4-2021

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Recommended Citation

Shawon, S. M. A. Z., Sun, A. X., Vega, V. S., Chowdhury, B. D., Tran, P., Carballo, Z. D., Tolentino, J. A., Li, J., Rafaqut, M. S., Danti, S., & Uddin, M. J. (2021). Piezo-tribo dual effect hybrid nanogenerators for health monitoring. Nano Energy, 82, 105691. https://doi.org/10.1016/j.nanoen.2020.105691

Piezo-Tribo Dual Effect Hybrid Nanogenerators for Health Monitoring

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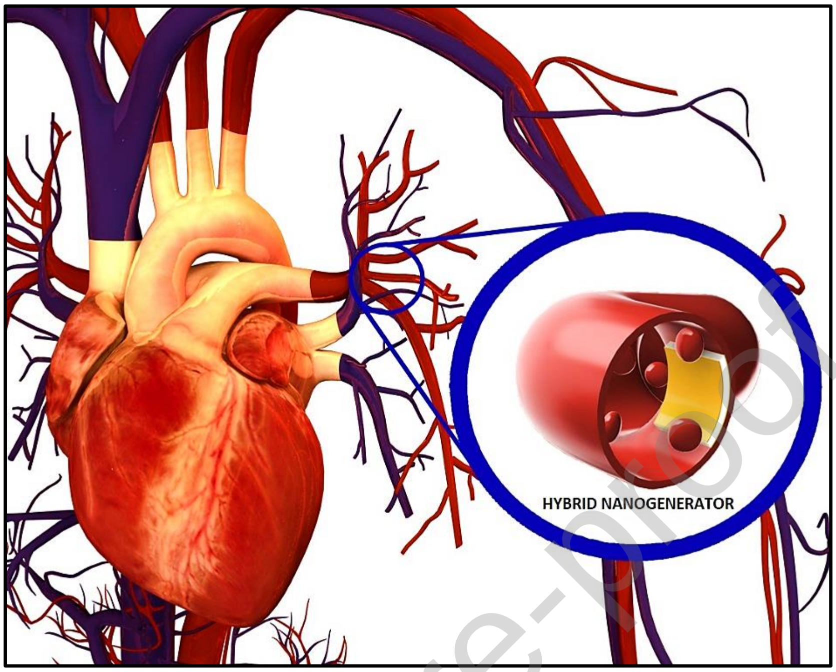
Abstract:

Over the years, nanogenerators for health monitoring have become more and more attractive as they provide a cost-effective and continuous way to successfully measure vital signs, physiological status, and environmental changes in/around a person. Using such sensors can positively affect the way healthcare workers diagnose and prevent life-threatening conditions. Recently, the dual piezo-tribological effect of hybrid nanogenerators (HBNGs) have become a subject of investigation, as they can provide a substantial amount of data, which is significant for healthcare. However, real-life exploitation of these HBNGs in health monitoring is still marginal. This review covers piezo-tribo dual-effect HBNGs that are used as sensors to measure the different movements and changes in the human body such as blood circulation, respiration, and muscle contractions. Piezo-Tribo dual-effect HBNGs are applicable within various healthcare settings as a means of powering noninvasive sensors, providing the capability of constant patient monitoring without interfering with the range of motion or comfort of the user. This review also intends to suggest future improvements in HBNGs. These include incorporating surface modification techniques, utilizing nanowires, nanoparticle technologies, and other means of chemical surface modifications. These improvements can contribute significantly in terms of the electrical output of the HBNGs and can enhance their prospects of applications in the field of health monitoring, as well as various in vitro/in vivo biomedical applications. While a promising option, improved HBNGs are still lacking. This review also discusses the technical issue which has prevented so far, the real use of these sensors.

Keywords: Hybrid Nanogenerator, Health Monitoring Sensor, Piezo-Tribo Dual Effect

Graphical Abstract:



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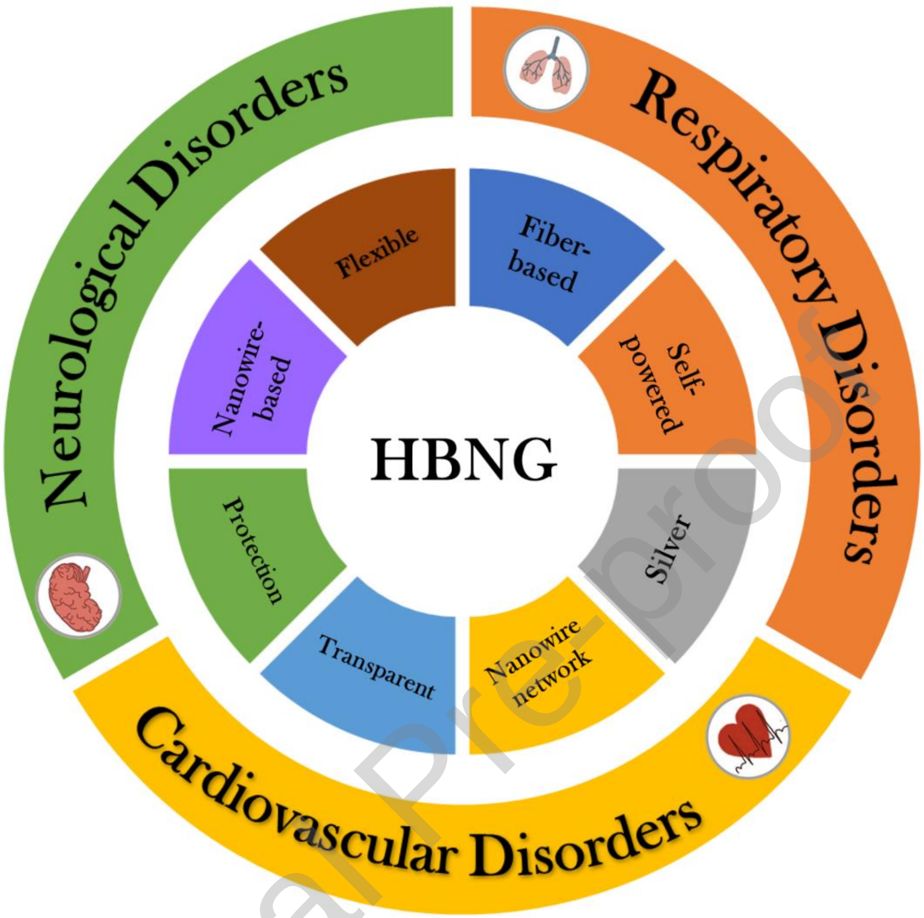
1. Introduction:

In recent years, the insistence for renewable energy has heightened as a result of energy cataclysm from exhausting resources, global warming caused by the greenhouse effect, and air pollution as a result of fossil fuel fragmentation that increasingly declined the quality of human life. Therefore, there has been an ongoing surge for new and ingenious research, seeking innovative forms of renewable energy due to its environmental benefits and impeccable multiuse performance, such as sensors, portable electronics, wearable devices, and wireless transport systems [1-8]. Extensive studies and efforts have been applied to the contribution of harvesting clean energy [9]. Advanced designs such as, effective energy conversion and storage instruments that produce sustainable energy have become products held at high regard in the medical field, as some distinct designs have been proved to be reliable sensors used for health monitors. Among the diversity of energy conversion apparatuses, nanogenerators have a promising capability to convert low-frequency mechanical energies to electrical energy through devices such as triboelectric nanogenerators (TENG) and piezoelectric nanogenerators (PENG). PENG-TENG hybrid nanogenerators have become very attractive in health monitoring due to its unlimited power capabilities. TENG and PENG are highly esteemed, due to their cost-effective structure and mechanically adept proficiency to harvest renewable energy; TENG has progressively been developed to seek extensively spread mechanical energy for independently powered sensors and systems utilized for a diversity of physical exerts [10-12]. Moreover, recent researches in the field of TENGs are constructing strategies to connect human beings with robots opening newer possibilities in the fields of artificial intelligence [13]. TENG has been established to produce more output power based on triboelectrification and electrostatic induction.

