Nanogenerators: A new paradigm in blue energy-harvesting

Arpita Adhikari[1], Joydip Sengupta[2*]

[1]Department of Electronics and Communication Engineering, Techno Main Salt Lake, Kolkata-700091

[2]Department of Electronic Science, Jogesh Chandra Chaudhuri College, Kolkata-700033

[*] Corresponding author, E-mail: joydipdhruba@gmail.com

The depletion of natural energy sources demands non-conventional efficient alternatives with sustainable utility. The outstanding performance of nanomaterials resolves the energy scarcity issue through the introduction of small-scale, energy-harvesting devices, called nanogenerators. A nanogenerator is an ambient energy-harvester with exotic features of being a lightweight, sustainable and stand-alone device which promises efficient utilization of energy. Conversion of mechanical/thermal energy into electricity is the basic working principle of a nanogenerator. The nanogenerators employ piezoelectric or triboelectric properties of a material to harvest electrical energy from mechanical energy whereas for the generation of electrical energy from thermal energy the pyroelectric or thermoelectric properties are utilized. The unique and variant range of applicability of nanogenerators makes them increasingly popular among the scientific communities having interdisciplinary research interests. Nanogenerators are employed successfully in different energy sectors such as solar energy, water (blue) energy, wind energy and many more. The present chapter will summarize the fundamentals of different types of nanogenerators along with their applicability in harvesting blue energy.

1. Introduction

The progress of civilization has undoubtedly reached its unprecedented peak with the
commencement of the fourth industrial revolution in the 21st century. The present age of
industrial advancement quite expectedly is facing an elevated demand for energy resources.
Limited storage of natural energy resources is making the situation more critical day by day.
Consequently, modern industries are confronting enormous energy challenges. Moreover, the
modern time of industrialization threatens the near future of the mankind with the rising level
of carbon pollution that paved the path of unpredictable changes of Earth's climate possibly
resulting in even scary extinction of life. The only way out of the critical situation may be the
search for alternative and sustainable energy resources[1]. In the perspective of climate change,
the added feature that a sustainable energy resource should have is that the energy utilization
needs to be pollution-free. Thus the futuristic growth of science and technology is
confronting the dual challenge of energy crisis and carbon pollution (Fig 1).
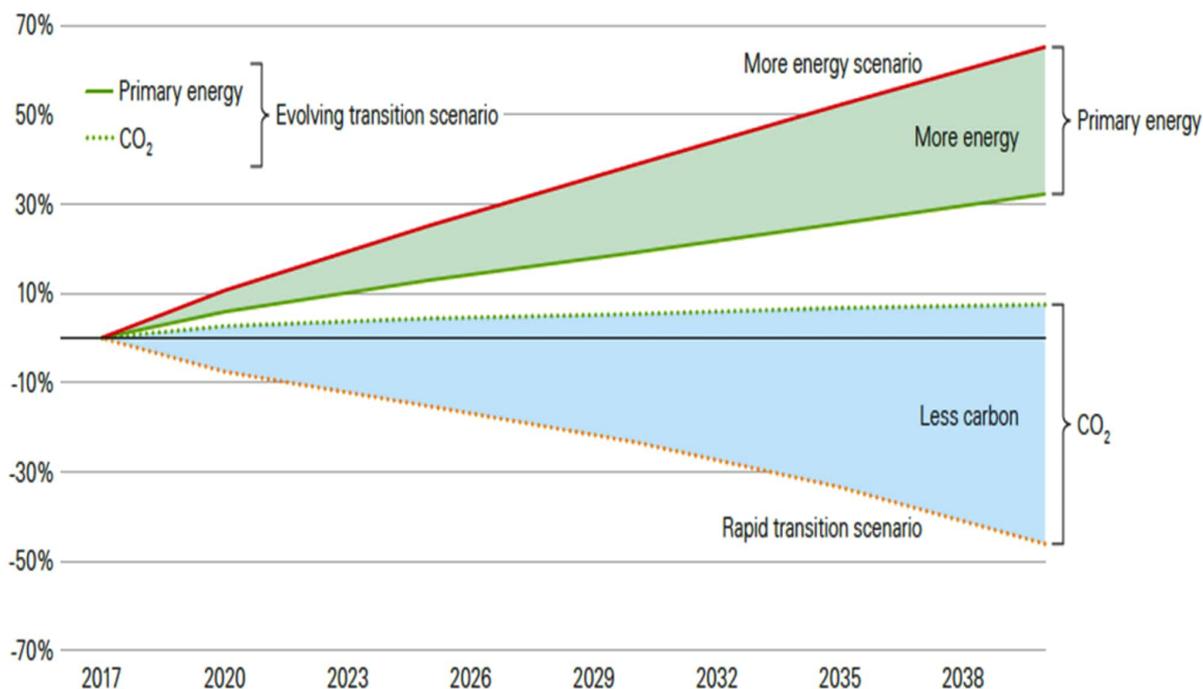
Fig.1. The global energy system faces a dual challenge: the need for 'more energy and less carbon[2].

2. Origin of Nanogenerators:

The search for alternative energy resources particularly in terms of the non-conventional and sustainable form is the essential prerequisite of modern society to maintain the futuristic scientific, technological and industrial drive towards a new era of automation. The novel advancement of mankind would not be possible without the revolutionary concept of the Internet of Things (IoT). All of this technological progress is the phenomenal consequence of the technological achievement of miniaturization science. Nanotechnology is the utmost discovery of miniaturization science which even outperformed the projection of technological growth that had been foreseen by Moore, decades before in 1975. Nanotechnology gives birth to nanodevices that need the power to operate. However, in general, the market-available battery size is much larger than the nanodevices, thus in turn governing the size of the entire system. Consequently, the practical realisation of a nano battery is highly desirable, preferably employing alternative energy resources. The nano-size battery usually has

a small lifetime posing a great hurdle to scientists. The desirable alternative is to develop a nano-sized battery that can harvest energy from the environment to become a self-sufficient green power resource for driving nanodevices. Nanogenerators are just fit in this scope. Firstly, they are of nano-size order and secondly, they are capable of converting naturally available mechanical energy into electrical energy. Moreover, this energy suffices to drive the nanodevice in self-power mode. The term nanogenerator was first coined in 1993[3] while the seed to the invention of nanogenerators is sowed long before in 1861 with the postulation of Maxwell's equation (Fig 2).

According to Maxwell's equation, the displacement current has two components. The first term of Maxwell's equation, $\varepsilon_0 \frac{\partial \boldsymbol{E}}{\partial t}$, postulates the origin of magnetic induction from the electric field. The term thus forms the basis of electromagnetic wave generation, the application of which extends to modern wireless communication technology. The second term $\frac{\partial \boldsymbol{P}}{\partial t}$ defines the polarisation of medium and from this key term, the fundamental features of nanogenerator were originated[4]. In nanogenerators, Maxwell's displacement current serves as the driving force for converting mechanical energy into electrical energy.
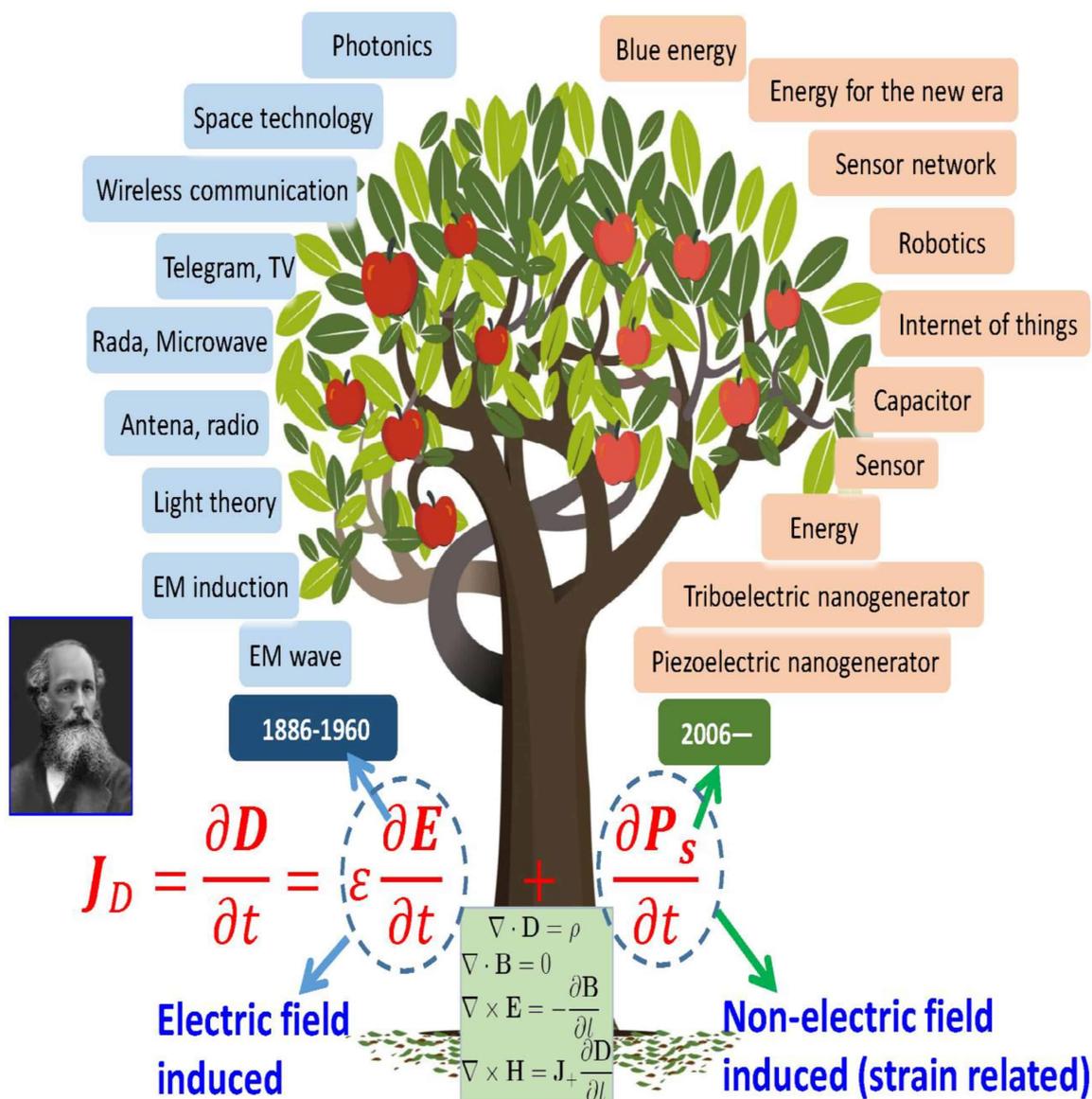
Fig 2: A tree idea to illustrate the newly revised Maxwell's displacement current: the first term $\varepsilon_0 \frac{\partial \boldsymbol{E}}{\partial t}$ is responsible for the electromagnetic waves theory; and the newly added term due to $\frac{\partial \boldsymbol{P}}{\partial t}$ is the applications of Maxwell's equations in energy and sensors, which are the nanogenerators.[5].

