



Recent Trends in Flexible Nanogenerators: A review

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Abstract

Harvesting energy from environment presents a remarkable practical way to supply energy for smart self-powered advanced devices such as remote sensing devices, wireless networks, biomedical and wearable devices. A nanogenerator converting mechanical/thermal energy into electricity is an interesting emerging technology since it produces energy from environment. The nanogenerators have different energy production approaches about which many significant studies are going on. In recent years, technological and scientific researches have been focused on flexible devices to increase the application fields. Besides, increasing work on nanogenerators showed that providing flexibility to these devices will contribute to producing more ergonomic smart systems. The devices, which are capable to be used in textile, medical, mechanical etc. industries are also designed especially in academic studies. In this review, recent trends in the field of flexible nanogenerators were presented by demonstrating new potential applications in different areas.



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Introduction

Ongoing national and international problems related to production, transportation, usage and conservation of energy and increasing serious environmental problems caused by use of conventional energy resources like fossil fuels etc. threaten sustainable development of modern life. Implementing stabilized, enduring and innovative energy policies is important for economic and social development in worldwide. Renewable energy technologies such as

hydropower, geothermal, wind, and solar energies are clean sources of energy and have a much lower environmental impact than conventional energy technologies as well as play an important role in reducing greenhouse gas emissions causing global warming.

On the other hand, with the growing development of nanotechnology-based devices, researchers and companies have concerns about power supply. Since

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especially micro/nano scale devices or systems become more important in wearable and implantable devices, power providers came to the agenda. Furthermore, self-powered and sustainable devices are preferred than the systems with conventional batteries.

In recent years, nanogenerators have attracted considerable great attention, since those devices are able to produce low-cost, clean, efficient and sustainable energy by harvesting energy from environment¹. Nanogenerators are structures that convert mechanical or thermal energy into electrical energy with small physical interactions². In addition, these devices are very convenient to build a system that generates their own energy when integrated into functional devices thanks to their nano/micro dimensions³.

Flexible Nanogenerators for Energy Harvesting

Nanogenerators mainly use three type approaches including triboelectric, piezoelectric and pyroelectric. Nanogenerators have added a new dimension to the principles of converting mechanical energy into electrical energy using piezoelectric and triboelectric effects. Additionally, some devices used to convert thermal energy into electricity with pyroelectric effect. It was reported that the piezoelectric systems perform better than triboelectric ones⁴.

There is a trend on nanogenerator researches; provide flexible property on these devices. Waste energy usually goes to be waste as multi-axially due to nature of waste mechanical energy. For example, joint, knee, finger movements; centrifugal force, stretching and compressing movement on mechanics are most common examples for multi-axial waste energy. Nanogenerators that is aiming to capture this multi-axial mechanical energy should be flexible.

Polymers, due to their stretchable characteristic and mechanical stability are preferred to produce nanogenerators. Polymers are used by two ways on nanogenerators. The first; polymers have been used as matrix in nanocomposite generators. The second way; piezoelectric polymers have been used to produce polymeric flexible nanogenerators⁵. Highest output values are approximately 500 V and 5.3 mA

for triboelectric nanogenerators⁶; 200 V and 1.5 μ A for piezoelectric nanogenerators⁷.

Piezoelectric Nanogenerators (PENGs)

When a piezoelectric material is subjected to a mechanical action, the net positive and net negative charges resulting from the collection of the load carriers on their surface will provide an electrical stress (Figure 1). Similarly, when a piezoelectric material is subjected to electrical voltage change, it deforms mechanically⁸. The piezoelectric effect is usually defect in crystal structures due to a molecular symmetric centre. It is evident that the piezoelectric effect is observed by means of opposing poles deposited in amorphous regions in polymers⁹.

Besides, the electronic differences of the atoms in the polymer chains cause the piezoelectric effect. Fukada, for example, explained in 1974 that he observed the piezoelectric effect in biopolymers, both in the form of β and in the form of α -helix. Here, the atomic composition of the polymer causes the formation of chiral carbon atoms in the polymer backbone, which leads to an electrical gradient¹⁰.

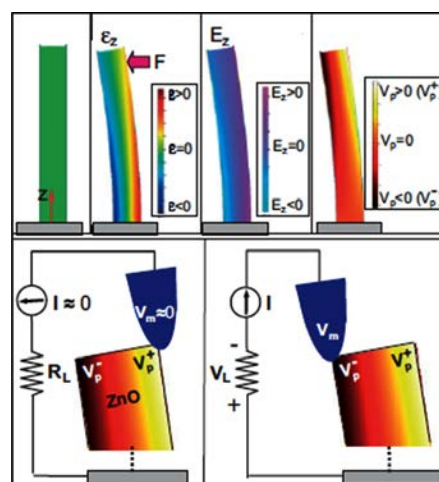


Fig. 1: Working Principle of Piezoelectric Nanogenerators⁸.

Both the threshold value and the energy produced are the levels that can be used directly in the piezoelectric effect. Another advantage of the piezoelectric method is that it can be produced and operated in both macro and micro dimensions¹¹⁻¹³.

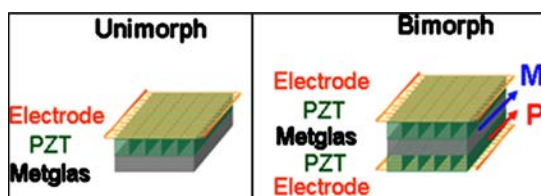


Fig. 2: Unimorph and Bimorph Piezoelectric Structures¹⁵.

The magnitude and direction of the piezoelectric effect is also parallel to the magnitude and direction of the mechanical force loaded. Among the various piezoelectric nanogenerator structures, unimorph and bimorph (Figure 2) type cantilevered beams are the simplest¹⁴.