Studies are ongoing to enhance the performance of the nanogenerators. Combining both of the energy harvesting systems (piezoelectric and triboelectric) into a single device has been an efficient approach to harvest more energy and enhance the energy conversion efficiency to a higher level, than the single system composed of only piezoelectric or only triboelectric devices [14-19]. Yang et al., initially suggested the multi-effects coupled nanogenerator to attain a greater extent of energy from one main structure [1]. Combining both piezoelectric and triboelectric effects does not demand for any intricate alteration in the apparatus structure, but only asks for one of the materials in the triboelectric apparatus to have the piezoelectric elements. Triboelectric nanogenerator devices are constructed by two distinct dielectric surfaces that sputter when they come into contact with each other opposite charges generate and flow by conducting electrodes. Additionally, it has been concluded that when distance is created through separation of the conducting surfaces, a potential drop is created, thus free electrons will transport from one active electrode to another for an electrostatic field to be created. The triboelectric charges created will cease once the separation gap is closed and electrons will flow back into the system. In addition to contact-separation, the sliding of two surfaces over each other can also generate triboelectric charges [20]. Additionally, work by Pierre and Jacques Curie first depicted a mechanical stress-dependent surface charge generator [21]. This brought to light piezoelectricity, the production of electric charge by exerting mechanical pressure. Piezoelectricity is created by linear electromechanical connections between electrical and mechanical states in crystalline matter that lack symmetry inversion. Piezoelectric materials have proved to be capable of producing a diversity of structural responses. Zhu et al., developed a piezo-photonic self-powered photodetector composed of a CdS NR array. The piezo-photonic effect can be used to regulate photodetection and pressure detection [22, 23].

The amalgamation of a TENG with a PENG would deliver substantial conversions of energy under low frequency mechanical impetus. Furthermore, counteracting impedance between PENG and TENG is considered unchallenging, due to the wide range of availability of piezoelectric material and their easiness to be incorporated with triboelectric materials. Thus, HBNGs are generally able to achieve higher electrical output compared to PENG or TENG under similar intensities and frequencies of mechanical stimuli. So far, researchers have fabricated tribo-piezo hybrid nanogenerators with advanced features such as flexibility, transparency, improved output capability, and the ability to be weaved into cloth [16, 24-27]. The device proved to have a well and stable linear relationship between the piezoelectric output and the speed of vibrations which displays the sensor's sensibility. Both piezoelectric and triboelectric material in the HBNG, demonstrated to have high sensitivity and flexibility in terms of structure and functionality, both of which are ideally desired in health monitoring. Application of nanogenerators in healthcare field can aid in monitoring a patient's vitals and other physiological signs and facilitate the process of diagnosis. Furthermore, hybrid TENG and PENG can utilize different types of materials with complex structures to improve sensitivity. In Scheme 1.0, a schematic representation of several classifications of HBNGs can be found as well as different physiological disorders that can be monitored with these promising dual effect sensors.



Scheme 1.0: Schematic overview of Hybrid Nanogenerators classifications and various physiological disorders that can be monitored.

Although the primary goal of this work is to summarize the health monitoring capabilities of HBNG, other health applications of PENG and TENG nanogenerators will also be explored. Due to the interconnectedness of their fundamental design and working mechanism, HBNGs and PENG/TENG share similar functionalities, so their roles are (to a certain extent) interchangeable. In other words, for the same health monitoring application, a suitably designed HBNG may be able to achieve equal, if not better, results compared to that of a TENG. Thus, introducing the health monitoring applications of PENG and TENG can help identify other potential applications of HBNGs. Overall, nanogenerators can be used for health monitoring in two primary ways: directly and indirectly. Nanogenerators can be directly used as physiologic signal sensors or be used as a compact, portable, and long-term power source for other sensors that rely on external energy. Though the paper focuses on the former, the latter will also be included as the energy-supplying application of nanogenerators for other heath sensors should not be overlooked.

2. Triboelectricity in sensory application for human health monitoring:

With time, considerable progress has been made in the utilization of triboelectricity in sensory applications. Triboelectric nanogenerators (TENG) generally have higher output voltages compared to other electric nanogenerators, which allows them to efficiently harvest energy and act as sensors. Additionally, TENG is more adept at being used to sense frequency since triboelectricity generally requires a contact-separation or rubbing motion.

The concept of using human skin as a triboelectric material shows the potential ease of integrating triboelectricity in human health monitoring. Yang and coworkers described a triboelectric nanogenerator that would use human skin and micro pyramid structured PDMS film as the two triboelectric materials, in which such a generator could serve as a tactile sensor [28]. The tactile sensor proposed would allow for a skin pressure sensor that requires only half of the components of a traditional TENG as only one triboelectric material is needed in conjunction with the skin. The working mechanisms are illustrated in Figure 2.1. The application of the device in healthcare comes from its ability to produce an output proportional to the force exerted on it by a finger or hand. Thus, it can be used in the field of occupation or physical therapy as a grip and finger strength monitor. Figure 2.1 (c) shows one way to employ the device as a strength sensor, wrapping the device around a cylinder that the patient can grip. For patients undergoing rehabilitation after having a stroke, injury, or carpal tunnel syndrome, the device can be used as a therapeutic tool to help exercise grip. Such an idea is not new since occupational therapists commonly provide non-technological equipment to patients undergoing long-term rehabilitation that can be used as exercise equipment outside the clinic to recover various motor functions [29]. However, these tools are usually unable to give the patient any objective feedback regarding how much pressure they are exerting, making it difficult for specific targets to be set. Thus, the implementation of a TENG tactile sensor can allow for therapeutic goals to be established, such as how much force should be applied each time the patient practices their grip on the device. Objective feedback could also promote self-management and improve their adherence to exercise programs [29]. Additionally, the long-term use of the TENG can help monitor the patient's progress in rehabilitation, tracking any changes in the patient's average gripping strength over time. Compared to other pressure sensors, the TENG requires inexpensive materials and is highly portable, two factors would allow form them to be easily provided to and taken home by the patient.

Furthermore, triboelectricity can offer unique sensory capabilities. In that same 2019 study, a triboelectric nanogenerator, modified with a polyethyleneimine film covering on the friction surface, was used as a carbon dioxide gas sensor to a range of 12,000 ppm [30]. The device uses chemical reactions between CO_2 and amine groups in the polyethyleneimine film, which changes its electroconductivity to monitor CO_2 levels. The research indicates potential for TENG generator to detect CO_2 in the blood to be fabricated, which would be extremely valuable in the healthcare field, namely for respiratory care.