Presently, four primary effects, namely, piezoelectric, triboelectric, pyroelectric, and thermoelectric, are employed to develop nanogenerators which are widely utilized in different potential application sectors (Fig 3).

(i) **Piezoelectric effect**

(ii) **Triboelectric effect**

(iii) **Thermoelectric effect**

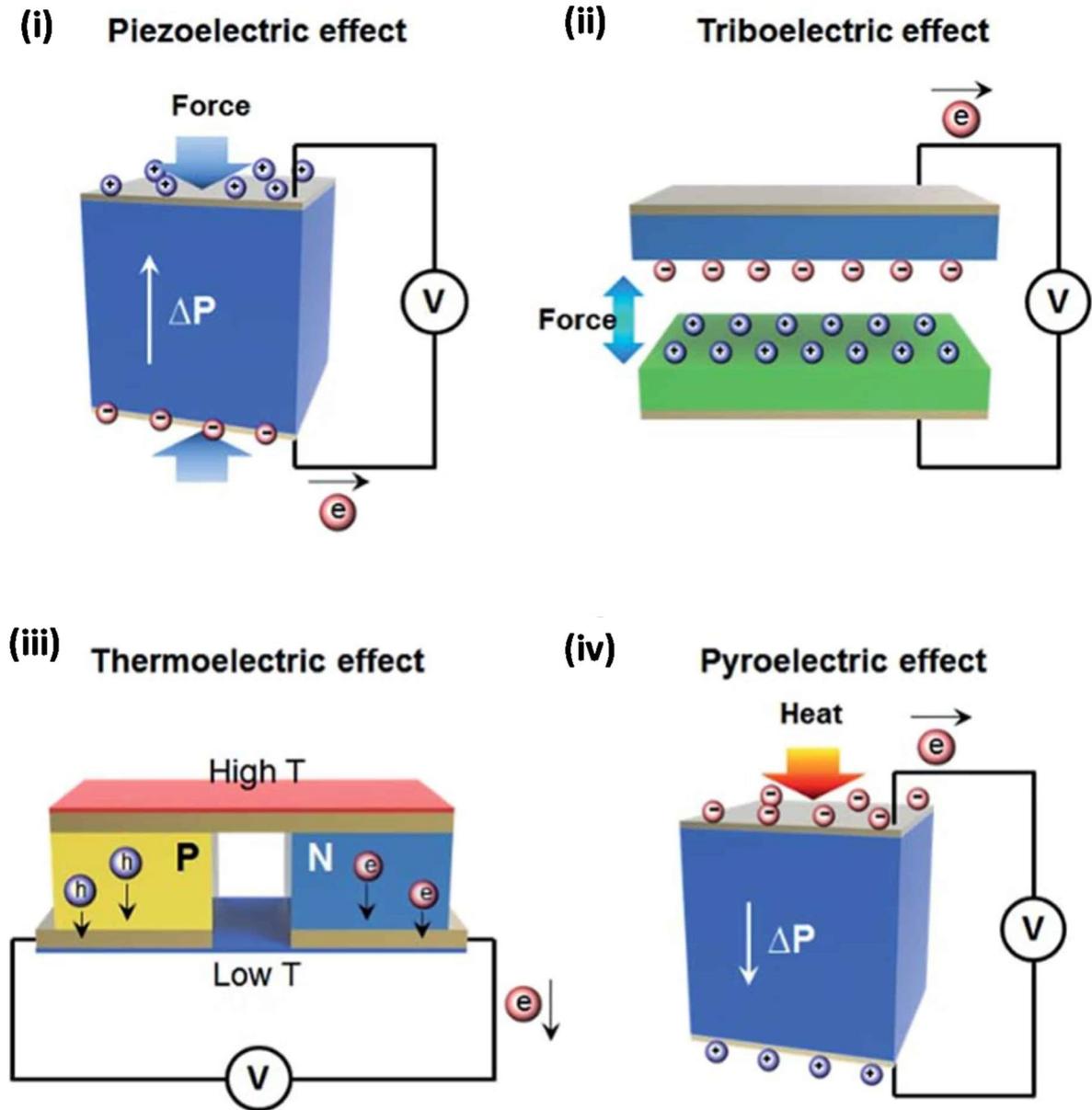**(iv)** **Pyroelectric effect**

Fig 3a. Schematic illustration of nanogenerators[6] based on (i) the piezoelectric effect, (ii) the triboelectric effect, (iii) the thermoelectric effect, (iv) the pyroelectric effect
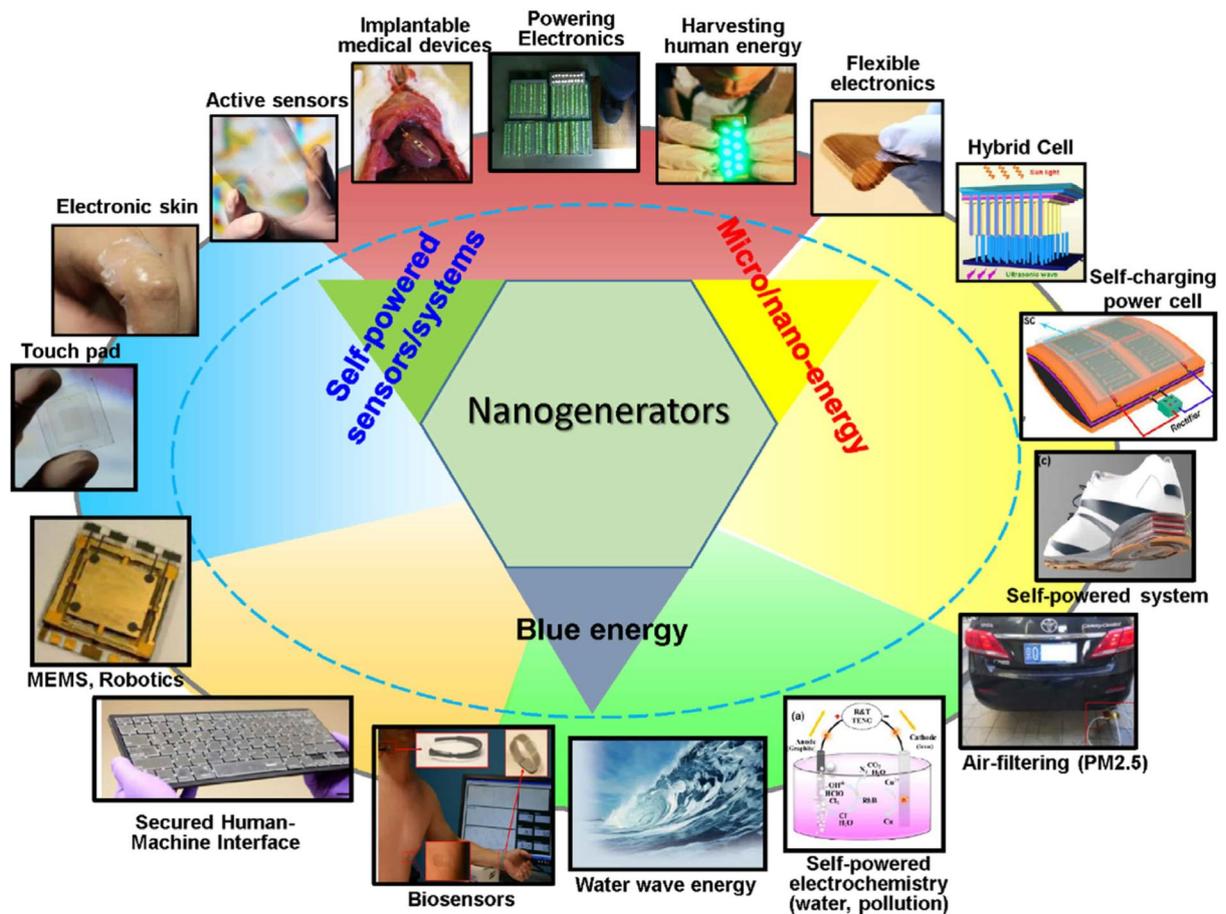
Fig 3b. Different application sectors of piezoelectric, triboelectric, pyroelectric*, and thermoelectric nanogenerator*[7].

3. Piezoelectric nanogenerator (PENG)

In some materials, if stress is applied then their atomic structure alters which prompts the formation of dipole moment and leads to the generation of a voltage difference across the material. This type of material is called piezoelectric material and the said effect is known as the direct piezoelectric effect. However, if electrical polarisation occurs within piezoelectric material, then material deformation takes place. This is known as a converse piezoelectric effect (Fig 4).
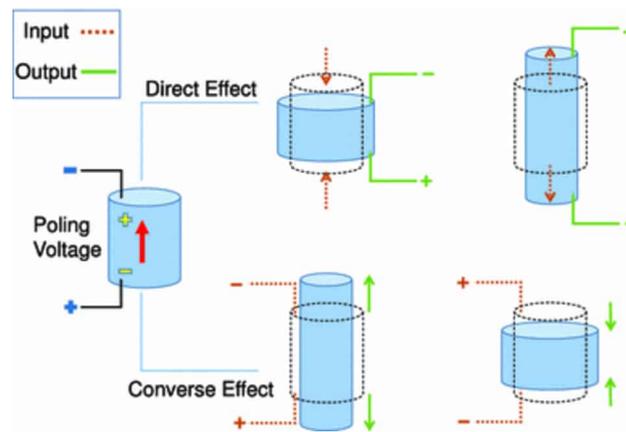
Fig 4. Direct and converse effects in piezoelectric ceramic[8].

A PENG is an energy harvesting nanodevice that can convert external mechanical energy into electrical energy employing the piezoelectric effect within a nanostructure piezoelectric material. PENG was first developed in 2006 by Wang's group[9].