Cantilevered beam type piezoelectric nanogenerators can produce electricity in d33 and d31 piezoelectric production modes. Here, "d" represents the piezoelectric constant of the material, and "31" or "33" represents the method of polarizing the material¹⁶. As seen in Figure 3, the d31 mode electrodes are perpendicular to the polarization

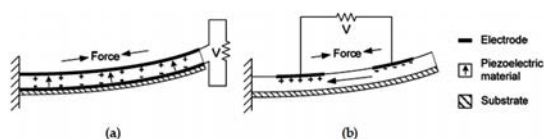


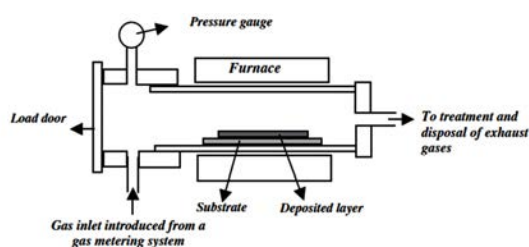
Fig. 3: (a) d31 and (b) d33 Piezoelectric Designs¹⁷.

direction; In the d33 mode, the electrodes have the same polarity direction¹⁷.

The alternating current generated by the piezoelectric nanogenerators must go through the rectifier and be stored in the supercapacitor in order to be usable. So an AC-to-DC conversion is necessary¹⁸. Another factor that is directly related to the performance of these devices is modeling. Because the performance of a nanogenerator is primarily due to the piezoelectricity of the piezoelectric layer; Secondly, it is shaped parallel to the electrical resistance of the external components¹⁹.

The crystals are usually piezoelectric materials and generally piezoelectric nanowires are placed on a

vertically conductive surface. This is accomplished by chemical vapour deposition (CVD), inductively coupled plasma (ICP) deposition, and chemical solution methods. With the nanowire grown by the CVD method, the initiators are attached to the surface so that the piezoelectric material to be used can grow. Subsequently, the base material of nanowire is atomized with high heat and sent to the surface (Figure 4). The particles sent to the surface are held only by the regions where the initiators are, and the nanowires are grown on the surface. It has recently been preferred to carry out the enlargement



- Uniform coating layer
- Thickness: 2–100 μm

Fig. 4: Film Creation Mechanism by CVD Method²¹.

process using the electric field and in solution after the same seeding process²⁰.

In the ICP method, as in CVD, the piezoelectric material is brought to the vapour phase; followed by passing through an induction coil with a high voltage applied and sent to the surface and nanostructures are grown (Figure 5).

Compounds that has ABO_3 formula are named as perovskites. Nowadays, nanoparticles of perovskite crystals were preferred on nanogenerator studies due to their dielectric properties. BaTiO_3 , $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ and $(\text{K}, \text{Na})\text{NbO}_3$ nanocrystals like nanorods, nanowires, nanobelts etc. are most commonly used perovskite piezoelectric materials^{23,24}. These nanostructures were usually synthesized by hydrothermal method and molten salt method (Figure 6).

Although nanostructure based nanogenerators have mechanical flexibility with small defects in their structures, most of the materials used are expensive because of their difficult and complicated

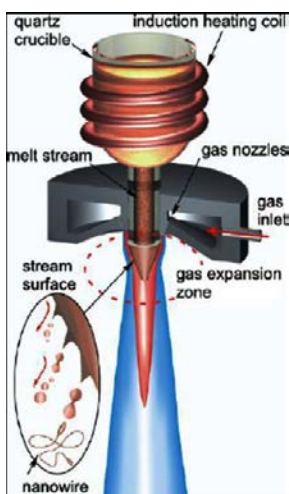


Fig. 5: ICP Material Storage System²².

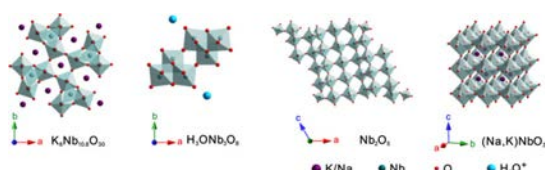


Fig. 6: Formation steps of $(\text{K,Na})\text{NbO}_3$ perovskite crystals²⁵.

manufacturing conditions, also brittle and not efficient in case of large scale applications due to low power output¹⁶.

Polymers having piezoelectric effect are good alternatives to inorganic ones with their good mechanical flexibility. Additionally, polymer-based nanogenerators are suitable for low weight applications¹⁶.

Bulk piezoelectric polymers (PVDF and PVDF copolymers, Parylene-C and Amorphous polyimide) are widely used. PVDF is the most commonly used piezopolymer since it has the largest piezoelectric coefficient (20–28 pC N⁻¹) among other bulk polymers. Although PVDF have five different polymorphs of β , α , γ , δ , and ϵ , mostly, α , β and γ phases are studied¹⁶.

Recently, nanofiber structures obtained by PVDF electro-production method have started to be preferred in piezoelectric nanogenerators. PVDF can be used in nanofibernanogenerators due to its

electronic properties and the mechanical strength of the polymer construction. The non-polarized alpha phase of the PVDF nanofibers turns to the polarized beta phase with high electric field effect. In this way PVDF nanofiber is used as a piezoelectric layer in nanogenerators. The linear mechanical effect exerted on the PVDF piezoelectric layer reveals a voltage opposite to that of the characteristic piezoelectric charge of PVDF (-) opposite to that of the polarity²⁶.

These new piezoelectric nanogenerators are a versatile electricity generation strategy that collects environmental waste energy for potential practical applications. Nanogenerators are particularly promising for miniaturization of more powerful packages than their implications for biological detection, environmental monitoring and personal electronics, and their powerful nanosystems. In particular, flexible and collapsible Nanogenerators are useful in areas having special mechanical and structural requirements, such as muscle or joint implanted biosensors. However, although there are many studies about electrospun PVDF nanofibres/ nanofibre mats²⁷⁻³³ there are still challenges related to low output power due to phase content of PVDF, high electrical resistance and lower surface charge density in and over the nanofibres, respectively.

Lin et al have produced a flexible and transparent piezoelectric nanogenerator. ZnO nanowires on PDMS were grown in solution. Piezoelectric film is coated with PMMA through the surface of the nanotubes. Top and bottom faces of the film were then coated with ITO to serve as electrodes. A voltage of 8V was obtained from the device³⁴.