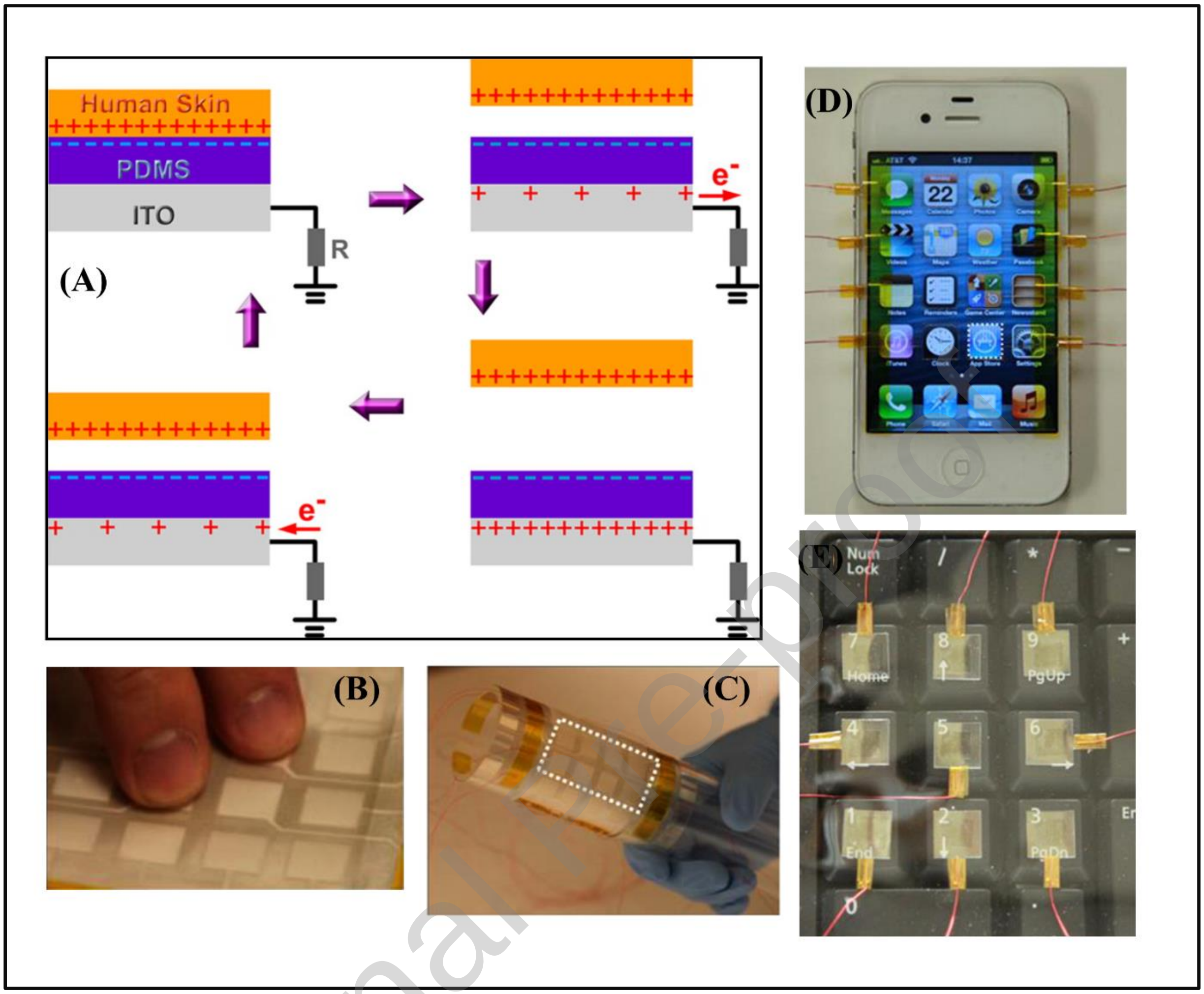


Figure 2.1: (A) The electricity generating cycle for TENG through contact electrification between PDMS and human skin, (B) small squares of this TENG has been organized into a grid to map out the exact location of pressure by finger pressing, (C) this flexible grid is attached to an acrylic tube to measure grip strength, (D) 1 cm x 1 cm TENG cubes attached to the screen of a cellphone, also (E) attached to the number pad, in order to harvest energy from daily cellphone activities.

In 2014, Bai et al. presented a membrane-based triboelectric sensor that was able to detect air pressure changes with a resolution of 0.34 Pa and 0.16 Pa [31]. These nanogenerators being integrated with signal processing units, are easily able to conform to the curvilinear shape of the skin and collect information such pulse, respiration, heart beats and joint motion. Thus, can take part in assessing health conditions and claimed to be used a human health monitoring self-powered device. In a similar fashion, TENG was proposed to detect displacements of the basilar membrane of the cochlea and transform them into electric signal, so as to act as a wireless cochlear implant [32, 33]

Figure 2.2 (a) illustrates the schematic diagram of a multilayered membrane-based triboelectric sensor (M-TES) and Figure 2.2 (b) depicts the device with a swollen latex membrane. Here the Latex membrane and the Fluorinated Ethylene Propylene film (FEP) are used as the two different triboelectric material due to the difference in their triboelectric polarities. When these two materials are attached on an acrylic sheet with two copper electrodes, this device produced electrical output with pressure changing variations. An air channel is also introduced to regain the latex membrane its initial state (separated from the FEP film). Figure 2.2 (c-f) depicts the operation principle. With the alternating constant contact and separation between the two triboelectric materials, the oscillating voltage output is produced. From Figure 2.2 (g-h), it is found that changing of 7.1 KPa air pressure at a frequency of 0.3 Hz produced 14.5 V. The electrical signal maximized to 20.4 V when the air pressure changes to 9.4 KPa, which is because a larger ΔP results in more deformation and separation of the latex membrane from the FEP film. The device reaches its saturation point at ΔP 9.9 KPa, the elastic limit of the latex membrane. Beyond this point, the triboelectric charges on the latex membrane surface do not have significant effects on the electron distribution around the electrodes [34].

The sensor has many applications in human health monitoring. As demonstrated in the study, an airbag can be attached to the abdomen of a patient and as the patient breathes, the pressure in the airbag changes and can be detected by the sensor, allowing for respiratory monitoring. A similar, smaller air-filled device attached to the chest even allowed for the heart to be monitored due the sensor's sensitivity.

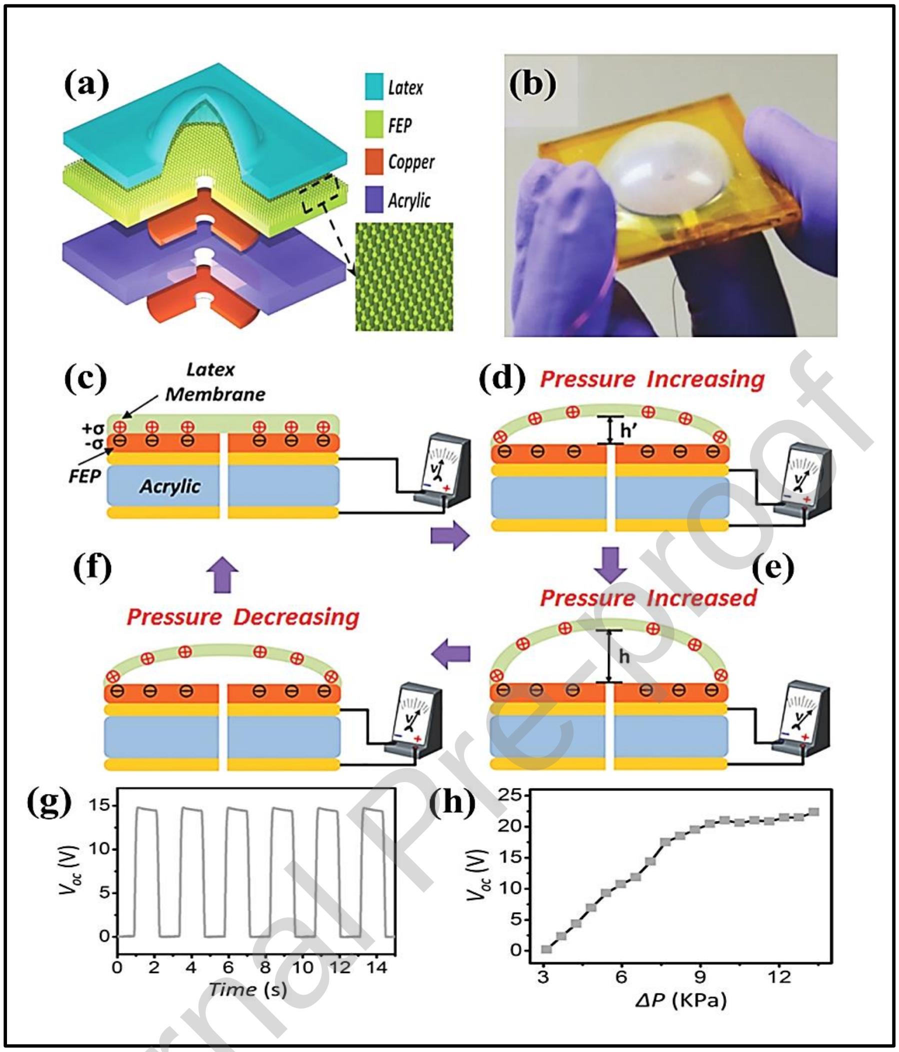


Figure 2.2: (a) Schematic of the M-TES, (b) M-TES with the latex membrane swelling, Working principle of the M-TES in open-circuit condition- (c) The initial state, (d) separation of the charged surfaces, (e) fully separated position and (f) the two surfaces are approaching to each other, g) V_{OC} of the M-TES when air pressure increases. (h) Dependence of V_{OC} on the increased air pressure.

A flexible wavy structured TENG (FTENG) has been developed based on wavy-structured Kapton film and a serpentine electrode and attached to human skin for health monitoring and sensing gentle body motions by Yang et al [35]. The as-fabricated FTENG can harvest ambient mechanical energy via both compressive and stretching modes. Moreover, the FTENG can be a bendable power source to work on curved surfaces. The FTENG was able to achieve a power density of 5 W/m^2 for a load resistance of 44 MΩ and claimed to be adaptive onto the human body skin for sensing gentle body motions (Fig: 2.3).