The basic working principle of a PENG relies on the piezo potential, which is produced within the piezoelectric material. In general, two electrodes are connected at the opposite sides of the piezoelectric material. Initially, the Fermi levels of the two electrodes are balanced electrostatically. When strain is employed to the material by external means, the piezo potential is developed within the material producing a difference in-between the internal and external Fermi levels at the contacts. To nullify the differences in-between the Fermi levels, the electrons start to flow through external circuits in-between two electrodes till two electrodes are electrostatically rebalanced. External mechanical forces can trigger strain within PENG in such a way that the strain undergoes periodical variations. This will give rise to an alternating current (AC) at the PENG output and establishes the PENG as a promising power source for the nanosystems.

The external mechanical force can be applied in two directions: one is perpendicular to the nanowire and the other is parallel to the nanowire (Fig 5a). However, in both cases, the top

contact behaves as Schottky contact and the bottom contact behaves like an ohmic contact.

To boost the output power of the PENG, several nanowires should be integrated in such a

way that the deformation of each nanowire is perfectly synchronized. Till now, there are two

types of structures of PENG, namely, lateral-nanowire integrated NG (LING)[10] and vertical-

nanowire integrated NG (VING)[11] (Fig 5b). In LING, the nanowires are grown parallel to a

flexible substrate and during bending deformation all the nanowires are deformed

synchronously with the substrate, resulting in elevated output power. While in VING, the

device is fabricated directly on vertically grown nanowire arrays and it can produce energy

from synchronous compression deformation of the NG.

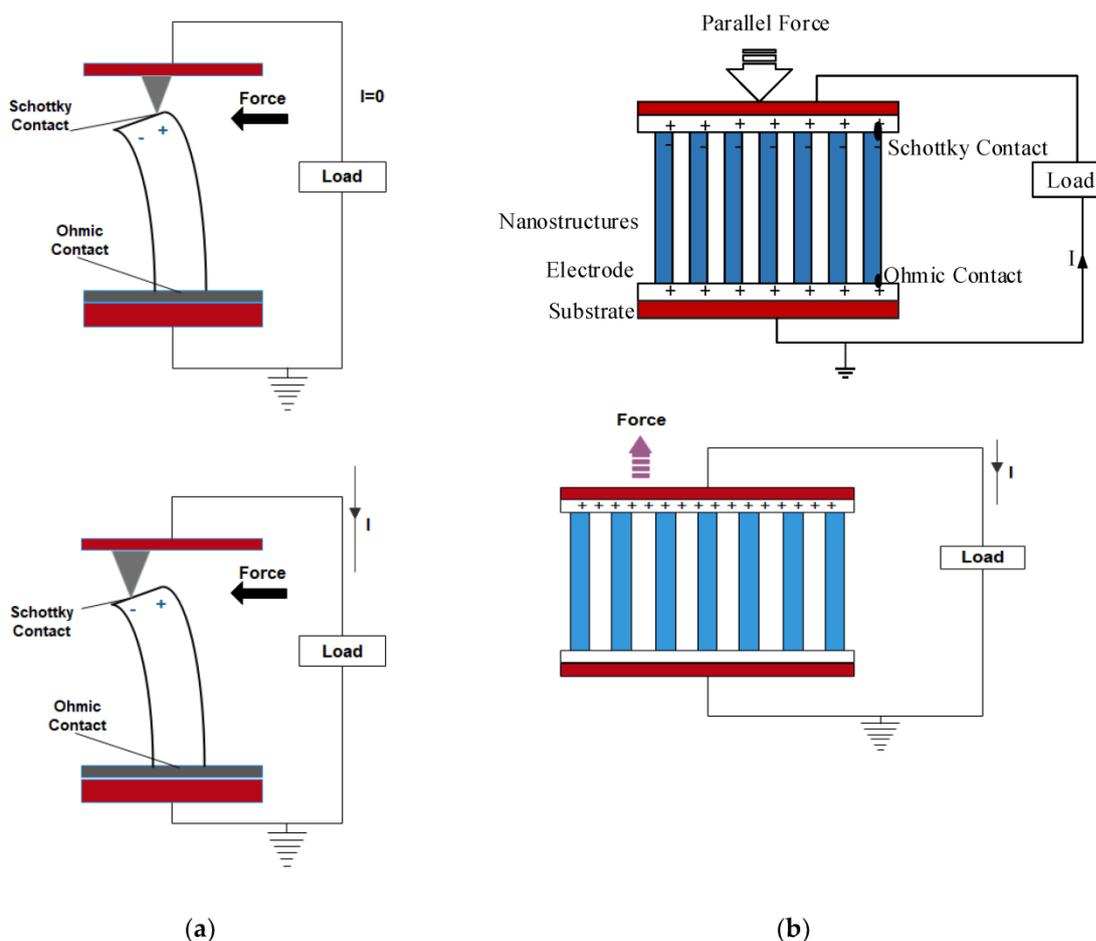

(a)   (b)

Fig 5a. Different mechanism of operation of PENG: (left) Force exerted perpendicular to the

growth of the nanowire and (right) Force exerted parallel to the growth of the nanowire
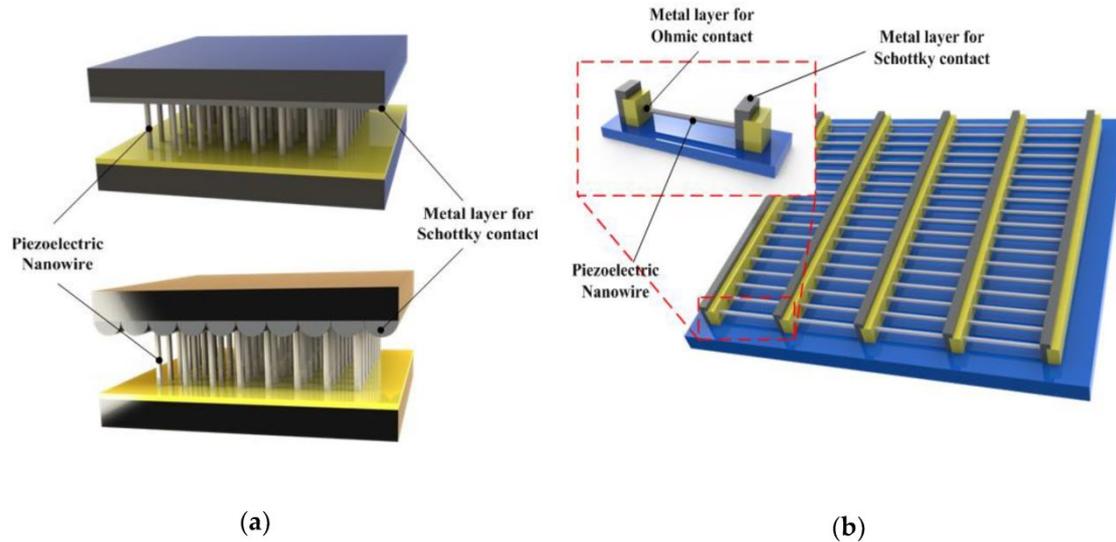
(**a**)   (**b**)

Fog 5b. Different structures of PENG: (left) VING and (right) LING [12].

Different piezoelectric materials such as lead zirconate titanate[13], barium titanate[14], zinc oxide[15], polyvinylidene fluoride[16], cadmium sulphide[17], molybdenum disulfide[18]were used for the fabrication of PENG.

4. Triboelectric nanogenerator (TENG)

Some materials get electrically charged when they make frictional contact with another dissimilar material[19]. This kind of contact-induced electrification is known as the triboelectric effect (Fig 6). After physical contact, the materials become oppositely charged, while, the strength of the charges is different for different materials[20].
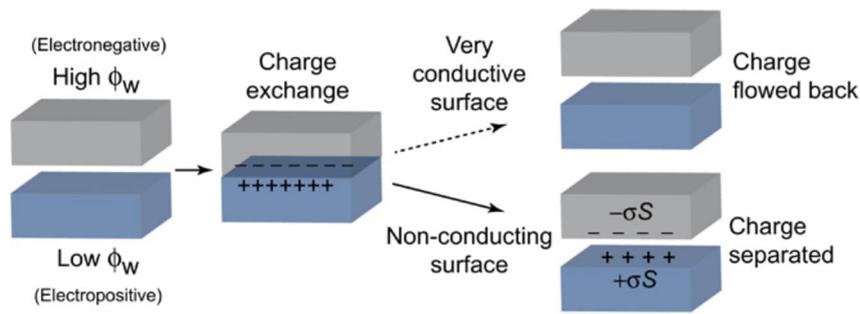
Fig 6. Triboelectric charge generation.[21].

Based on triboelectrification and electrostatic induction effects, Wang's group[22] first put forward the idea of TENG in 2012. There are four basic modes for TENG, namely vertical contact-separation (CS) mode[23], lateral-sliding (LS) mode[24], single-electrode (SE) mode[25], and freestanding triboelectric-layer (FT) mode[26]. In all the four kinds of TENGs, there is a minimum of one pair of triboelectric surfaces with at least two electrodes (For SE mode, the ground is the other electrode). In the triboelectric effect, transport of electrostatic charges occurs from one surface to the other. Upon displacement of one of the triboelectric surfaces, the electrostatic status of the system changes resulting in the generation of the potential difference in-between the two electrodes. Subsequently, the generated potential difference causes a current to flow via the external circuit to balance the electrostatic status. Displacement of the triboelectric layers in the opposite direction creates a reverse potential difference in-between the electrodes, and therefore the current flows in the opposite direction. Thus, an AC output is generated from the TENG via periodical displacement of triboelectric layers.

