surfaces back into contact. The electrode's potential difference will eventually charge, causing current to flow in the opposite direction, resulting in a continuous AC output.

Figure 4a,b depicts the open circuit voltage and current response with a force of 33.8 N on constructed TENG. The iodine-doped PVDF unit is thought to become positively charged, whereas the other component that comes into touch with PET and copper is thought to become negatively charged. When the iodine-doped sheet moves away from the TENG, an electrical potential difference develops, which forces electrons from the PVDF electrode to the copper electrode through an external circuit to offset the produced triboelectric potential. As seen in Fig. 4a this produces an alternating electrical output. Under these conditions, the TENG could produce an open circuit voltage (V_{oc}) of around 25 V and enhanced with the force applied. The undoped TENG resulted in open circuit voltage variation between 0 to 12 V, whereas in this work, when compared to the undoped, their better findings showed that iodine doping had an impact on TENG performance in terms of conductivity and output voltage [12].

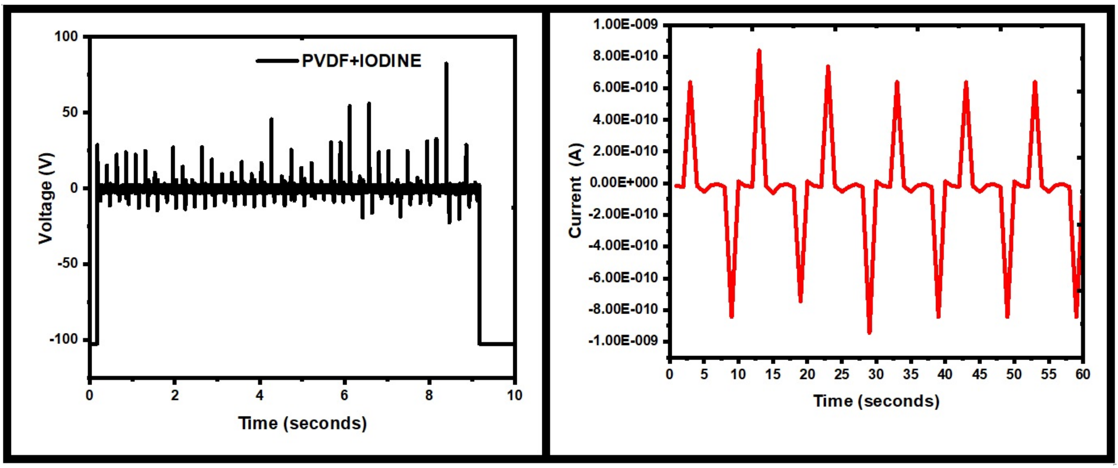

FIG. 4. Open-circuit voltage response (a) and current waveform of the TENG during press and release (b)

We also examined the TENG's current output and presented in Fig. 4b, when it was in contact with free-standing triboelectric layers constructed of iodine doped PVDF and with copper foil at a normal applied force of 33.8 N, the peak-to-peak current was approximated as 8 pA.

4. Conclusions

Finally, we demonstrated an iodine doped structural TENG that captures mechanical energy from applied force using iodine doped PVDF and PET. A free-standing triboelectric layer that moves relative to the TENG surface generates the power. The thin films are fabricated on the specified substrate using the thermal evaporation process. The proposed TENG can capture mechanical energy from a force of 33.8 N and produce a peak-to-peak current of 8 pA. As a consequence, the proposed TENG shows promise as a power source for variable devices and has the potential to be developed to a wide range of other applications.

References

[1] Tayyab M., Wang J., Wang J., Maksutoglu M., Yu H., Sun G., Yildiz F., Eginligil M., Huang W. Enhanced output in polyvinylidene fluoride nanofibers based triboelectric nanogenerator by using printer ink as nano-fillers. *Nano Energy*, 2020, **77**, P. 105178.

[2] Cheng L., Xu Q., Zheng Y. A self-improving triboelectric nanogenerator with improved charge density and increased charge accumulation speed. *Nature Communications*, 2018, **9**, P. 3773.

[3] Bazaka K., Jacob M. Effects of Iodine Doping on Optoelectronic and Chemical Properties of Polyterpenol Thin Films. *Nanomaterials*, 2017, **7**(1), P. 11.

[4] Harold O. Lee III, Sam-Shajing Sun. Properties and mechanisms of iodine doped of P3HT and P3HT/PCBM composites. *AIMS Materials Science*, 2018, **5**(3), P. 479–493.

[5] Kise H., Ogata H., Nakata M. Angewandte Makromolekulare Chemie. 1989, **168**(1), P. 205–216.

[6] Lee J., Lee J., Baik J. The Progress of PVDF as a Functional Material for Triboelectric Nanogenerators and Self-Powered Sensors. *Micromachines*, 2018, **9**(10), P. 532.

[7] Garcia C., Trendafilova I., De Villoria R.G., Del Rho J.S. Triboelectric nanogenerator as self-powered impact sensor. *MATEC Web of Conferences*, 2018, **148**, P. 14005.

[8] Madhuri P.K., Santra P.K., Bertram F., John N.S. Current Mapping of Lead Phthalocyanine Thin Films in the Presence of Gaseous Dopants. *Physical Chemistry Chemical Physics*, 2019, **21**, P. 22955–22965.

[9] Zhu Y., Ye X., Jiang H., Wang L., Zhao P., Yue Z., Jia C. Iodine-steam doped graphene films for high-performance electrochemical capacitive energy storage. *Journal of Power Sources*, 2018, **400**, P. 605–612.

[10] Lee J., Lee J., Baik J. The Progress of PVDF as a Functional Material for Triboelectric Nanogenerators and Self-Powered Sensors. *Micromachines*, 2018, **9**(10), P. 532.

[11] Bahrami S., Yaftian M.R., Najvak P., Dolatyari L., Shayani-Jam H., Kolev S.D. PVDF-HFP based polymer inclusion membranes containing Cyphos§IL 101 and Aliquat§336 for the removal of Cr(VI) from sulfate solutions. *Separation and Purification Technology*, 2020, **250**, P. 117251.

[12] Wang Y., Yang Y., Wang Z.L. Triboelectric nanogenerators as flexible power sources. *Npj Flexible Electronics*, 2017, **1**, article 10.

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