Figure 2.3 shows a photograph of a fully assembled FTENG (a) and several applications of the device (Figure 2.3: c-h). As visible from Figure 2.3 (a), the copper electrodes are uniquely serpentine shaped, which helps increase the copper's resistance to tensile strain. The wavy-structured Kapton thin film is sandwiched in between two layers of copper serpentine-shaped electrodes, which are in turn each covered by a flexible PDMS substrate. The Kapton film acts both as a spacer and triboelectric material, separating the top and bottom electrodes from itself through minimal contact when there are no external forces. By applying a vertical compressive force or a stretching force along the FTENG, the copper electrodes and Kapton thin film are bought into complete contact as the force causes the wavy Kapton film to flatten, leading to contact electrification as electrons are transferred to the Kapton surface. When the force is released, the Kapton film and copper electrodes are separated again. Electrons move from a grounded wire attached to each electrode into the copper due to the potential difference and a current is created. When the film and copper are brought near each other again, the negative Kapton film causes the electrons in the copper electrode to move back into the ground. Thus, an AC output current is created from compression or a stretching movement.

Therefore, the device can generate electricity compressed or stretched (Figure 2.3 b. I) and be easily applied to uneven surfaces like human skin (Figure 2.3 b. II). Additionally, it showed great consistency output (Figure 2.3 i-k) when attached to different curvature acrylic surfaces, demonstrating its ability to work with all types of irregularly shaped surfaces, such as the ones found on the human body. Indeed, as seen from Figure 2.3 (c-d), when attached major joints such as the elbow and knee, FTENG's output could be used to identify flexion and extension movements. In Figure 2.3 (e), the tension from the flexion of the biceps muscle was captured by FTENG. Evidently, the device is not limited to the locations of joints and can capture minute movements. Figure 2.3 (f-h) shows the device attached to the neck. Distinct electrical outputs resulted from swallowing and neck tilting. These examples show FTENG's feasibility in human motion monitoring as an epidermal device.

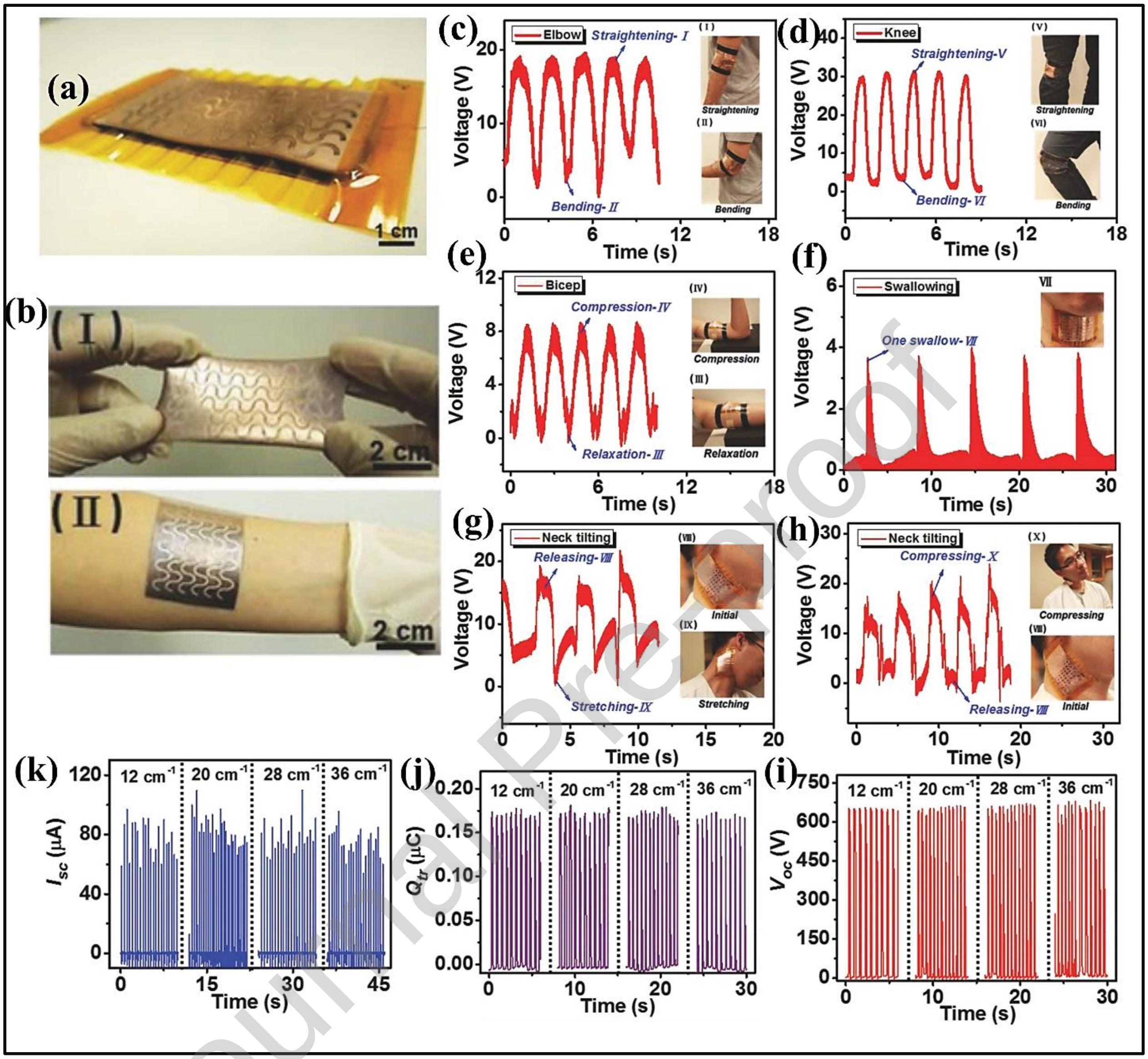


Figure 2.3: Structure and photographs of the FTENGs. (a) Photograph of the fully assembled wavy-FTENG. (b) FTENG under stretching condition & on human skin and; Application of the FTENG for body motion monito ring in terms of voltage versus time for monitoring motions in: (c) elbow, (d) knee, (e) bicep, (f) swallowing, (g) left neck tilting , and (h) right neck tilting , respectively. TheV_{oc} (i), Q_{tr} (j), and I_{sc} (k) outputs when FTENG was applied to different curvature acrylic surfaces ranging from 12 to 36 cm^{-1}.

Readily detection of physiological and pathological parameters, such as- blood pressure, blood flow rate, heartbeat rate, respiratory rate, holds great importance to ensure a highly efficient and fully automatic health care system. Failure to detect abrupt changes in these parameters results in life-threatening conditions and the worst-case scenario may lead to death. In addition to this, implantable devices often cause health threats because of their additional sizes and when changing power sources of those devices under surgical procedures. Ma et al. proposes a self-powered, flexible, and implantable triboelectric active sensor (iTEAS) that can provide continuous monitoring of important pathological and physiological parameters including heart rates, cardiac arrhythmias, such as- atrial fibrillation and ventricular premature contraction multiple physiological and pathological signs [36]. As demonstrated in Figure 2.4 (a), the device can be implanted in heart walls and was tested on the heart of human-scale animals. Figure 2.4 (b) shows a schematic diagram of iTEAS.

Figure 2.4 (c) offers a side-by-side comparison of the outputs of an electrocardiogram (ECG) as compared to that from iTEAS during different stages of a heartbeat. The output from iTEAS is comparable to the more conventional device for heart monitoring and can be similarly used to distinguish the different stages of a heartbeat (i.e. diastole from systole). Thus, the device can replace some of the functionalities of an ECG. Figure 2.4 (d) shows the heart rates of a pig when resting (~60 bpm, rHR), active (~90 bpm, aHR), and stressed (~120 bpm, sHR) detected from iTEAS and an ECG. An accuracy of ~99% was recorded when measuring the heart rates. The typical voltage and current outputs of the device are graphed in Figure 2.4 (e-f).

Additionally, several other measurements could be obtained through a mathematical analysis of the output from iTEAS. An estimate of blood pressure can be derived from the device's output. Additionally, the researchers created a formula to find average blood flow velocity as follows:

$$V_{avg} = S/LT$$

V_{avg} is the average velocity of blood flow, S is the length of the heart to the femoral artery, and LT is the leading time (difference in time between the peaks of iTEAS and a separate arterial pressure implanted in the right femoral artery. Finally, researchers also postulated the possibility for iTEAS to detect respiratory rate through being implanted on the left lateral, right lateral, and posterior wall of the heart.