The triggering process is different in all four modes of TENG (Fig 7). Contact and separation process of the two triboelectric layers causes triggering of CS mode while relative sliding between triboelectric layers is responsible for the triggering of LS mode. In both CS and LS

mode TENG, the external load is connected between the back electrodes of moving
triboelectric layers and thereby imposing a limitation in the movement of the triboelectric
layers. However, this limitation is waived off in the SE and FT mode of operation. In SE
mode a triboelectric layer moves freely with respect to one static electrode, while in FT mode
a triboelectric layer moves freely between the two static electrodes to trigger the NG. To
increase the output power of TENG via structural optimization, different structures like the
multi-layer integrations[27] and grating structures[28] have been fabricated.
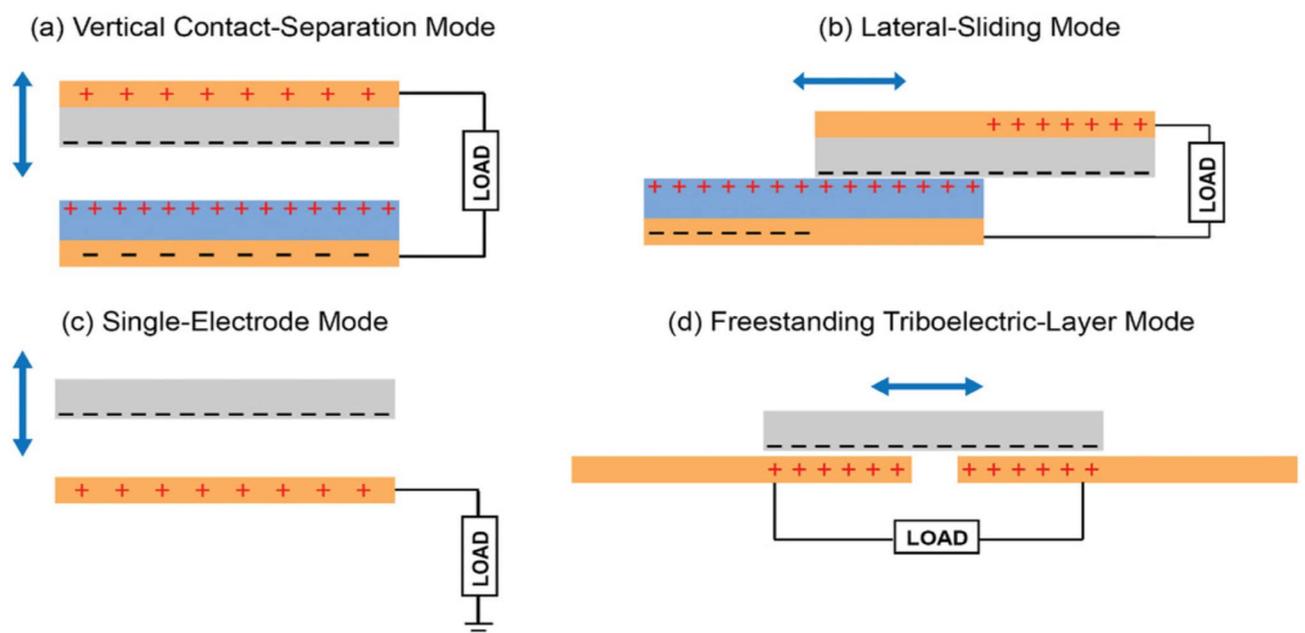
*Figure 7. Four working modes of TENG. a) Vertical CS mode. b) LS mode. c) SE mode. d)
FT mode[29].*

Different natural and eco-friendly materials that can be used to fabricate TENG are described
in recent reviews by Slabov et al.[30] and Kim et al.[31].

5. Pyroelectric nanogenerator (PyENG)

The time-dependent temperature fluctuation often causes spontaneous polarization in certain
anisotropic solids, which is known as the pyroelectric effect. The key parameter of the
pyroelectric effect is the pyroelectric coefficient which can be described as the differential

change in spontaneous polarization owing to an alteration in temperature. The pyroelectric coefficient is the attribute of two phenomena, namely primary pyroelectric effect and secondary pyroelectric effect[32]. If all the dimensions of material remain constant (strain-free case), then the primary pyroelectric coefficient is employed to express the amount of charges generated due to an alteration in temperature. On the other hand, if the dimensions of a material are altered due to the temperature variation, then such anisotropic deformation of the material will produce a strain causing an additional contribution of piezoelectrically induced charges. This process is called secondary pyroelectric effect. In lead zirconate titanate, potassium niobate, barium titanate and some other ferroelectric materials the primary pyroelectric effect dominates while in zinc oxide, cadmium sulfide and some other wurtzite-type materials the secondary pyroelectric effect will predominate.

Based on the pyroelectric effect, Wang's group[33]devised the first pyroelectric nanogenerator (PyENG) in 2012. The principle of generation of current via primary pyroelectric coefficient can be explained through the example of potassium niobate nanowire PyENG. In potassium niobate dipole moments readily exist along with the spontaneous polarization density (Fig 8(a)-top). With increasing temperature, the random oscillations of the ions will intensify with a greater magnitude of spread around their corresponding aligning axes. This causes a reduction in effective dipole moments and consequently, the polarization density is decreased[34]. To regain the previous electrostatic status, charge carriers flow through the external circuit (Fig 8(a)-middle). Even if the PyENG is cooled down from ambient temperature, the oscillations of the ions are reduced with a smaller amplitude of spread across their respective aligning axes and thereby causing an enhancement in effective dipole moments. The resulting increase in polarization density prompts the flow of charge in the reverse direction (Fig 8(a)-bottom).

The principle of generation of current via secondary pyroelectric coefficient can be explained via the example of zinc oxide nanowire[33] PyENG were vertically grown zinc oxide nanowires are sandwiched between two electrodes (Fig 8b). With the increase in temperature, a pyroelectric potential is created along zinc oxide nanowire, thus one electrode becomes electrically positive and the other electrode becomes electrically negative. As the Fermi level of the electrically negative electrode is enhanced, it will drive the electrons to flow from the negative electrode to the electrically positive electrode. After the temperature goes down to the initial value, the electrons accumulated at the positive electrode are released and flow back to the negative electrode as the pyroelectric electrical potential is faded away. Here, a difference in piezoelectric potential is created across the material by the anisotropic thermal deformation and because of the emerged potential difference, the electrons flow through the external circuit. Thus the output of secondary pyroelectric effect based nanogenerator is the combined effect of the piezoelectric coefficient and the anisotropic thermal deformation of the material.

Fig 8a. Primary pyroelectric effect[35].

Fig 8b. Secondary pyroelectric effect (Where D denotes electrical displacement, S denotes constant strain, E denotes electric field, T denotes elastic stress, σ denotes entropy, θ denotes temperature)[34].

Different materials like triglycine sulfate[36], gallium nitride[37], zinc oxide[33], perovskite-based pyroelectrics were used to fabricate PyENG.

6. Thermoelectric nanogenerator (ThENG)

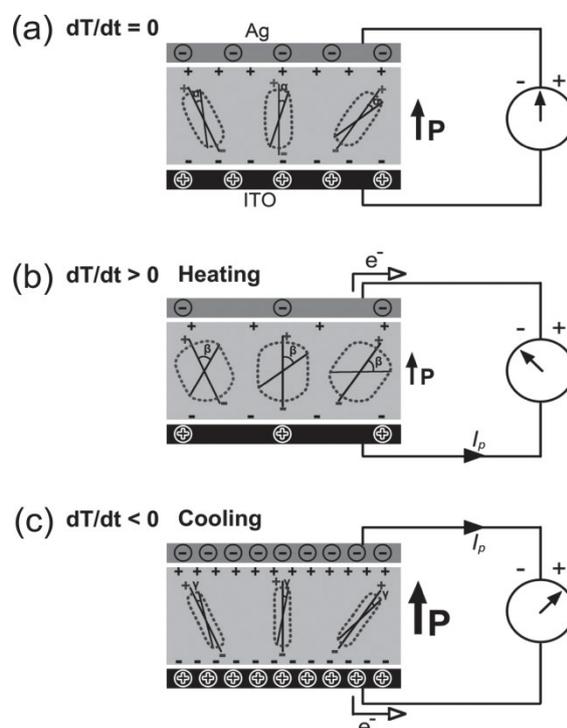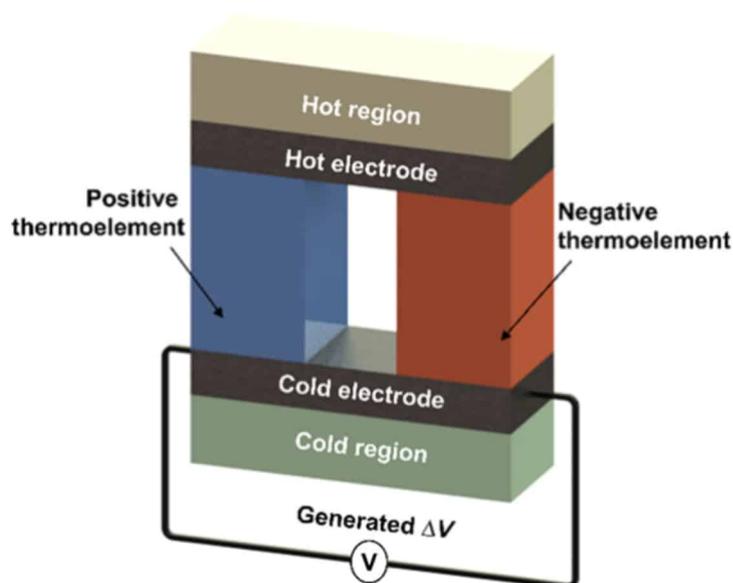If two interconnected dissimilar conductors are maintained at different temperatures, then a potential difference is created between the conductors that are directly proportional to the

temperature difference and such potential difference results in the flow of current in the loop.

This thermoelectric phenomenon is called the Seebeck effect (Fig 9).

Fig 9 Diagram of energy generation mechanism using the thermoelectric effect[38].

The Seebeck effect is utilized to fabricate ThENG. If a thermal gradient exists in the environment, then a ThENG can convert the heat into electrical energy. In 2012 Wang's group first fabricated ThENG using single Sb-Doped ZnO Micro/Nanobelts[39] (Fig 10a). They had placed the ZnO belt on a glass substrate and used silver paste to fix the two ends, which eventually acted as electrodes with a separation of 3 mm. They found that 30 K temperature difference between two electrodes of ThENG can produce output current and voltage of about 194 nA and 10 mV, respectively.

To explain this phenomenon, a π-type model can be employed. In the π-type model, the structure is made up of one p-type and one n-type semiconductor, which is connected via a conducting wire/strip to complete the electrical circuit (Fig 10b). When one side of p-type and n-type material is heated and another one is cooled, the majority charge carriers (holes) of p-type materials and that (electrons) of n-type materials will diffuse from the hot side to

the cold side. This diffusion process results in building-up charge carriers at the cold end.