In another study³⁵ for mamidium lead halide perovskite(FAPbBr_3) which is a piezoelectric material dominantly was used as "piezoelectric reinforcing material" in a piezoelectric matrix. FAPbBr_3 nanoparticles were added into PVDF in different concentrations (6-9-12-15-18 %wt). Nanocomposite solution was poured onto a glass substrate. And then annealed 2 hours at 80°C and 2 hours at 130°C to dominate the β phase PVDF. PET foils are deposited with Cr (10 nm) and Au(90 nm) to form top and bottom electrodes of nanogenerator. PET/ Cr/Au electrodes were integrated to piezoelectric layer and the nanogenerator was kept under an

electric field of 50 kV/cm for 1 hour. Piezoelectric nanocomposite was characterized by fourier transform infrared spectrum analysis. Absorption peaks of analysis at 840 cm^{-1} and 1275 cm^{-1} were shown the β phase domination of PVDF after thermal treatment. Piezoelectric voltage and current outputs of nanogenerators were measured under compress/release process with 0.5 MPa at frequency of 5 Hz. 12 %wt nanocomposite was shown the best piezoelectric performance with 30 V.

Jung *et. al.* has been manufactured a piezoelectric nanogenerator based on piezoelectric perovskite nanocomposite³⁶. NaNbO_3 nanowires and nanocubes were synthesized by hydrothermal method. Nanowires and nanocubes were mixed with PDMS resin with %1 volume ratio. Then nanocomposite solution was spin coated on Au/Cr coated polyimide film and another Au/Cr coated polyimide film integrated with nanocomposite/electrode polyimide film to form the nanogenerator. As a last step, sandwiched nanocomposite is attached to a polyester film. 80 V/cm electric field and a periodic bending force were

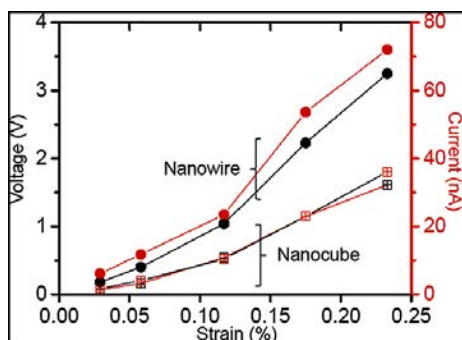


Fig. 7: Comparison of Output Voltage and Current of Nanowire and Nanocube Based Nanogenerators³⁶.

applied to the piezoelectric nanocomposite. Nanowire based device has shown better performance than nanocube based nanogenerator with 3.2 V and 72 nA (figure 7).

In a similar study, zinc stannatnanocubes were mixed with PDMS with different concentrations³⁷. PDMS/ ZnSnO_3 solution was spin coated onto indium tin oxide coated polyethylene naphthalate. Nanocomposite surface of film was coated with

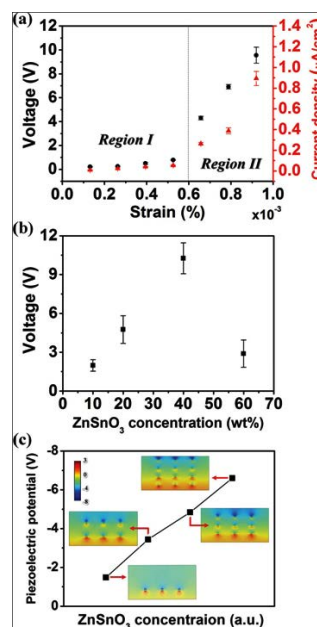


Fig. 8: (a) Output current and voltage of ZnSnO_3 :PDMS with %40 concentration. (b) Output voltage comparison with ZnSnO_3 concentration. (c) Output piezoelectric potential distribution of HP-NG with different ZnSnO_3 concentration³⁷.

10 nm thick Cr and 100 nm thick Au. The best performance among nanogenerators under %0.91 vertical compress strain was shown by %40 wt. nanocomposite (12 V and 0.9 μA) (Figure 8).

Fuh and Wang used polyvinylidene fluoride (PVDF), which is a dielectric material with high dielectric properties, as a piezoelectric layer by electrospinning in the form of nanofibers. Nanofibers are produced in parallel with each other by electrospinning in the near field (1-2 mm). It has been determined that the performance of the obtained nanogenerator is improved in this way³⁸. Produced nanogenerators were used to electrically identify some human gestures.

In a study conducted in 2017, PVDF electrospinning method was used to produce a 200 μm thick nanofiber film. Top and bottom surfaces of the film are coated with gold and silicon substrate is mounted³⁹. Here, the piezoelectric nanofiber layer is polarized under a voltage of 5 kV and the device is intended to be used as a respiration sensor by affixing it to

a bandage. Examination of respiratory signals can be used both in detailing the respiratory event, both in the diagnosis of respiratory diseases and in the monitoring of the current situation of the hospitalized patient.

Hadimani et al. melted pure PVDF homopolymer and drawn fiber; they were polarized at 13 kV voltage at the end of the fiber drawing process. The drawn fibers were placed between two PET films coated with ITO and the voltage sensitive test was carried out in the impact tester. This device weighs 1.02 kg and is lowered on the film from a height of 5 cm. The same test was also carried out on a commercial piezoelectric PVDF filament and it was observed that the drawn PVDF fibers performed about 2 times lower (5 V / 2.2V) than the commercial PVDF filament. The main reason for the loss of performance is that PVDF used for fiber drawing is selected from a cheap raw material that is not specifically manufactured for the piezoelectric effect as it is in the commercial film. This shows that; harvesting

energy from piezoelectric polymers by lowering costs is a strong candidate for renewable energy sources, despite a 50% loss⁴⁰. In another flexible nanogenerator operation⁴¹, a two-step mechanism was used to produce BaTiO₃ nanowires. PDMS film cured on a silicon plate; BaTiO₃ nanoparticles coated on PDMS; A layer of PDMS is further coated on the nanowire. This dielectric layer was removed from the silicon plate and placed between two ITO coated thin and thick PET films (Figure 9).