The feasibility of the sensor is also supported by testing. The device nearly perfectly maintained its monitoring capabilities 72 hours after chest closure after implantation and no significant loss of sensitivity was observed after ~350,000 cycles of separation and contact. Thus, the device exhibits good in vivo durability, a necessity for its utilization. Additionally, the device shows little biotoxicity after it was extracted from a pig after two weeks of implantation. The myocardial tissue samples extracted display little cellular rejection of the device and no apoptosis. Therefore, the device also shows promise in biocompatibility.

Another implantable TENG design is demonstrated to be able to monitor a different physiological measurement of the heart. An endocardial pressure sensor (SEPS), based on TENG, was created and showed good linearity and sensitivity of R^2 = 0.997 and 1.195 mV mm/Hg respectively [37]. The device was small enough to be minimally invasively implanted through a catheter, compared to the invasive cardiac catheterization used currently to monitor endocardial pressure. Endocardial pressure is a valuable measurement because it is an indicator of a variety of heart conditions, including heart failure, and it is especially important for those with impaired cardiac function.

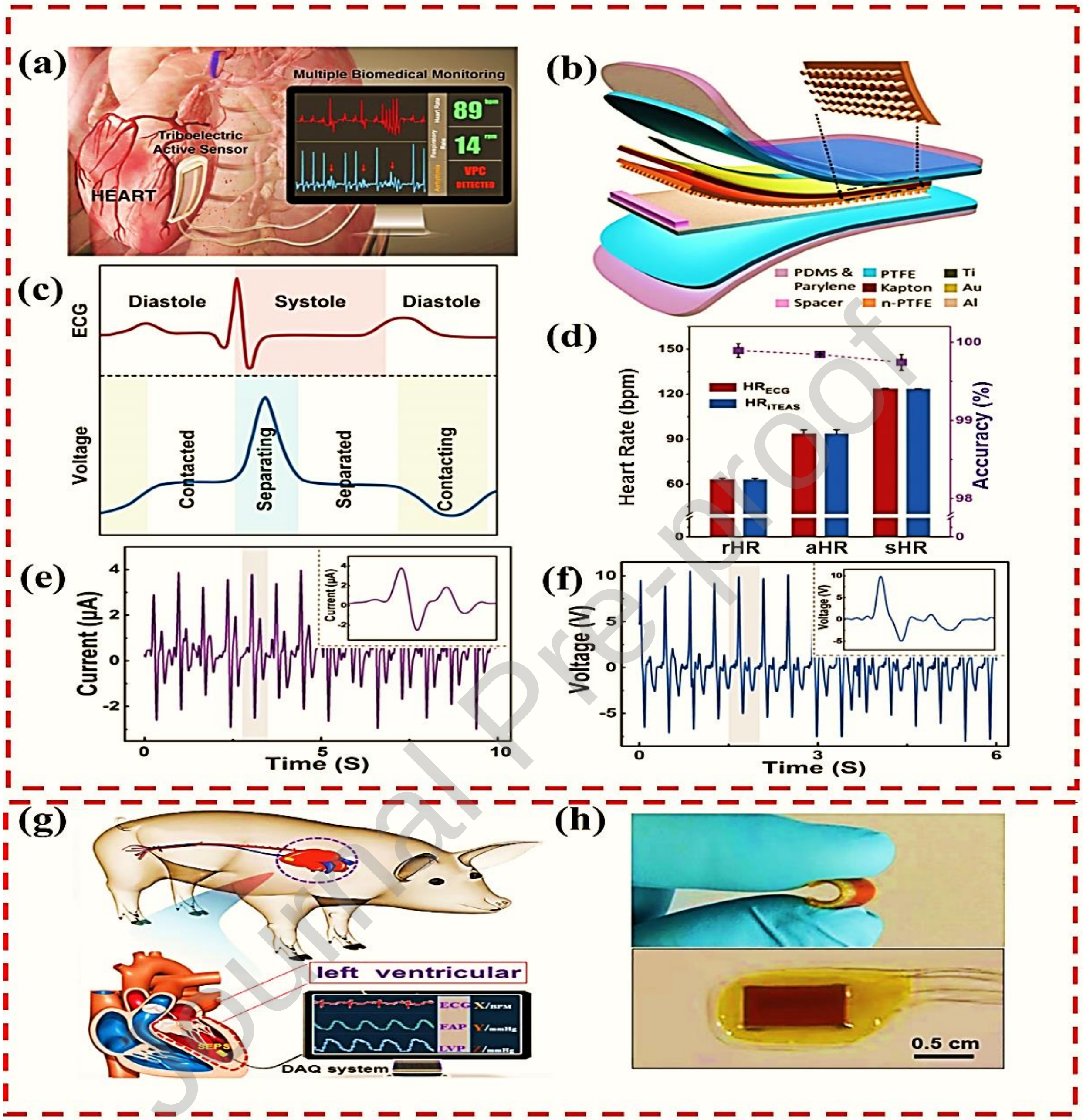


Figure 2.4: (a) Schematic diagram of the iTEAS implanted in the heart walls. (b) Schematic illustration of the structure of the iTEAS. (c) Schematic correspondence between voltage output of the iTEAS and different phases of heart motion indicated by ECG. Typical in vivo. (d) Analysis of HRs under different states using continuous intervals (e) V_{OC} and (f) I_{SC} of the implanted device. (g) Schematic diagram of the semaphore acquisition from the SEPS implanted into an Adult Yorkshire swine's heart. (h) Photograph of the SEPS in bending and original state.

In Figure 2.4 (g), a diagram of the SEPS being tested in vivo into a pig is illustrated. The device was implanted in the left ventricle through a stretchable catheter commonly used in bypass surgery. The operation was minimally invasive, with only a 2 cm- small incision, and the device generated an electrical output during cycles of contraction and relaxation of the heart, where the ventricular pressure fluctuates. The SEPS output, like iTEAS, showed good consistency with a simultaneous ECG output. Figure 2.4 (h) shows the SEPS in a bent and relaxed state. The device was of small size (1 cm × 1.5 cm × 0.1 cm), so minimal disruption of the heart was achieved after implantation. The device also shows great flexibility, durability, and is leak-proof, which facilitates its monitoring of the heart.

More recently, in 2020, some designs have focused on external, noninvasive cardiovascular monitoring. Wang et al. used polyvinyl alcohol (PVA) to create a biocompatible, flexible TENG suitable for human health monitoring because of its stable outputs [38]. They attached the device to the wrist and a modified band-aid with copper tape inside was applied above the PVA film to act as the counter electrode. Due to the sensitivity of the device, the output showed three peaks for each heartbeat, representing blood ejection, blood reflection from the lower body, and blood reflection from the closed aortic valve. Another design by Yu et al. based on an ultra-flexible micro-frustum-array polydimethylsiloxane (mf-PDMS) film focused on high sensitivity and flexibility [39]. A linearity of $R^2 = 0.99$ of voltage and stability of over 80,000 cycles was reported, which makes it a good sensor. The researchers used the device to mimic the three-fingered pulse-taking in traditional Chinese medicine, a technique believed to be able to aid in disease diagnosis.

Electronic skins (e-skins) based on all-nanofiber triboelectric nanogenerators have been used to monitor whole-body physiological signal and join movement. These e-skins have promising applications in the fields of health monitoring, patient rehabilitation, athletic performance monitoring and even driver fatigue monitoring. All these applications are owed to their high sensitivity, flexibility, and comfortability. Another e-skin is one based on PANI/PTFE/PANI sandwich. This e-skin differs from the earlier examples because it is non-wearable. This electronic skin can visually identify drunken drivers without an external electricity source [40-42].

3. **Piezoelectricity in sensor application for human health monitoring**:

Piezoelectricity potential in sensory applications is widely recognized by the scientific community. The main advantage of this technology is its ability in responding to pressure with an electrical output without an external power source. This characteristic allows for designs to be engineered with convenience and practicality in mind. Piezoelectricity sensory applications for human health monitoring has been steadily advanced by previous research, and several studies have created biomedical sensors centered on piezoelectric properties [43]. In 2018, Han et al. constructed a compact battery-free and wireless full-body sensor for temperature and pressure [44]. Using a spiral structure of thin, monocrystalline silicon membrane, a piezoresistive material, the researchers were able to integrate a pressure-sensing element into the sensor along with temperature sensing capabilities achieved through a thermometer detector in a near-field communication (NFC) chip [44]. Here, temperature sensor is the NFC microchip; the pressure sensor is made of silicon membrane and PDMS covers the sensor. The sensor could be charged, and data retrieved, wirelessly through radio waves from a phone or a similar device. Such sensor designs have immense applications in the human healthcare field as it offers 24-hour full-body monitoring that can be used to detect and prevent bedsores in bed-ridden patients. The structure and function of the sensors can be seen in the following Figure 3.1.