Such build-up of charge carriers at one end produces a potential difference across the

semiconductor, proportional to the temperature difference across the semiconductor. If the

cold ends of both the semiconductors are electrically connected, then a current flows from the

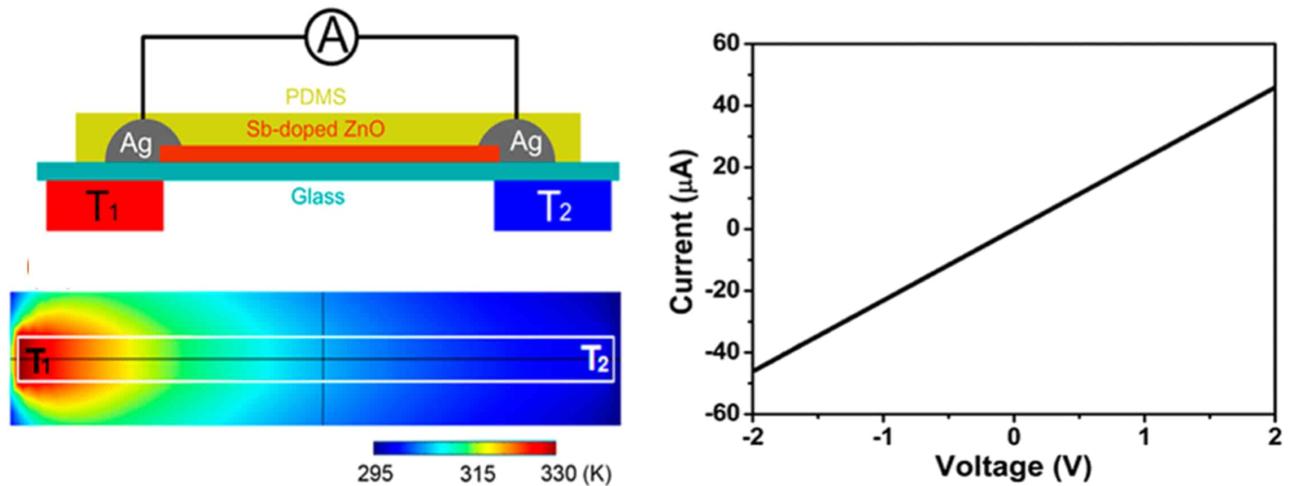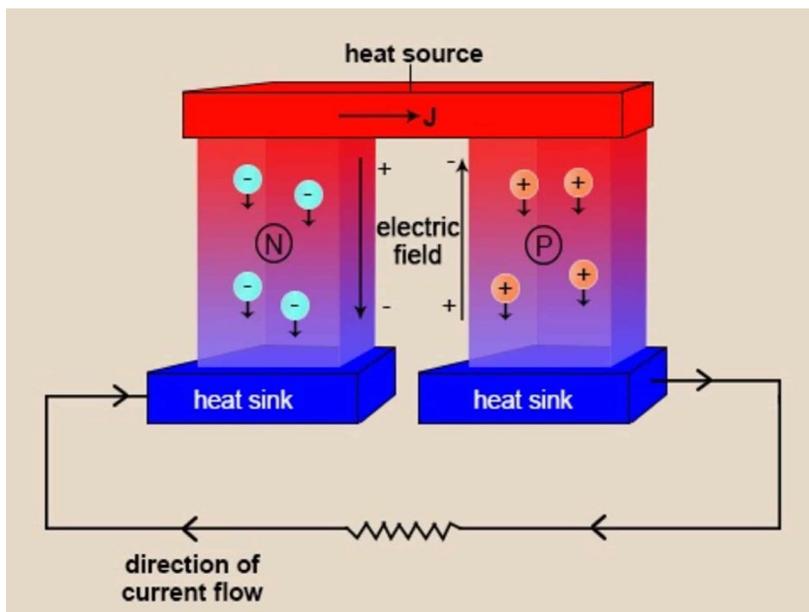p-type material to the n-type material.

Fig 10a. A Zno ThENG based on the Seebeck effect (top left) Schematic diagram of a single
Sb-doped ZnO micro belt NG. (bottom left) Calculated temperature distribution along a glass
substrate. (right) I-V characteristic of a fabricated NG.[39]

Fig 10b A π-type model to explain the working principle of ThENG[40].

7. Blue Energy and its harvesting using NG

As the futuristic growth of science and technology is confronting the dual challenge of energy crisis and carbon-pollution so renewable energy sources must be extensively explored and the use of fossil fuels should be restricted to a minimum.

Among the different renewable energy resources ocean energy is one of the least explored renewable energy sources on the earth. The total blue energy content of the Ocean was estimated to be 7.66×10^{13} W[41]. Both the thermal and mechanical energy can be harvested from the ocean. The temperature gradient that exists across the warm surface waters and the cool deeper waters can be utilized to generate thermal energy and mechanical energy can be harvested from the tides, waves and currents of the ocean. Blue energy has several advantages over the other available renewable energy resources. Firstly, blue energy is invariant to weather, time of the day, or temperature[42]. Secondly, tides, waves and currents are predictable globally and more reliable than wind and solar energy. Finally, harvesting blue energy requires minimal use of land and small environmental interaction, thereby offering one of the most lenient techniques for large-scale, eco-friendly and sustainable electricity generation[43].

Among different NGs, TENG has a huge potential for harvesting blue energy[44]. TENG can effectively harvest blue energy even at frequencies < 5 Hz which is perfectly suitable to harvest energy from a low-frequency ocean wave[45]. Since the invention of TENG, much effort has been made to harvest blue energy via various designs of prototypes.

7.1 Water-involved TENG

In this type of TENG water is used as one of the triboelectric materials and liquid-solid contact electrification harvests the output energy (Fig 11). The first water-involved TENG was reported by Lin et al.[46] in 2013, where periodic contact and separation between water and polydimethylsiloxane (PDMS) pyramid array give rise to the output energy. The frequency response test revealed that the optimized power density is 50 mW/m^2 at 5 Hz. while the peak power density is nearly 0.13 W/m^2. Here, the water remaining on the PDMS array will affect the output power. To overcome this hurdle Lin et al.[47] modified their design and used superhydrophobic polytetrafluoroethylene (PTFE) in place of PDMS and could achieve an output power of 20 mW/cm^2. Later different kinds of polymer material with varied structures were employed by Zhu et al.[48] and Zhao et al.[49] for the fabrication of water involved TENG. By modification of the structures, they were able to achieve the output power up to 1.1 mW while initially; it was only 0.12 mW. When water flows through the air or an insulating tube, because of the contact with the air/solid surface, triboelectric charges will be induced on its surface and the water will contain the mechanical energy as well as the electrostatic energy. For harvesting the mechanical and electrostatic energies of flowing water, simultaneously, a dual-mode TENG was fabricated by Lin et al.[50] employing a superhydrophobic TiO$_2$ layer with hierarchical micro/nanostructures. Cheng et al.[51] developed a dual-mode TENG consisting of a disk-TENG part and a water-TENG part. The water-TENG was composed of 8 wheel blades covered by PTFE film to harvest the electrostatic energy from flowing water. Kinetic energy can be harvested through the rotational movement of disk-TENG caused by the flowing water. A hybrid TENG comprising interfacial electrification enabled TENG and an impact-TENG was developed by Su et al.[52] with an internal wavy-electrode structure to harvest mechanical energy and electrostatic energy from water. A novel cylinder-shaped structure TENG, based on contact electrification in-between water and PTFE filtration membranes, was proposed by Zhang et al.[53]. The

recommended device can achieve a short-circuit current of 1.5 µA and an open-circuit voltage of 12 V. Fluorinated ethylene propylene (FEP) nanowire-based TENG was proposed by Li et al.[54]. Due to the presence of nanowires the contact area had been significantly increased and thus more friction between polymer and water took place which in turn had produced an output current of 10 µA and an output voltage of 200 V. Shi et al.[55] proposed a buoy ball type symmetric spherical-shaped water-based TENG employing Al electrodes wrapped by Polytetrafluoroethylene (PTFE) thin film to produce the arbitrary directional and irregular water wave energy. A U-tube shaped TENG based on FEP was fabricated by Pan et al.[56] to harvest blue energy. A further modified structure with sandwich-like water-FEP U-tube TENG was developed to harvest blue energy with a power density of 2.04 W/m^3. Xu et al.[57] developed a tower-shaped TENG which was composed of multiple units, made of PETF balls and nylon film-coated arc surface, connected in parallel. The tower-shaped TENG containing 10 units in parallel can harvest blue energy from random directions with a power density of 10.6 W/m^3. Blue energy harvesting by regular fabric using a nontoxic and low-cost hydrophobic coating of Hydrophobic Cellulose Oleoyl Ester Nanoparticles (HCOENPs) was demonstrated by Xiong et al.[58]. Li et al.[59] designed and fabricated a buoy-like liquid-solid contact-based TENG which magnifies the output energy via increased friction by 48.7 times, in comparison to the solid-solid contact-based TENG having an identical area. Nie et al.[60] developed a novel liquid-liquid TENG that can harvest blue energy with a peak power of 137.4 nW by passing a liquid droplet through a freely suspended liquid membrane.
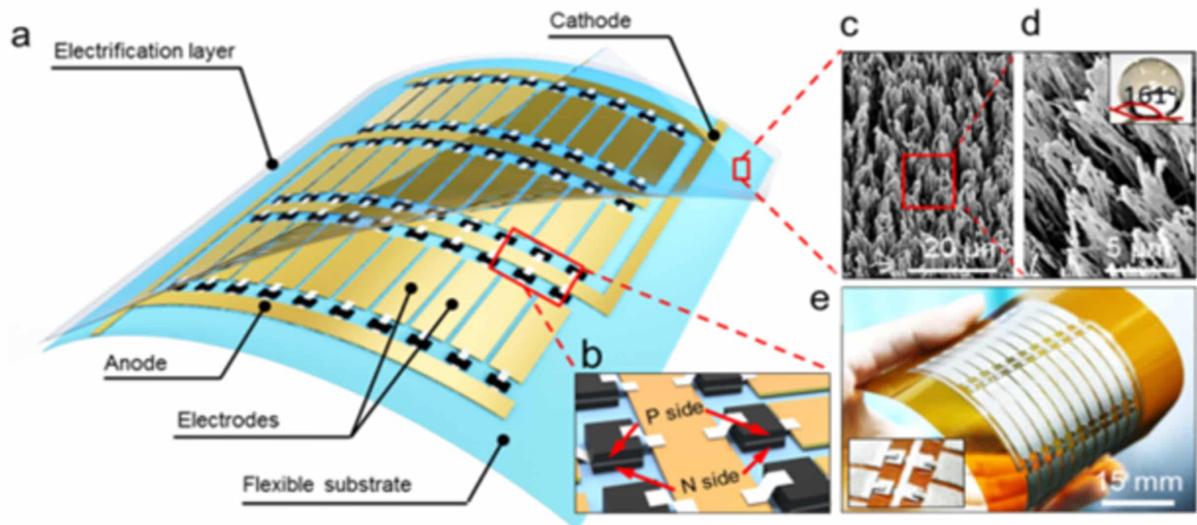
Fig. 11. Structure of a networked integrated triboelectric nanogenerator (NI-TENG). (a) Schematic diagram of a NI-TENG. (b) Enlarged sketch of the arrayed bridge rectifiers; c) SEM image of the PTFE nanowires on the electrification layer. (d) Enlarged view of the nanowires, inset: contact angle on the nanostructured surface. (e) Picture of a bendable as-fabricated NI-TENG, inset: Enlarged view of the rectifying diodes. [61]

However, one major problem of water involved TENG is that the seawater can corrode polymer films via direct contact. Thus to overcome this problem researchers are intending to use fully enclosed TENG to harvest blue energy as discussed in the next subsection.