Seung et al (2015)⁴², piezoelectric nanogenerator fabrics were fabricated to produce wearable technology in their work (Figure 10).

The "Sungkyunkwan University" logo was displayed using the power generated by the nanogenerator in polarized LCD manufactured from the nanogenerator fabric, and six LEDs were lit at the same time (Figures 11a-11b). A remote control used for the keyless entry system was operated using a commercial capacitor (1200 μ F) charged by the nanogenerator only (Figure 11c-11e) without any assistance from an external charging source⁴².

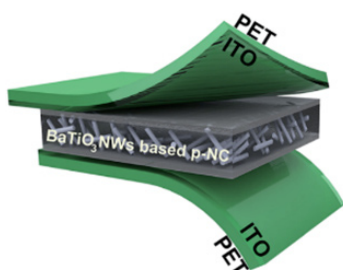


Fig. 9: BaTiO₃ nanowire based piezoelectric nanogenerator⁴¹.

Two different designs in the d_{31} mode have been studied by Shenck and Paradiso (2001). At first, multi-layered flexible PVDF is mounted under the shoe soles. Multi-layer PVDF film is formed as PVDF-Epoxy-Flexible plastic. In the second case, two PZT / metal unimorph components are placed underneath the ball, and this design is called bimorph. When pressure is applied and released, load accumulates along the surface of the PZT; This charge is transferred from the bimorph device via

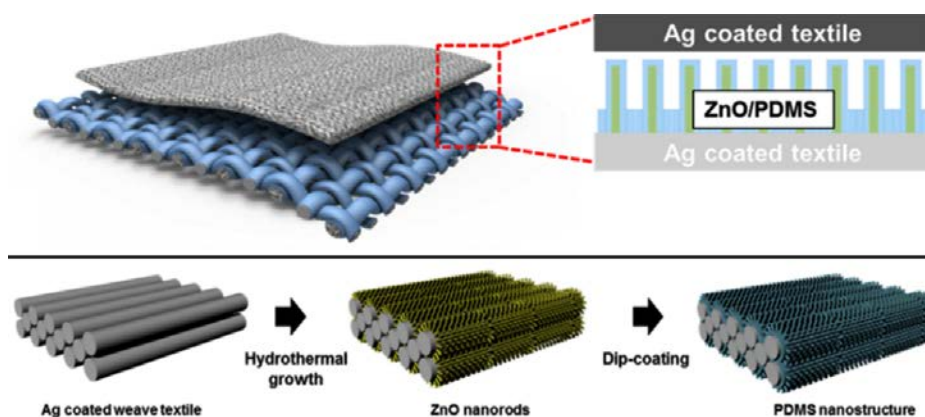


Fig. 10: Fabrication of piezoelectric nanogenerator fabrics⁴².

the Be / Cu electrode. These devices provide energy efficiency of 0.5% and 20% respectively⁴³.

In another example⁴⁴, PVDF was dissolved in DMF or DMAc followed by films of 20-60 μm thickness. The two surfaces of the films were covered with gold, and these layers served as electrodes. Produced film is attached to shoe soles with shaker. The shaker has strengthened the vibration that occurs during walking. A maximum voltage of 6 V was produced from 28 μm film.

Footwear applications of piezoelectric nanogenerators give high accuracy results in describing human walking cycles⁴⁵, walked gym⁴⁶, acceleration and deceleration tendencies due to high output voltages, voltage sensitivities and easy application.

In a work done for industrial machines, a piezoelectric impulse excitation approach was developed. Here, a cylindrical mass is actuated by a series of piezoelectric bimorph-beam magnetic attraction⁴⁷. With the first warning, transducers start vibrating naturally frequency. Using this approach, the working frequency range can be extended while the electromechanical coupling increases significantly. The principle of current excitation is shown using an integrated circuit on the market for voltage regulation. With a 2 Hz frequency and an acceleration of 2.7 m

s⁻², the nanogenerator has a maximum power output of 2.1 mW. Here, the mass starts to move under the magnetic field and generates energy at the same level because it stimulates the magnets connected to the piezoelectric beams at the same level in each cycle. If the frequency of the mass increases, the energy produced will also increase. Steel was used as a mass in the study.

In another work proposed for electric generation from the knee motion, a circular design was prepared and the bimorph strata were horizontally extended to the outer edge from the centre of the field. At the edge of the outer circumference, polyimide pens were placed at regular intervals. Positioned parallel to the knee, this device caused the bimorph films to stuck and stretch and produce electrical stress when the step was taken⁴⁸. The bimorph layer is a metal film between two layers with a thickness of 125 μm . A voltage of 2.7 mV (2 Ω -300 Hz) to 24 V (1 M Ω -320 Hz) was obtained from the device at different electrical loads.

In flexible piezoelectric films, a shell layer is required to achieve high voltage output and to allow both flexing and deformation protection. Promise; a PVDF film cambered polymer film used as a piezoelectric layer may be an example of this⁴⁹. Here, the polyester film was subjected to heat treatment to make it



Fig. 11: Wearable self-powered textile⁴².

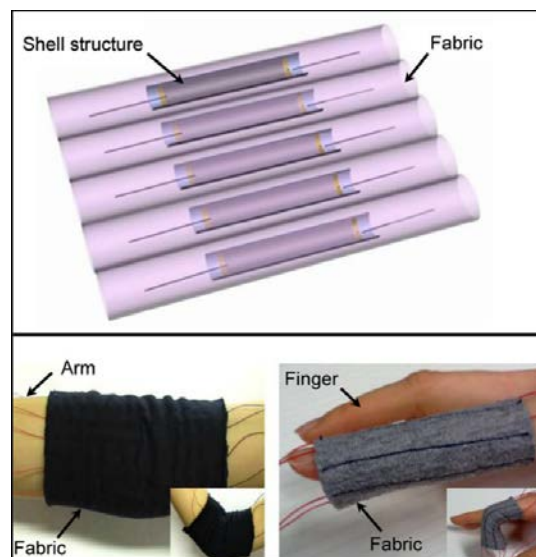


Fig. 12: Flexible nanogenerator with convex shell layer⁴⁹.

convex, followed by a PVDF layer having copper electrodes at both ends on its inner side (Figure 12). A marked increase in performance was observed when compared to the samples made using the flattened PET film. When the output voltage is about 10 V in the flat structure and folded with the angle of 80° in the convex structure, this value increases to 60 V.