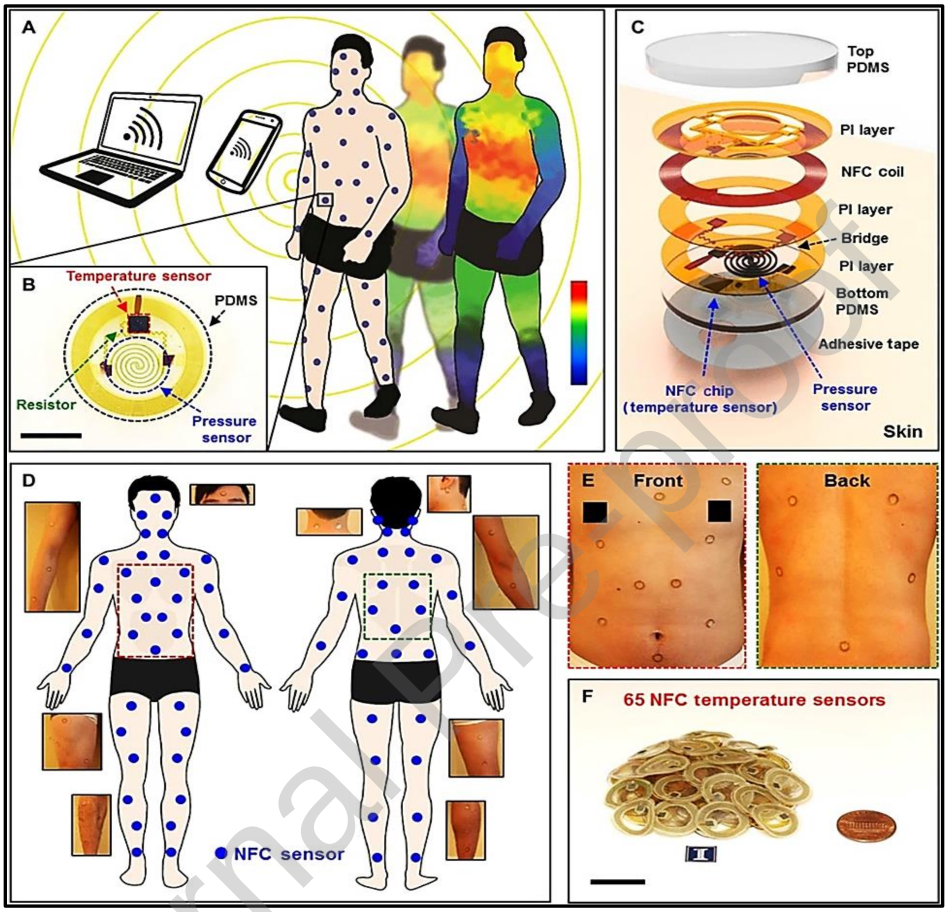


Figure 3.1: Overview of the wireless, battery-free sensors for full-body monitoring. (A) Illustration of the sensors applied for full-body monitoring and wirelessly transmitting information about temperature and pressure; and (B) top-view illustration of the sensor with 8mm scale bar; (C) schematic diagram showing the device structure; (D) illustration showing the distribution of 65 wireless sensors on the body and corresponding photographs; (E) images showing the distribution sensors on the front and back of the body, with red and green boxes; (F) images of 65 sensors with a penny for scale and a 16mm scale bar.

Another potential of PENG in health monitoring is in wearable fabrics. A fiber-based PENG is fabricated using zinc oxide nanowires and polyvinylidene fluoride around a conducting fiber [45]. Under ~ 0.1% strain, the device was able to reach a 32mV open-circuit output of voltage and a 2 $nAcm^{-2}$ closed-circuit current density. The fiber devices can also be superimposed by connecting them in series resulting in an open-circuit with higher output voltage (~85 mV) than either device individually (~40 mV and ~55mV). These results can be seen in Figure 3.2 (a-f).

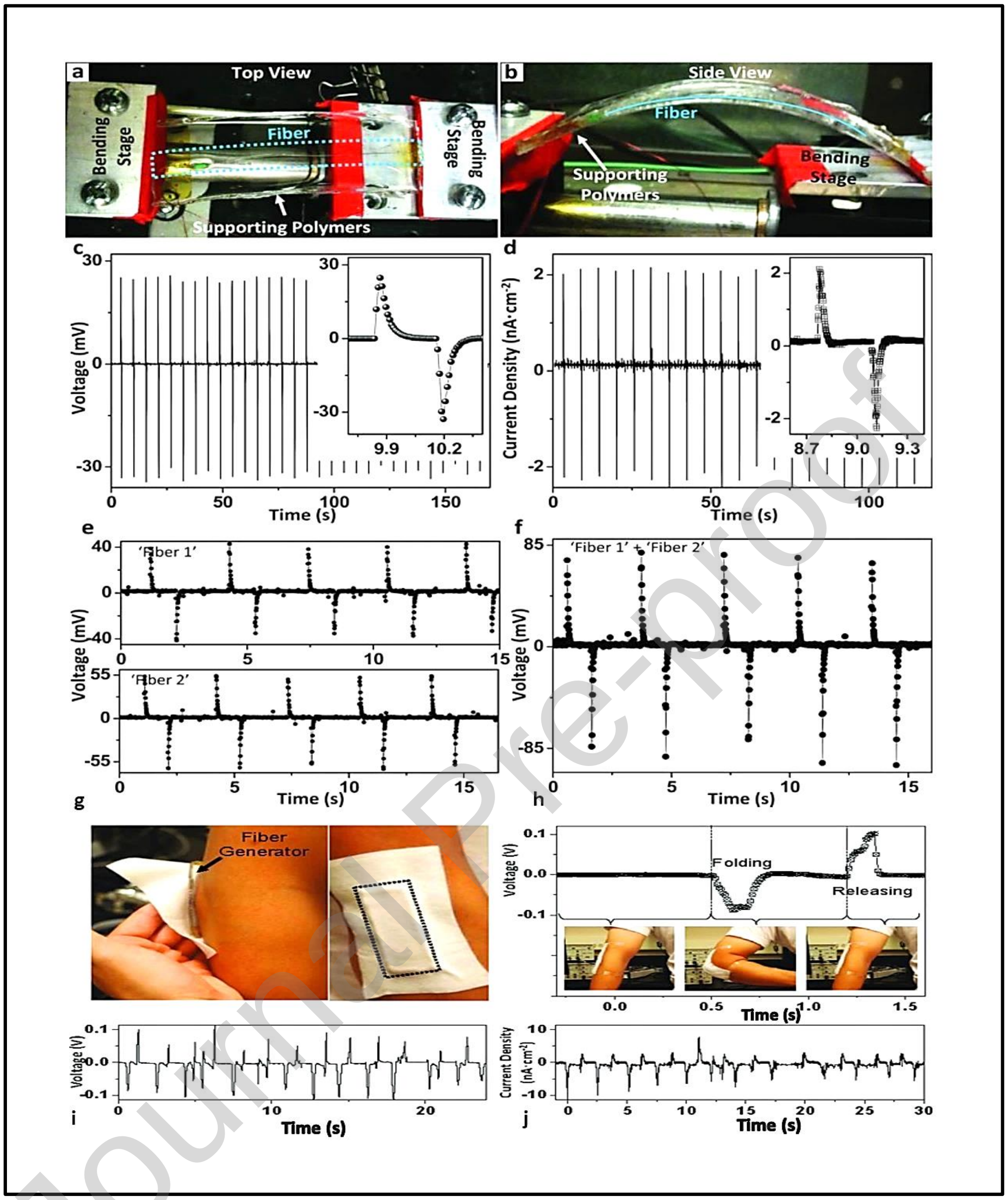


Figure 3.2: Photographs and electrical outputs of hybrid-fiber nanogenerators. Top-view (a) and side-view (b) of a hybrid-fiber device attached to a PS substrate and covered in PDMS for uniform stress, on a bending stage. Open-circuit output voltage (c) and closed-circuit output current density of a fiber device (d) under a strain of ~ 0.1%. Open-circuit voltage outputs (e) of two different fiber devices, labeled 'Fiber 1' and 'Fiber 2', under a strain of ~ 0.1%. Open-circuit voltage output of Fiber 1 and Fiber 2 (f) connected in series under a strain of ~ 0.1% and at a strain rate of ~ 2.3% s^{-1}. Photographs of the hybrid-fiber device (g), and PDMS/PS were attached in the same way and for the same reason as in (a). Open-circuit voltage output (h) of a fiber device from the flexion and extension (folding and releasing respectively) of the elbow. Open-circuit voltage (i) and closed-circuit current-density output (j) of a fiber device from several cycles of flexion and extension.