7.2 Non-water-involved TENG

In general, a waterproof layer is employed in the non-water-involved TENG (Fig 12). In July 2013, the first non-water-involved TENG was fabricated in a fully enclosed spherical shell by Yang et al. [62] using PTFE-polyamide (PA) film. A suspended three-dimensional spiral structured TENG was designed and fabricated by Hu et al. [63] for harvesting blue energy with a power density of 2.76 W/m^2. Wen et al. [64] developed a wavy-structured based TENG

comprised a Cu-Kapton-Cu film sandwiched in-between two flat nanostructured PTFE to collect blue energy with a power density of 0.4 W/m^2. Zhang et al.[65] further modified the structure and designed a regular dodecahedron device containing 12 sets of wavy-structured TENGs. Each TENG consists of a wavy-structured Cu-Kapton-Cu film sandwiched between two flat nanostructured FEP thin films. This TENG can harvest 0.64 MW power from a 1 km^2 surface area of water. Chen et al.[66] created a network of TENGs that can generate an average output power of 1.15 MW from a 1 km^2 surface area. A water treatment system was designed by Jiang et al.[67] employing a TENG which will harvest energy from the water itself. Xu et al.[68] designed an array of integrated TENG based on air-driven membrane structures with an optimized peak power density of 13.23 W/ m^3. Here air pressure was used to distribute and transfer harvested water wave energy and a spring-levitated oscillator helped it to achieve resonance in a short period. Jiang et al.[69] developed a spring-assisted TENG comprising two Cu-PTFE-based TENGs connected through spring. They found that due to the presence of the spring, the energy conversion efficiency can be augmented by 150.3%. The spring-based structure was modified by Xiao et al.[70] by employing silicone rubber/carbon black composite electrode which can provide better contact with the dielectric film. While triggered by the water waves it can generate output with a maximum power density of 2.40 W/m^3. Later they fabricated a TENG array consisting of four spherical TENGs[71] based on the spring-assisted multilayered structure to harvest power up to 15.97 mW. A box-shaped TENG consisting of wavy-structured Cu-Kapton-Cu and FEP films, with an enclosed metal ball, was designed and fabricated by Jiang et al.[72]. Later they optimised the charging behaviour under the enclosed ball collision and direct water wave impact[73]. They reported that in case of the direct water wave impact, deformation depth governs the energy storage efficiency, whereas for the enclosed ball collision the size of the ball is responsible for energy storage efficiency. A ball-shell structured TENG network was developed by Xu et

al.[74] with flexible connections. They found that the charge output of the coupled units is 10 times more in comparison to that without coupling. Cheng et al.[75] devised a new methodology of soft-surface-contact based spherical TENG employing silicone rubber to maximize the transferred charge during the triboelectric effect by 10 folds in comparison to conventional PTFE based hard-contact TENG. A torus structured TENG enclosing a ball was fabricated by Liu et al.[76] which can harvest blue energy with a power density of 0.21 W/m^2. Self-assembly of a self-healable and reconfigurable TENG network was developed by Yang et al.[77] with an average power density of 8.69 W/m^3. A pendulum structured robust TENG was fabricated by Lin et al.[78] which can deliver frequency multiplied output. Zhong et al.[79] fabricated a TENG with an open book-like structure. Owing to its unique structure, many TENGs can be accommodated in a small area with a high packing density to harvest blue energy with a peak power density of 7.45 W/m^3. To harvest multidirectional blue energy, Lei et al.[80] designed a butterfly-shaped TENG using spring-assisted four-bar linkage to achieve a maximum output power density of 9.559 W/m^3. A bimodal, highly stretchable, superhydrophobic TENG was developed by Chen et al.[81] which was made of an ionic conductor and hierarchical micro-nano structures with self-cleaning properties. The proposed TENG can harvest blue energy with a power density of 0.36 mW. The principle of the pendulum was applied to fabricate a TENG with a compact disk-track structure to achieve a peak power density of 14.71 W/m^3 via an area contact mechanism. An oblate spheroidal TENG was designed and fabricated by Liu et al.[82] which is much superior compared to the traditional sphere shell and can harvest blue energy with a power density of 21.356 mW. The performance of spherical-shaped TENG was further improved by Liang et al.[83] using a spring-assisted multilayered structure with an integrated power management module (PMM) to control the harvested energy.
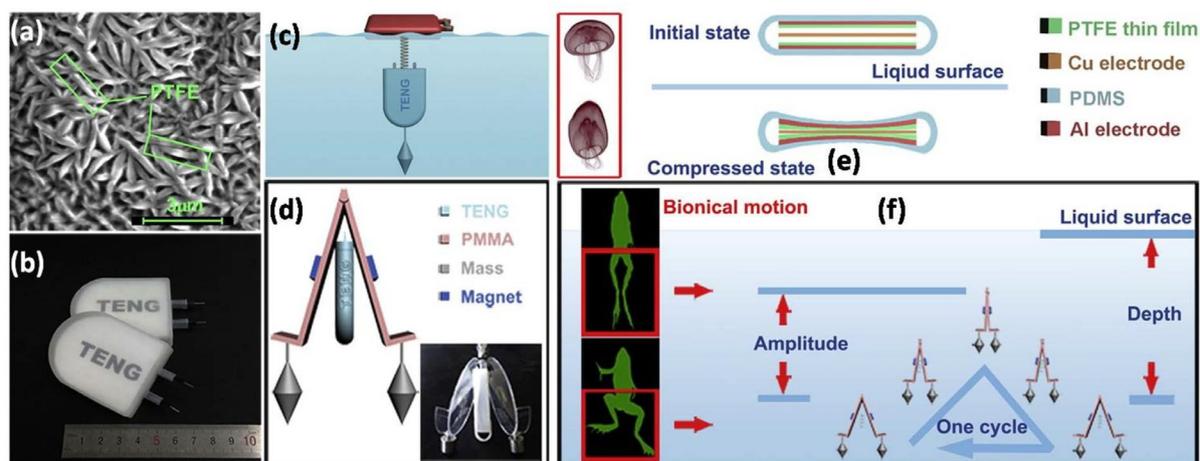
Fig 12. The structure and fabrication process of the bionic-jellyfish triboelectric nanogenerator (bjTENG). (a) SEM images of the tribo-material PTFE thin film, (b) digital image of bjTENG (c) Illustration of an application. (d) Schematic diagrams of the optimized structure (e) Working process of the interface self-powered fluctuation sensor (f) five steps working process of the undersea bjTENG[84].

8. Summary and perspective

Mankind moves towards modernization of every aspect of technology and modernization needs energy. However, the conventional energies are limited and thus the continuous proliferation of technological progress necessitates an alternative one. The process to harvest alternative energy should be inexpensive, self-powered, eco-friendly, sustainable and preferably maintenance free for a seamless growth of technology. The evolution of nanogenerator in 2006 created a revolution in harvesting alternative energy from the ambient environment by various means. The four physical processes, namely, piezoelectric effect, triboelectric effect, pyroelectric effect, thermoelectric effects were employed in the nanogenerators to harvest energy. The rapid growth in the development of the different nanogenerators has marked the foundation for self-powered modern electronic systems. However, to harvest ambient energy like blue energy on a large scale, a nanogenerator with

long durability, efficient energy conversion and enhanced output power density is desirable.

The futuristic research on nanogenerators should be focused on the efficient integration

methodology and improved power management module.

[1] 'BP Energy Outlook | Energy Economics | Home', BP global, accessed 18 March 2020, https://www.bp.com/en/global/corporate/energy-economics/energy-outlook.html.

[2] 'Home', BP global, accessed 27 May 2020, https://www.bp.com/en/global/corporate.html.

[3] F. Gazeau et al., 'Energy Conversion in Ferrofluids: Magnetic Nanoparticles as Motors or Generators', *Physical Review E* 56, no. 1 (1 July 1997): 614–18, https://doi.org/10.1103/PhysRevE.56.614.

[4] Zhong Lin Wang, 'On Maxwell's Displacement Current for Energy and Sensors: The Origin of Nanogenerators', *Materials Today* 20, no. 2 (1 March 2017): 74–82, https://doi.org/10.1016/j.mattod.2016.12.001.

[5] Zhong Lin Wang, 'On the First Principle Theory of Nanogenerators from Maxwell's Equations', *Nano Energy* 68 (1 February 2020): 104272, https://doi.org/10.1016/j.nanoen.2019.104272.

[6] Ju-Hyuck Lee et al., 'All-in-One Energy Harvesting and Storage Devices', *Journal of Materials Chemistry A* 4, no. 21 (24 May 2016): 7983–99, https://doi.org/10.1039/C6TA01229A.

[7] Zhong Lin Wang, 'Nanogenerators, Self-Powered Systems, Blue Energy, Piezotronics and Piezo-Phototronics – A Recall on the Original Thoughts for Coining These Fields', *Nano Energy* 54 (1 December 2018): 477–83, https://doi.org/10.1016/j.nanoen.2018.09.068.

[8] Abdulrahman Jbaily and Ronald W. Yeung, 'Piezoelectric Devices for Ocean Energy: A Brief Survey', *Journal of Ocean Engineering and Marine Energy* 1, no. 1 (1 February 2015): 101–18, https://doi.org/10.1007/s40722-014-0008-9.