When the produced flexible nanogenerators are embedded in the fabrics, there is a system that transforms the mechanical energy of the joint movements into electrical energy. When the transformation of the mechanical energy in the elbow and finger joints on this system is examined, it is seen that the highest values have the highest slope values (Figure 13).

In 2012, a design has been signed for the conversion of waste mechanical energy of rotating devices for residential use of flexible nanogenerators. In the

design, a rigid PZT piezoelectric beam and a flexible beam are placed perpendicular to the axis of rotation of a rotating household article. During rotation, the flexible beam physically stimulates the piezoelectric beam, causing the load carriers to polarize⁵⁰.

Lee has produced a piezoelectric nanogenerator by using a ZnO film. 3 different piezoelectric layer design have been used in this work; ZnO film, ZnO/P3HT layer and ZnO/PCBM-P3HT. The resulting tests revealed a voltage of 0.05 V in the resulting ZnO nanogenerator, which increased to 0.2 V in ZnO / P3HT devices. The energy conversion efficiency increased by 28% with a potential of 0.5 V output in ZnO / P3HT-PCBM nanogenerators, increasing by 36 times⁵¹.

In another study, the electrodes were selected from conducting polymers that connecting the piezoelectric films. The fiber drawing method originally used for this work was made possible by conductive solid filled LDPE films. In this fiber drawing method, different piezoelectric layers and carbon black doped LDPE electrodes are placed on top of each other and twisted to form fiber. For piezoelectric films, BaTiO_3 , PZT or CNT is dispersed in the PVDF matrix. Once the overlaid films are allowed to soften at temperature, the polycarbonate is bent in one direction around an axis. The fabric woven with these fibers produced power up to about 5 V by folding and releasing movements like the photo⁵².

Soin et al demonstrated "3D spacer" technology based all-fibre piezoelectric fabrics as power generators and energy harvesters. The knitted single-structure piezoelectric generator consists of high β -phase (80%) piezoelectric PVDF monofilaments as the spacer yarn interconnected between silver (Ag) coated polyamide multifilament yarn layers acting as the top and bottom electrodes. The novel and unique textile structure provides an output power density in the range of $1.10\text{--}5.10\text{ mW cm}^{-2}$ at applied impact pressures in the range of $0.02\text{--}0.10\text{ MPa}$, thus providing significantly higher power outputs and efficiencies over the existing 2D woven and nonwoven piezoelectric structures⁵³.

Yu *et. al.* PVDF nanofiber-based piezoelectric nanogenerators are directly prepared via

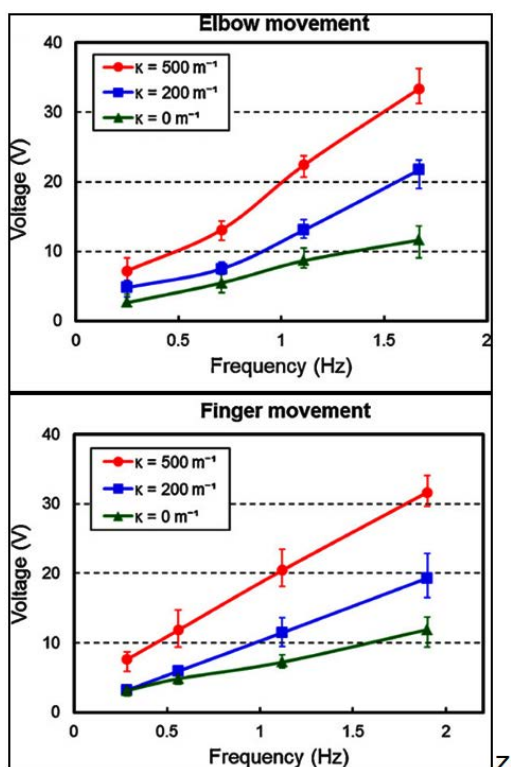


Fig. 13: Stimulation of convex nanogenerator with elbow and finger movement; responses from the nanogenerator. (K: curvature degree of shell layer)⁴⁹.

electrospinning without any post-poling treatment. The effect of the addition of multi-walled carbon nanotubes (MWCNTs) on the fibre diameter, mechanical properties, β -phase composition, surface and volume conductivities, output voltage and output power are investigated. Increased surface conductivity of the polyvinylidene fluoride (PVDF) nanofibre mats, which plays an important role in the enhancement of output power, is first found by the addition of an appropriate amount of MWCNTs. The maximum generated piezo-voltage exhibited by PVDF nanofibre mats in the presence of 5 wt% MWCNTs is as high as 6 V, while the average capacitor charging power is 81.8 nW, increases of 200% and 44.8%, respectively, compared with bare PVDF nanofibre mats⁵⁴.

Hu⁵⁵ has synthesized nanotubes horizontally aligned on a polyurethane substrate by thermochemical method. Then, a portion of the nanotube surface is coated with ZnO by means of an ADL reactor and filled with MWCNT by polymerizing the parylene to mechanically stabilize it. The prepared layered structure was glued with silver paste from two sides and after the electrodes were prepared, the torsion test was carried out. It was observed that the output voltage of 1.7 V was reached. In addition, measurements were taken with the same test, parallel and anti-parallel connection of two generators. Up to 2V of voltage was obtained in

parallel measurements and no significant movement was observed in the anti-parallel test.