The device depicted in Figure 3.2 opens the opportunity for wearable nanogenerators that could monitor a patient's motion and have applications in physical therapy where tracking the speed or strength of muscle movements is valuable. This application is further supported by the device's output in response to movement when attached to the elbow, as shown in Figure 3.2 (g-j).

Additionally, in 2019, researchers were able to create a multifunctioning monitoring system by including a piezoelectric micromachined ultrasonic transducer (pMUT) array to detect relative humidity and room temperature [30]. The pMUT array was partially coated in polyethyleneimine (PEI)/graphene oxide (GO) and exhibited a high sensitivity of 748 Hz/%RH along with good linearity. The study demonstrates a way to utilize piezoelectricity to sense factors beyond pressure. Therefore, it is evident that piezoelectricity has a high potential versatility regarding its sensory capabilities.

Recent works demonstrated factors that promise the feasibility of piezoelectricity in widespread biomedical sensor applications. Interestingly, Onion Skin Based Piezoelectric Nano Generator (OSBPNG) could monitor the output sensitivity [48] of the throat movement during coughing (≈0.30 V), swallow pass (≈0.86 V), and drinking of water (≈0.20 V). In addition to this, the device could harvest green energy from throat voice signals by generating the sound of "START" and "STOP" and it could also differentiate these two sounds in terms of electrical output. The high sensitivity of OSBPNG was further confirmed by harvesting energy from up-down neck movement and generating output signals in the range of ≈2.0 V to ≈3.5V from the falling of leaves from different height with various weights. These results strongly supported the onion skin based nanogenerator as a highly sensitive and potential energy harvester which can continuously produce output for longer cycles (up to 10000 cycles, 2000s), concluding it as a durable and mechanically stable alternate source of energy. All these applications are depicted through Figure 3.3 (a-i) [49] [50]. Additionally, in Figure 3.3 (j-k), prawn shell based nanogenerators are depicted that can produce electrical output upon throat movement and artery movement. Furthermore, prawn shell-based nanogenerators are also found to generate electricity from throat movement [51].

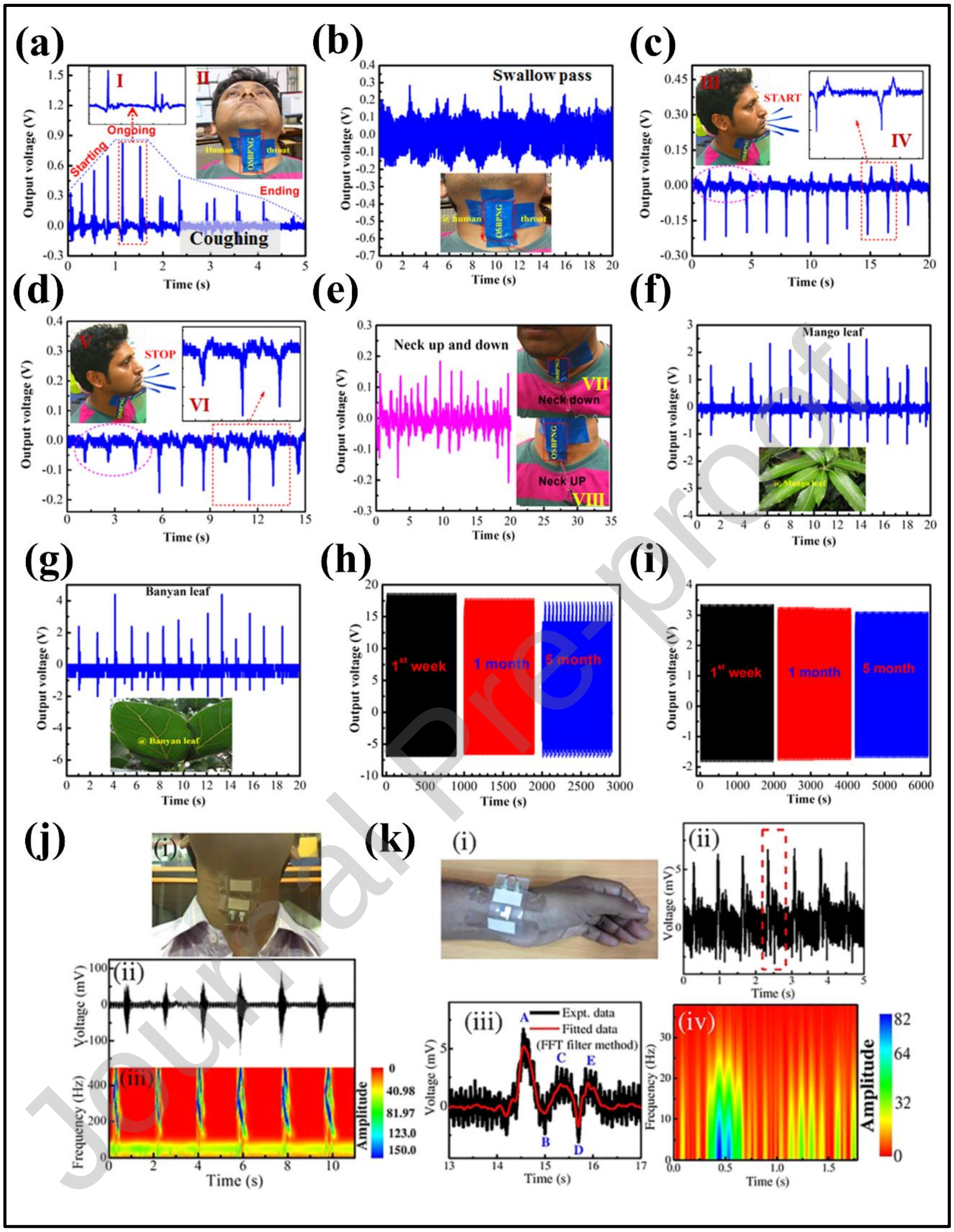


Figure 3.3: Output voltage of onion skin based nanogenerator attached to the throat when (a) coughing, (b) swallowing, (c) saying “start”, (d) saying “stop”, (e) nodding up and down. The voltage output when a (f) mango leaf and (g) banyan leaf was dropped, showing the sensitivity of the generator. The stability of the nanogenerator when (h) hand punching and (i) sewing machine vibration. A prawn shell based nanogenerator attached to the throat (j-i) with its corresponding output values (j-ii). A prawn shell based nanogenerator attached to the wrist (k-i), with its corresponding outputs of (j-ii) wrist pulse vibration. The data was enlarged, and noise was removed (k-iii) and an STFT spectrogram was selected for a single pulse wave (k-iv).

Piezoelectric nanogenerators made of biodegradable materials offer several unique advantages. Firstly, biodegradability is important in reducing pollution. Secondly, cost-efficiency allows these sensors to be integrated into the healthcare system without huge financial barriers. Finally, the high sensitivity of these biodegradable piezoelectric sensors allows them to play a key role in monitoring the often-minute mechanical motions of the human body.

In recent years, detectors for certain chemical markers have been developed based on the piezoelectric effect. A self/powered breath analyzer based on PANI/PVDF Piezo-Gas-Sensing Arrays for diagnostics application was developed in 2018. The device works by converting energy from blowing of exhaled breath into electrical sensing signal without any external power sources. There five sensing units in a single device can be used for diagnosis of liver cirrhosis, airway inflammation, diabetes, and asthma. Another detector based on the piezoelectric effects, is a noninvasive electronic skin that couples the piezoelectric effect with a biosensing unit. The piezo-biosensing unit matrix is comprised of enzymes modified on the surface of ZnO nanowires. The electronic-skin can detect lactate, glucose, uric acid and urea in the perspiration through actively outputting piezoelectric signal (driven by body movement) [46, 47]. These two sensors use the piezoelectric effect, and they couple it with other chemical detectors to identify body metabolites.