[9] Zhong Lin Wang and Jinhui Song, 'Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays', *Science* 312, no. 5771 (14 April 2006): 242–46, https://doi.org/10.1126/science.1124005.

[10] Guang Zhu et al., 'Flexible High-Output Nanogenerator Based on Lateral ZnO Nanowire Array', *Nano Letters* 10, no. 8 (11 August 2010): 3151–55, https://doi.org/10.1021/nl101973h.

[11] Youfan Hu et al., 'Self-Powered System with Wireless Data Transmission', *Nano Letters* 11, no. 6 (8 June 2011): 2572–77, https://doi.org/10.1021/nl201505c.

[12] Sridhar Sripadmanabhan Indira et al., 'Nanogenerators as a Sustainable Power Source: State of Art, Applications, and Challenges', *Nanomaterials* 9, no. 5 (May 2019): 773, https://doi.org/10.3390/nano9050773.

[13] Horim Lee et al., 'Pure Piezoelectricity Generation by a Flexible Nanogenerator Based on Lead Zirconate Titanate Nanofibers', *ACS Omega* 4, no. 2 (28 February 2019): 2610–17, https://doi.org/10.1021/acsomega.8b03325.

[14] Saqib Siddiqui et al., 'High-Performance Flexible Lead-Free Nanocomposite Piezoelectric Nanogenerator for Biomechanical Energy Harvesting and Storage', *Nano Energy* 15 (1 July 2015): 177–85, https://doi.org/10.1016/j.nanoen.2015.04.030.

[15] Jasleen Kaur and Harminder Singh, 'Synthesis and Fabrication of Zinc Oxide Nanostrands Based Piezoelectric Nanogenerator', *Journal of Materials Science: Materials in Electronics* 30, no. 5 (1 March 2019): 4437–45, https://doi.org/10.1007/s10854-019-00732-3.

[16] Jing Yan et al., 'Performance Enhancements in Poly(Vinylidene Fluoride)-Based Piezoelectric Nanogenerators for Efficient Energy Harvesting', *Nano Energy* 56 (1 February 2019): 662–92, https://doi.org/10.1016/j.nanoen.2018.12.010.

[17] Yi-Feng Lin et al., 'Piezoelectric Nanogenerator Using CdS Nanowires', *Applied Physics Letters* 92, no. 2 (14 January 2008): 022105, https://doi.org/10.1063/1.2831901.

[18] Wenzhuo Wu et al., 'Piezoelectricity of Single-Atomic-Layer MoS2 for Energy Conversion and Piezotronics', *Nature* 514, no. 7523 (October 2014): 470–74, https://doi.org/10.1038/nature13792.

[19] Roger G. Horn and Douglas T. Smith, 'Contact Electrification and Adhesion Between Dissimilar Materials', *Science* 256, no. 5055 (17 April 1992): 362–64, https://doi.org/10.1126/science.256.5055.362.

[20] R. G. Horn, D. T. Smith, and A. Grabbe, 'Contact Electrification Induced by Monolayer Modification of a Surface and Relation to Acid–Base Interactions', *Nature* 366, no. 6454 (December 1993): 442–43, https://doi.org/10.1038/366442a0.

[21] Jun Peng, Stephen Dongmin Kang, and G. Jeffrey Snyder, 'Optimization Principles and the Figure of Merit for Triboelectric Generators', *Science Advances* 3, no. 12 (1 December 2017): eaap8576, https://doi.org/10.1126/sciadv.aap8576.

[22] Feng-Ru Fan, Zhong-Qun Tian, and Zhong Lin Wang, 'Flexible Triboelectric Generator', *Nano Energy* 1, no. 2 (1 March 2012): 328–34, https://doi.org/10.1016/j.nanoen.2012.01.004.

[23]Feng-Ru Fan et al., 'Transparent Triboelectric Nanogenerators and Self-Powered Pressure Sensors Based on Micropatterned Plastic Films', *Nano Letters* 12, no. 6 (13 June 2012): 3109–14, https://doi.org/10.1021/nl300988z.

[24]Guang Zhu et al., 'Linear-Grating Triboelectric Generator Based on Sliding Electrification', *Nano Letters* 13, no. 5 (8 May 2013): 2282–89, https://doi.org/10.1021/nl4008985.

[25]Ya Yang et al., 'Single-Electrode-Based Sliding Triboelectric Nanogenerator for Self-Powered Displacement Vector Sensor System', *ACS Nano* 7, no. 8 (27 August 2013): 7342–51, https://doi.org/10.1021/nn403021m.

[26]Sihong Wang et al., 'Freestanding Triboelectric-Layer-Based Nanogenerators for Harvesting Energy from a Moving Object or Human Motion in Contact and Non-Contact Modes', *Advanced Materials* 26, no. 18 (2014): 2818–24, https://doi.org/10.1002/adma.201305303.

[27]Peng Bai et al., 'Integrated Multilayered Triboelectric Nanogenerator for Harvesting Biomechanical Energy from Human Motions', *ACS Nano* 7, no. 4 (23 April 2013): 3713–19, https://doi.org/10.1021/nn4007708.

[28]Yannan Xie et al., 'Grating-Structured Freestanding Triboelectric-Layer Nanogenerator for Harvesting Mechanical Energy at 85% Total Conversion Efficiency', *Advanced Materials* 26, no. 38 (2014): 6599–6607, https://doi.org/10.1002/adma.201402428.

[29]Changsheng Wu et al., 'Triboelectric Nanogenerator: A Foundation of the Energy for the New Era', *Advanced Energy Materials* 9, no. 1 (2019): 1802906, https://doi.org/10.1002/aenm.201802906.

[30]Vladislav Slabov et al., 'Natural and Eco-Friendly Materials for Triboelectric Energy Harvesting', *Nano-Micro Letters* 12, no. 1 (28 January 2020): 42, https://doi.org/10.1007/s40820-020-0373-y.

[31]Dong Wook Kim et al., 'Material Aspects of Triboelectric Energy Generation and Sensors', *NPG Asia Materials* 12, no. 1 (24 January 2020): 1–17, https://doi.org/10.1038/s41427-019-0176-0.

[32]A. S. Bhalla and R. E. Newnham, 'Primary and Secondary Pyroelectricity', *Physica Status Solidi (a)* 58, no. 1 (1980): K19–24, https://doi.org/10.1002/pssa.2210580146.

[33]Ya Yang et al., 'Pyroelectric Nanogenerators for Harvesting Thermoelectric Energy', *Nano Letters* 12, no. 6 (13 June 2012): 2833–38, https://doi.org/10.1021/nl3003039.

[34]Sidney B. Lang, 'Pyroelectricity: From Ancient Curiosity to Modern Imaging Tool', *Physics Today* 58, no. 8 (1 August 2005): 31–36, https://doi.org/10.1063/1.2062916.

[35]Ya Yang et al., 'Flexible Pyroelectric Nanogenerators Using a Composite Structure of Lead-Free KNbO3 Nanowires', *Advanced Materials* 24, no. 39 (2012): 5357–62, https://doi.org/10.1002/adma.201201414.

[36]R. Ghane-Motlagh and P. Woias, 'A Pyroelectric Thin Film of Oriented Triglycine Sulfate Nano-Crystals for Thermal Energy Harvesting', *Smart Materials and Structures* 28, no. 10 (August 2019): 104002, https://doi.org/10.1088/1361-665X/ab3910.

[37] C. R. Bowen et al., 'Pyroelectric Materials and Devices for Energy Harvesting Applications', *Energy & Environmental Science* 7, no. 12 (12 November 2014): 3836–56, https://doi.org/10.1039/C4EE01759E.

[38]Krishna Veni Selvan, Md Nazibul Hasan, and Mohamed Sultan Mohamed Ali, 'Methodological Reviews and Analyses on the Emerging Research Trends and Progresses of Thermoelectric Generators', *International Journal of Energy Research* 43, no. 1 (2019): 113–40, https://doi.org/10.1002/er.4206.

[39]Ya Yang et al., 'Thermoelectric Nanogenerators Based on Single Sb-Doped ZnO Micro/Nanobelts', *ACS Nano* 6, no. 8 (28 August 2012): 6984–89, https://doi.org/10.1021/nn302481p.

[40]'A Simple Explanation of Seebeck Effect With Its Applications', *Science Struck* (blog), 19 December 2014, https://sciencestruck.com/seebeck-effect-with-applications.

[41] Omar Ellabban, Haitham Abu-Rub, and Frede Blaabjerg, 'Renewable Energy Resources: Current Status, Future Prospects and Their Enabling Technology', *Renewable and Sustainable Energy Reviews* 39 (1 November 2014): 748–64, https://doi.org/10.1016/j.rser.2014.07.113.

[42] António F. de O. Falcão, 'Wave Energy Utilization: A Review of the Technologies', *Renewable and Sustainable Energy Reviews* 14, no. 3 (1 April 2010): 899–918, https://doi.org/10.1016/j.rser.2009.11.003.

[43] Gouri S. Bhuyan, 'World-Wide Status for Harnessing Ocean Renewable Resources', in *IEEE PES General Meeting*, 2010, 1–3, https://doi.org/10.1109/PES.2010.5589292.

[44] Zhong Lin Wang, 'Triboelectric Nanogenerators as New Energy Technology and Self-Powered Sensors – Principles, Problems and Perspectives', *Faraday Discussions* 176, no. 0 (6 March 2015): 447–58, https://doi.org/10.1039/C4FD00159A.

[45] Yunlong Zi et al., 'Harvesting Low-Frequency (<5 Hz) Irregular Mechanical Energy: A Possible Killer Application of Triboelectric Nanogenerator', *ACS Nano* 10, no. 4 (26 April 2016): 4797–4805, https://doi.org/10.1021/acsnano.6b01569.

[46] Zong-Hong Lin et al., 'Water–Solid Surface Contact Electrification and Its Use for Harvesting Liquid-Wave Energy', *Angewandte Chemie International Edition* 52, no. 48 (2013): 12545–49, https://doi.org/10.1002/anie.201307249.

[47] Zong-Hong Lin et al., 'Harvesting Water Drop Energy by a Sequential Contact-Electrification and Electrostatic-Induction Process', *Advanced Materials* 26, no. 27 (2014): 4690–96, https://doi.org/10.1002/adma.201400373.

[48] Guang Zhu et al., 'Harvesting Water Wave Energy by Asymmetric Screening of Electrostatic Charges on a Nanostructured Hydrophobic Thin-Film Surface', *ACS Nano* 8, no. 6 (24 June 2014): 6031–37, https://doi.org/10.1021/nn5012732.