In a study of 2016, PVDF solutions (0-0.1-1.0-3.0-5.0) with different amounts of graphene in DMF were prepared. From these solutions, nanofibers produced by the electrospinning method were sandwiched between two metal electrodes and piezoelectric nanogenerators were produced. In piezoelectric measurements, the output voltage was 2 times higher than that of graphene-free device⁵⁶.

Triboelectric Nanogenerators (TENGs)

The triboelectric effect is that a material becomes electrically charged after contact with a different material by friction⁵⁷. TENGs are based on the principle that when two different surfaces come into contact with each other, electrons are transferred from one to another and that a surface maintains electrons more than the other while the contact is cut off. When these two surfaces are isolated, electron transfer takes place between the positive and negative poles formed. Thus, electrical stress is produced⁵⁸. TENGs are separated by four types according to contact modes:

- Vertical Contact: Electrodes are placed on one surface of the two-pole dielectric film. The physical contact between the two dielectric films creates oppositely charged surfaces.

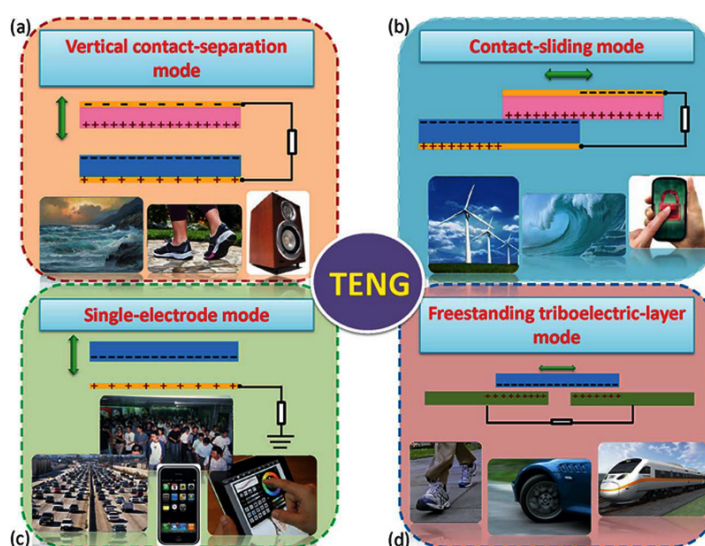
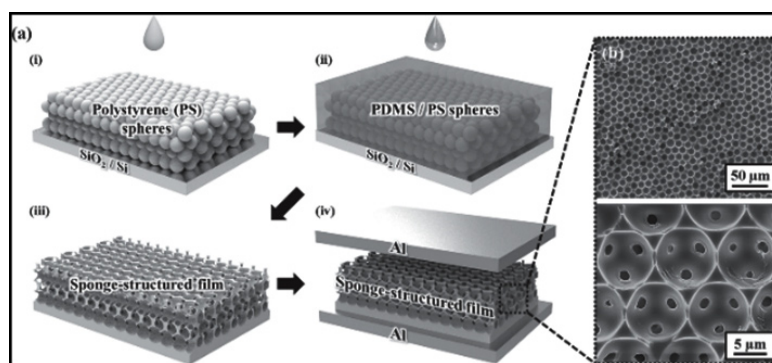


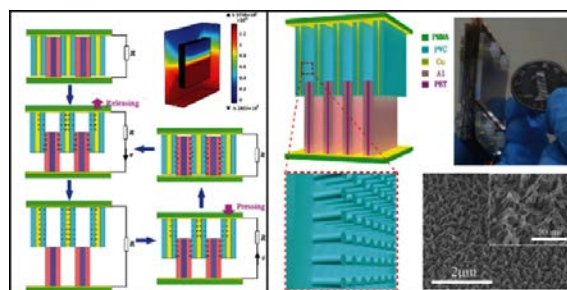
Fig. 14: Triboelectricnanogenerators according to contact modes⁵⁷.

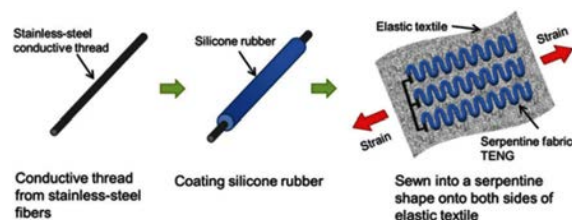
Fig. 15: PDMS foam layered TENG⁵⁹.

- Electron flows when the plates contact, and charge accumulation when the contacts are cut (Figure 14a).
- Lateral slip: Slip parallel to the surface when two dielectric films are in contact, creating triboelectric charges on two surfaces. Polarization in the direction of friction directs electrons in the upper and lower electrodes to flow to completely balance the charges (Figure 14b).
 - Single-Electrode: Approach or separation of TENG to the ground of dielectric filament changes local electric field distribution; so that electrons exchange between the bottom electrode and the ground to maintain the film potential change (Figure 14c).
 - Non-Connected Electrode: When a symmetric electrode pair is placed underneath a dielectric layer, a self-charged object is moved to the electrodes when moving, and the object moves away from the electrodes, creating a charge distribution in the medium (Figure 14d)⁵⁷.

Among the factors that affect the performance of TENGs, sufficient load separation and friction area are two main factors. The load separation depends on the electronegativities of the materials used in the device. For the frictional field, developing a device from a 2D layered structure to a 3D device would be an efficient choice. In past studies, PDMS foam was produced to increase the contact surface and TENG was designed from this foam layer (Figure 15)⁵⁹. In another study that used this idea, both a 3D structure and a surface were coated with nanostructures to increase the surface area of the electrodes (Figure 16)⁶⁰.

TENGs have been attracting attention among energy collectors because of advantages such as simple production, high stability, low cost. In past studies, textile applications of TENGs are always based on the contact of two threads or the cutting of contact. However, since the textile products are soft, the net contact distinctions become more difficult as the triboelectric mechanism is required. So wearable electronics are suffering from loss of comfort. Lai

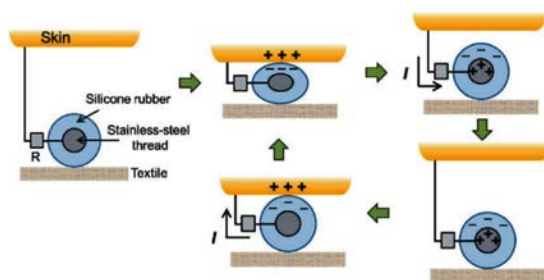
Fig. 16: Lateral shift type 3D TENG⁶⁰.

Fig. 17: Non-woven textile based TENG⁶¹.

et al. came up with a TENG they produced from untamed yarn from above⁶¹.

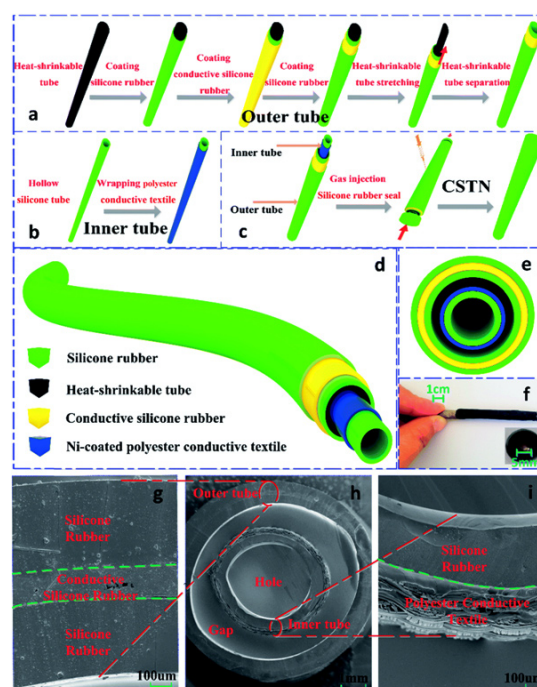
Stainless steel thread is covered with silicone rubber. This yarn was sewn on both sides of a flexible fabric in a curved manner (Figure 17). The triboelectric wire on the inner surface of the fabric acts as the second triboelectric electrode when it contacts human skin. Silicone electron transfer occurs when the skin is in contact with the silicon layer; when contact is interrupted, the negative charge on the silicon provides positive pole formation as long as it is a contact with the conductive thread (Figure 18).

In a similar study⁶², a core shell coaxially triboelectric thread was produced. A heat shrinkable tube was coated by silicone rubber/conductive silicone rubber/silicone rubber. This structure is used as outer triboelectric surface. On second step a silicone rubber hollow tube which has smaller diameter than outer triboelectric layer was wrapped by Ni coated polyester fabric. This structure was used as inner triboelectric surface. Then inner tube was inserted into outer tube and two ends of triboelectric tube was coated with silicone rubber to prevent contamination. In the last step air was injected into the triboelectric core-shell structure to form a gas bag (Figure 19). Core-shell triboelectric structure was produced 380 V and 11 μ A under 300 N pressure and 3 Hz frequency.

Fig. 18: Energy convert mechanism of non-woven textile based TENG⁶¹.

A rectifier circuit was used for convert alternative current to direct current and use the electrical energy from parallel linked six core-shell structures. By this way the device could powered up 60 LEDs and an electronic watch.

Lin *et al.* have produced a sleeping sensor which is working with triboelectric effect⁶³. Triboelectric sensor is consisting of wavy shaped PET tapes between two conductive fabric. Carbon fibres are washed by organic solvents and water. Then carbon fibres were kept on 100 °C after coating with silver nitrate and dipping edetic acid solution. Thus Ag coated conductive fibres could be produced. Conductive fibres are mounted on two fabrics with perpendicular

Fig. 19: Production processes, schematic illustrations and SEM images of core-shell triboelectric nanogenerator⁶².

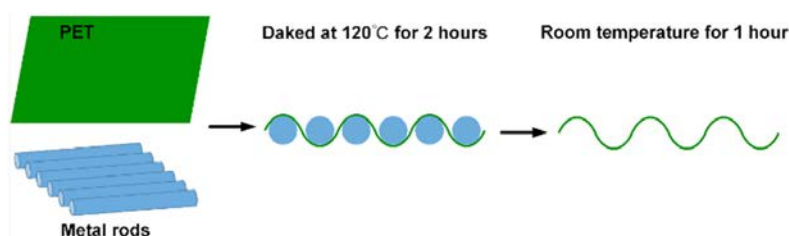


Fig. 20: Schematic illustration of wavy shaped PET foil⁶³.

orientation. Wavy shaped PET foils were cut 50 mm X 60 mm. Then PETs foils were kept at 120°C and wavy shape was brought with metal rods (Figure 20).

Wavy shaped PET foils were placed on intersections of conductive lines on fabrics (Fig B). Triboelectric nanogenerator based sleeping sensor was working with 0.77 V/Pa definition. The sensor is comprised 4 X 4 (16 point) intersection point with a rectangular shape. Sensor has shown enough synchronization with external force (Figure 21).

Conjugated polymers are preferred as electrode in nanogenerators because of their conductive disposition. Electrode designs that cannot be realized with metals can be realized with conductive polymers due to their polymeric character⁶⁴.

Wang *et al.* have offered an innovative device design to nanogenerator-supercapacitor systems. A triboelectric electrode is additionally coated onto

top electrode and electrical contact is provided with polyimide based films. In this study, nanogenerator produced 28 V potential at 10 Hz; besides supercapacitor stored this potential⁶⁵.

Cui has electro-polymerized pyrrole on an anodic aluminium oxide porous pattern which was used for production of polypyrrole nano-forest. Polypyrrole is preferred as electrode due to its fast redox performance, flexibility and low cost. Triboelectric electrode of the device consists of respectively Ag/PE/PVDF film. Triboelectrode is fixed on polypyrrole electrode and four acrylic sheets are used as spacer. While PVDF layer charges under stable condition, on the other hand, discharge is observed when the PVDF layer touches to polypyrrole nanowires with wind power⁶⁶.