[49] Xue Jiao Zhao et al., 'Triboelectric Charging at the Nanostructured Solid/Liquid Interface for Area-Scalable Wave Energy Conversion and Its Use in Corrosion Protection', *ACS Nano* 9, no. 7 (28 July 2015): 7671–77, https://doi.org/10.1021/acsnano.5b03093.

[50] Zong-Hong Lin et al., 'Dual-Mode Triboelectric Nanogenerator for Harvesting Water Energy and as a Self-Powered Ethanol Nanosensor', *ACS Nano* 8, no. 6 (24 June 2014): 6440–48, https://doi.org/10.1021/nn501983s.

[51] Gang Cheng et al., 'Simultaneously Harvesting Electrostatic and Mechanical Energies from Flowing Water by a Hybridized Triboelectric Nanogenerator', *ACS Nano* 8, no. 2 (25 February 2014): 1932–39, https://doi.org/10.1021/nn406565k.

[52] Yuanjie Su et al., 'Hybrid Triboelectric Nanogenerator for Harvesting Water Wave Energy and as a Self-Powered Distress Signal Emitter', *Nano Energy* 9 (1 October 2014): 186–95, https://doi.org/10.1016/j.nanoen.2014.07.006.

[53] Xiaolong Zhang et al., 'Liquid–Solid Contact Triboelectrification and Its Use in Self-Powered Nanosensor for Detecting Organics in Water', *Nano Energy* 30 (1 December 2016): 321–29, https://doi.org/10.1016/j.nanoen.2016.10.025.

[54] Xiaoyi Li et al., 'A Nanowire Based Triboelectric Nanogenerator for Harvesting Water Wave Energy and Its Applications', *APL Materials* 5, no. 7 (6 March 2017): 074104, https://doi.org/10.1063/1.4977216.

[55] Qiongfeng Shi et al., 'Self-Powered Triboelectric Nanogenerator Buoy Ball for Applications Ranging from Environment Monitoring to Water Wave Energy Farm', *Nano Energy* 40 (1 October 2017): 203–13, https://doi.org/10.1016/j.nanoen.2017.08.018.

[56] Lun Pan et al., 'Liquid-FEP-Based U-Tube Triboelectric Nanogenerator for Harvesting Water-Wave Energy', *Nano Research* 11, no. 8 (1 August 2018): 4062–73, https://doi.org/10.1007/s12274-018-1989-9.

[57] Minyi Xu et al., 'High Power Density Tower-like Triboelectric Nanogenerator for Harvesting Arbitrary Directional Water Wave Energy', *ACS Nano* 13, no. 2 (26 February 2019): 1932–39, https://doi.org/10.1021/acsnano.8b08274.

[58] Jiaqing Xiong et al., 'Wearable All-Fabric-Based Triboelectric Generator for Water Energy Harvesting', *Advanced Energy Materials* 7, no. 21 (2017): 1701243, https://doi.org/10.1002/aenm.201701243.

[59] Xiaoyi Li et al., 'Networks of High Performance Triboelectric Nanogenerators Based on Liquid–Solid Interface Contact Electrification for Harvesting Low-Frequency Blue Energy', *Advanced Energy Materials* 8, no. 21 (2018), https://doi.org/10.1002/aenm.201800705.

[60] Jinhui Nie et al., 'Power Generation from the Interaction of a Liquid Droplet and a Liquid Membrane', *Nature Communications* 10, no. 1 (22 May 2019): 2264, https://doi.org/10.1038/s41467-019-10232-x.

[61] Xue Jiao Zhao et al., 'Highly Adaptive Solid–Liquid Interfacing Triboelectric Nanogenerator for Harvesting Diverse Water Wave Energy', *ACS Nano* 12, no. 5 (22 May 2018): 4280–85, https://doi.org/10.1021/acsnano.7b08716.

[62] Ya Yang et al., 'Fully Enclosed Triboelectric Nanogenerators for Applications in Water and Harsh Environments', *Advanced Energy Materials* 3, no. 12 (2013): 1563–68, https://doi.org/10.1002/aenm.201300376.

[63] Youfan Hu et al., 'Triboelectric Nanogenerator Built on Suspended 3D Spiral Structure as Vibration and Positioning Sensor and Wave Energy Harvester', *ACS Nano* 7, no. 11 (26 November 2013): 10424–32, https://doi.org/10.1021/nn405209u.

[64] Xiaonan Wen et al., 'Harvesting Broadband Kinetic Impact Energy from Mechanical Triggering/Vibration and Water Waves', *ACS Nano* 8, no. 7 (22 July 2014): 7405–12, https://doi.org/10.1021/nn502618f.

[65] Li Min Zhang et al., 'Multilayer Wavy-Structured Robust Triboelectric Nanogenerator for Harvesting Water Wave Energy', *Nano Energy* 22 (1 April 2016): 87–94, https://doi.org/10.1016/j.nanoen.2016.01.009.

[66] Jun Chen et al., 'Networks of Triboelectric Nanogenerators for Harvesting Water Wave Energy: A Potential Approach toward Blue Energy', *ACS Nano* 9, no. 3 (24 March 2015): 3324–31, https://doi.org/10.1021/acsnano.5b00534.

[67] Qianwen Jiang et al., 'Self-Powered Electrochemical Water Treatment System for Sterilization and Algae Removal Using Water Wave Energy', *Nano Energy* 18 (1 November 2015): 81–88, https://doi.org/10.1016/j.nanoen.2015.09.017.

[68] Liang Xu et al., 'Integrated Triboelectric Nanogenerator Array Based on Air-Driven Membrane Structures for Water Wave Energy Harvesting', *Nano Energy* 31 (1 January 2017): 351–58, https://doi.org/10.1016/j.nanoen.2016.11.037.

[69] Tao Jiang et al., 'Spring-Assisted Triboelectric Nanogenerator for Efficiently Harvesting Water Wave Energy', *Nano Energy* 31 (1 January 2017): 560–67, https://doi.org/10.1016/j.nanoen.2016.12.004.

[70] Tian Xiao Xiao et al., 'Silicone-Based Triboelectric Nanogenerator for Water Wave Energy Harvesting', *ACS Applied Materials & Interfaces* 10, no. 4 (31 January 2018): 3616–23, https://doi.org/10.1021/acsami.7b17239.

[71] Tian Xiao Xiao et al., 'Spherical Triboelectric Nanogenerators Based on Spring-Assisted Multilayered Structure for Efficient Water Wave Energy Harvesting', *Advanced Functional Materials* 28, no. 35 (2018): 1802634, https://doi.org/10.1002/adfm.201802634.

[72] Tao Jiang et al., 'Structural Optimization of Triboelectric Nanogenerator for Harvesting Water Wave Energy', *ACS Nano* 9, no. 12 (22 December 2015): 12562–72, https://doi.org/10.1021/acsnano.5b06372.

[73] Yanyan Yao et al., 'Charging System Optimization of Triboelectric Nanogenerator for Water Wave Energy Harvesting and Storage', *ACS Applied Materials & Interfaces* 8, no. 33 (24 August 2016): 21398–406, https://doi.org/10.1021/acsami.6b07697.

[74] Liang Xu et al., 'Coupled Triboelectric Nanogenerator Networks for Efficient Water Wave Energy Harvesting', *ACS Nano* 12, no. 2 (27 February 2018): 1849–58, https://doi.org/10.1021/acsnano.7b08674.

[75] Ping Cheng et al., 'Largely Enhanced Triboelectric Nanogenerator for Efficient Harvesting of Water Wave Energy by Soft Contacted Structure', *Nano Energy* 57 (1 March 2019): 432–39, https://doi.org/10.1016/j.nanoen.2018.12.054.

[76] Wenbo Liu et al., 'Torus Structured Triboelectric Nanogenerator Array for Water Wave Energy Harvesting', *Nano Energy* 58 (1 April 2019): 499–507, https://doi.org/10.1016/j.nanoen.2019.01.088.

[77] Xiaodan Yang et al., 'Macroscopic Self-Assembly Network of Encapsulated High-Performance Triboelectric Nanogenerators for Water Wave Energy Harvesting', *Nano Energy* 60 (1 June 2019): 404–12, https://doi.org/10.1016/j.nanoen.2019.03.054.

[78] Zhiming Lin et al., 'Super-Robust and Frequency-Multiplied Triboelectric Nanogenerator for Efficient Harvesting Water and Wind Energy', *Nano Energy* 64 (1 October 2019): 103908, https://doi.org/10.1016/j.nanoen.2019.103908.

[79] Wei Zhong et al., 'Open-Book-like Triboelectric Nanogenerators Based on Low-Frequency Roll–Swing Oscillators for Wave Energy Harvesting', *Nanoscale* 11, no. 15 (11 April 2019): 7199–7208, https://doi.org/10.1039/C8NR09978B.

[80] Rui Lei et al., 'Butterfly-Inspired Triboelectric Nanogenerators with Spring-Assisted Linkage Structure for Water Wave Energy Harvesting', *Advanced Materials Technologies* 4, no. 3 (2019): 1800514, https://doi.org/10.1002/admt.201800514.

[81] Xiaoliang Chen et al., 'Transparent and Stretchable Bimodal Triboelectric Nanogenerators with Hierarchical Micro-Nanostructures for Mechanical and Water Energy Harvesting', *Nano Energy* 64 (1 October 2019): 103904, https://doi.org/10.1016/j.nanoen.2019.103904.

[82] Guanlin Liu et al., 'Oblate Spheroidal Triboelectric Nanogenerator for All-Weather Blue Energy Harvesting', *Advanced Energy Materials* 9, no. 26 (2019): 1900801, https://doi.org/10.1002/aenm.201900801.

[83] Xi Liang et al., 'Spherical Triboelectric Nanogenerator Integrated with Power Management Module for Harvesting Multidirectional Water Wave Energy', *Energy & Environmental Science* 13, no. 1 (21 January 2020): 277–85, https://doi.org/10.1039/C9EE03258D.

[84] Bao Dong Chen et al., 'Water Wave Energy Harvesting and Self-Powered Liquid-Surface Fluctuation Sensing Based on Bionic-Jellyfish Triboelectric Nanogenerator', *Materials Today* 21, no. 1 (1 January 2018): 88–97, https://doi.org/10.1016/j.mattod.2017.10.006.