According to a study in 2015, textile product is prepared by using both supercapacitors and TENGs to produce a wearable electronics. TENG fabric is

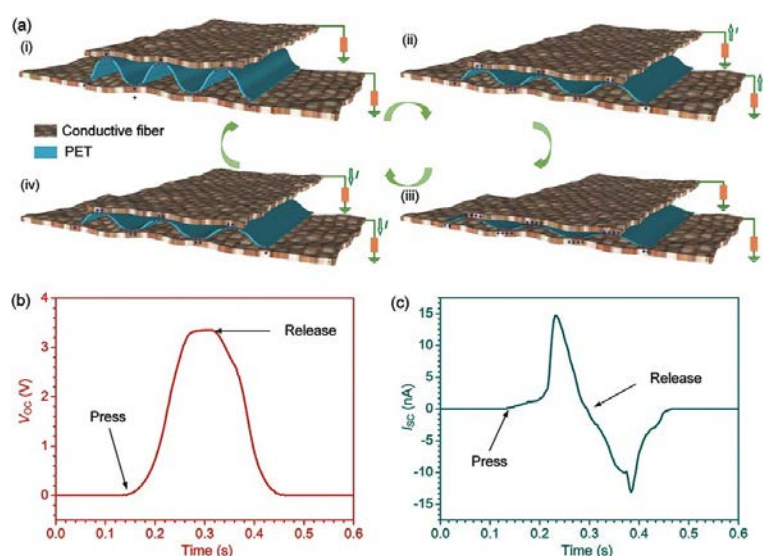


Fig. 21: Schematic illustration and electrical characterization of sleeping sensor⁶³.

woven with Ni coated polyester yarn is used as weft, while parylene-Ni coated polyester yarn is used as warp. TENG device fabrication is completed by combining TENG fabric and a cotton fabric. When the cotton layer touch the TENG fabric charge is observed on both weft and warp yarn⁶⁷.

Huang *et al.* have developed a nanogenerator shoe sole. In this study, PVDF nanofiber layer is used as triboelectric electrode thanks to high electronegativity difference between side groups of PVDF. Counter triboelectric electrode was copper and nickel coated polyethylene terephthalate fabrics. TENG shoe sole could achieved to produce electrical potential till 210 V68.

Pyroelectric Nanogenerators

Pyroelectric property is at least one of the known properties of the solids is defined as the temperature dependence of polarization in certain anisotropic layer. Pyroelectric materials, net dipole moment and the temperature change (or bound charge) they introduce the changes. Pyroelectricnanogenerator are widely used in petroleum refining, steelmaking, glassmaking, such as waste heat of industrial processes or natural geothermal heat obtained from volcanic heat using the solar heat sources such as hot water / cold water charging by utilizing the difference / discharge occur is provided (Figure22).

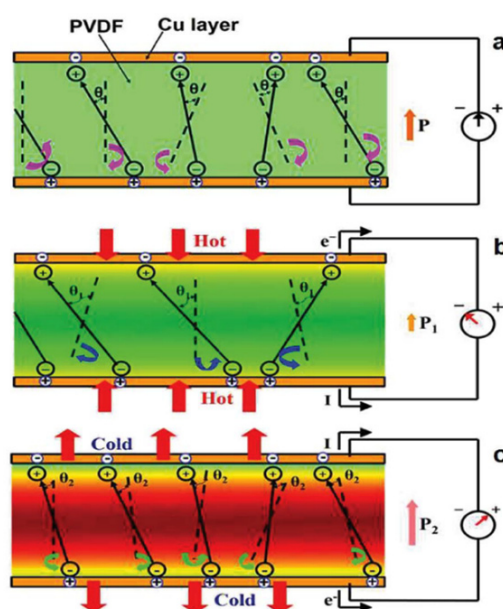


Fig. 22: Pyroelectric effect⁶⁹.

Made of a pyroelectricnanogenerator studies⁶⁹ the two faces of the copper-plated of a PVDF film (electrode), a contact wire from the electrodes for measuring the electricity generated is removed, then the entire device is coated with PVC. The temperature difference between the hot and cold water is 80 °C 192 V voltage and 12 mA / cm² current density reached.

Conclusions

Nanogenerators have emerged to target the recovery of energy used mechanically, biologically or radially inefficiently; in the case of macro sizes, the possibility of producing these quantities of energy producing devices, in small quantities with simple devices that require energy to produce their own energy has produced systems. Electronically, electrostatically, or piezo-electrically, these devices are particularly well suited to revolutionize device design as well as electric energy production, particularly in factories, vehicles, and in areas where mechanical energy is present in high amounts, such as human body, in small quantities or high frequency. The fact that these devices come to the flexible form promises higher efficiency by capturing more mechanical force on the axle compared to the rigid construction when the energy is harvested. In addition, these devices, which are more sensitive to the force axis, may even have a sensor system on their own. Flexible nanogenerators can be predicted to play a large role, especially in biomedical developments. For example, they can be used as breathe sensors³⁹, joint motion sensors^{48,49} etc.

With the growing development of wearable and implantable devices, nanogenerators (NGs) have been paid attention in recent years due to their high conversion efficiency and low-cost with organic nanomaterials^{13,15,21}. The powers of micro/nano scale devices or systems supplied by traditional batteries have some problems such as miniaturization, compatibility and long lifetime^{14,60}. Thus harvesting the energy from environments by NGs can be a potential and effective alternative to meet such requirements. The traditional mechanisms of nanogenerators have been reviewed^{9,32-41}, including electrostatic^{3,46,62,63,66,67}, piezoelectric^{4,10} and electromagnetic^{19,50} methods. However, those devices usually cannot satisfy the need of power supply for electronic devices due to their complex fabrication processes, low output

power and biocompatibility for medical applications. Moreover, most of devices work under single mechanism and their output performance is actually limited in service. Advances in nanotechnology, novel and viable device designs as well as applications of new nanomaterials will enhance better results in flexible nanogenerators.

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Conflict of Interest

"The author(s) declare(s) that there is no conflict of interests regarding the publication of this article".

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