The innovation of flexible piezoelectric material increases the practicality of piezoelectricity as a human health monitor. Perovskite-structured ceramics, such as lead zirconate titanate (PZT), and lead magnesium niobate (PMN) show excellent piezoelectric properties. Although the toxicity of lead oxides in ceramics is debated, for biomedical applications, this concern has focused the research efforts on lead-free piezo materials, including polymers, ceramics, and composites, both in the form of film and fibers [52, 53]. Among them, a low-cost lead-free piezoceramic entitled with piezoelectric effects is barium titanate ($BaTiO_3$). Anyway, the use of $BaTiO_3$, PZT, and PMN-PT perovskite salts to construct piezoelectric thin films has allowed for greater mechanical-to-electrical conversion efficiency and thereby a more sensitive sensor [54]. PZT thin films were even used for detecting cellular deformations in the nanometer range. A key advantage of a flexible piezoelectric nanogenerator is its ability to conform to the irregular shapes of human skin and internal organs, being able to effectively monitor and harvest the mechanical motions of the human body. For example, a flexible piezoelectric material can be implanted on the surface of the heart, detecting the frequency and pressure of its beats while harvesting the energy to possibly maintain a pacemaker. Flexibility opens many opportunities for PENG to be used as a health sensor.

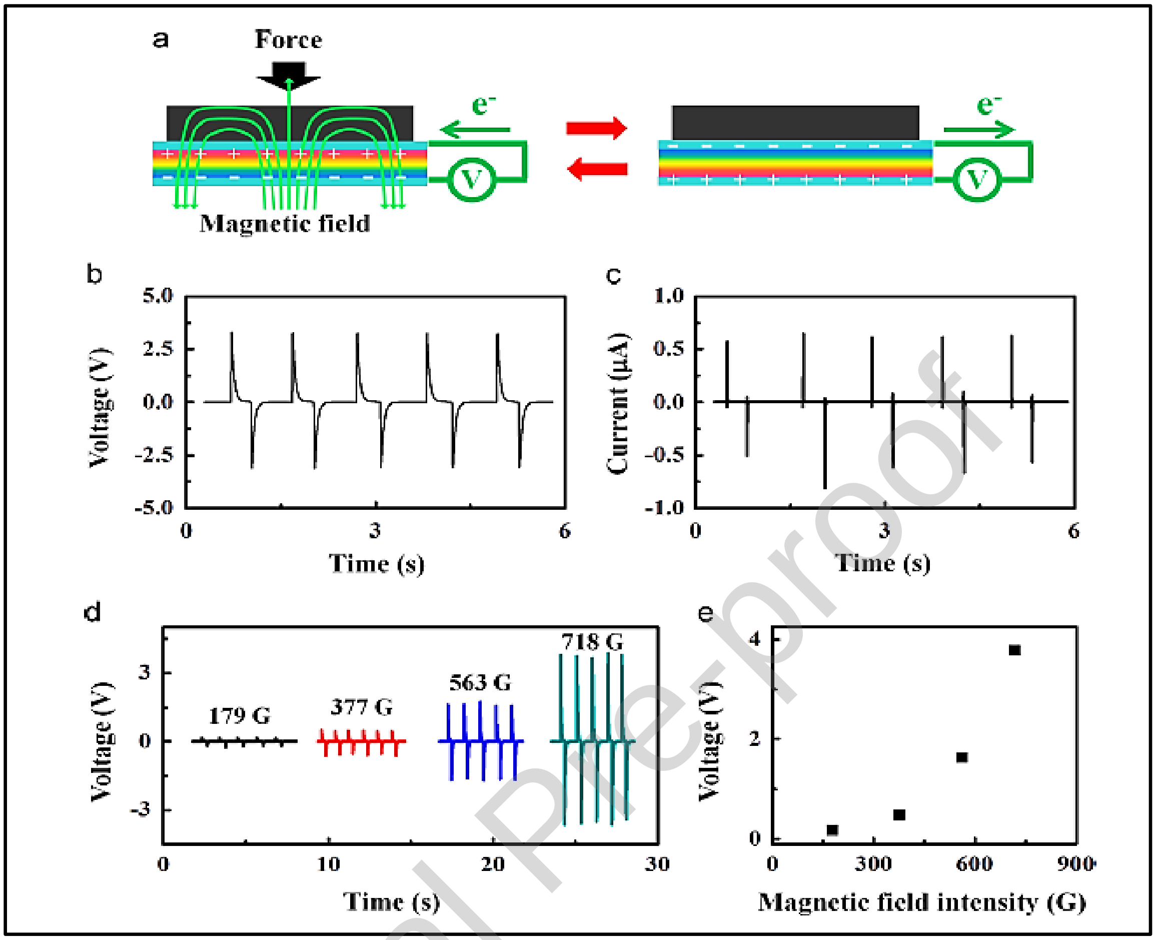


Figure 3.4: (a) Schematic diagram of WLNG and its working mechanism, (b) Output voltage of the WLNG, (c) Output current of the WLNG, (d) Voltage vs time plotted for different magnetic field intensities, and (e) peak output voltage plotted vs magnetic field intensity.

Another application for biomedical sensing is to use a piezoelectric generator as the power source of another sensor. Cheng and coworkers created a PENG using BZT-BCT nanowires that, instead of harvesting the body's mechanical energy, generates electricity through an external changing magnetic field [55]. Challenges to this design include the inconsistent mechanical motion of the human body which makes it difficult for PENG to power another device without a storage battery. The design presents a significant approach integrating piezoelectricity into a sensor system to eliminate the need for wires or batteries. More information about the working mechanism of the device can been seen in Figure 3.4 (a). Under a changing magnetic field created by an electromagnet, the current and voltage can reach 810 nA and 3.3 V respectively as shown in Figure 3.4 (b-c). Additionally, Figure 3.4 (d-e) shows voltage output under different values of magnetic field intensity, with an increase in field intensity exponentially affecting voltage. The output reaches a voltage of 3.9 V and a current of 1.17 μA.

4. Piezo-Tribo Dual effect hybrid Nanogenerators in sensory application for human health monitoring and biomedical sectors:

The use of hybrid nanogenerators, combining the triboelectric and piezoelectric effects, as sensors have been explored less compared to solely PENG or TENG. The concept of hybrid nanogenerator focuses mainly on power enhancement due to its hybrid mode of operation. These devices attract researchers due to their compact size with respect to their electrical output. Being introduced as a health monitoring sensor, the device should be capable of harvesting enough energy even in small spaces. Unlike, TENGs the HBNGs require limited separation distance for operation, which is very necessary for these devices, as they are often incorporated in sophisticated human organs. In addition to this, health monitoring sensors require enriched signal detection and quick response capability. All these features can be met by HBNGs, instead of the individual incorporation of PENG or TENG devices. Thus, hybrid nanogenerators could provide a direction for future innovations of more precise, practical, and self-sufficient biomedical nanogenerators to be discovered.

Scientists have made some progress on using hybrid nanogenerators as sensors, which demonstrates their potential to be more advantageous than PENG or TENG. In Table 1, a summary of hybrid nanogenerators with healthcare applications is presented with their electrical output and key features. Each of these nanogenerators is thus discussed in this and the following section.

Table 1. Hybrid Nanogenerators for Human Health Monitoring.

HNG Used for Human Health Monitoring	Total Electrical Output (Hybrid)	Healthcare Capabilities	Features	Corresponding References
Polarization-controlled PVDF-based hybrid nanogenerator	180 V & 5.3 μA	• Self-detection of human motion for safety. • Self-monitoring of pressure distribution. • Energy harvesting from vibrational energy.	• Reduced manufacturing. • High-susceptibility to mechanical impulse • Easy installation in a thin shoe insole.	Lee, D.W., et al., Nano Energy, 2020: p. 105066.
Self-Powered Cotton Sock Hybrid Nanogenerator	196 V & 4.5 μA	• Sensing gait, contact force, sweat levels. • Walking pattern recognition and motion tracking.	• Wearable device. • Self-sustained: self-powered monitor and self-functional.	Zhu, M., et al., ACS nano, 2019. 13(2): p. 1940-1952.
Flexible one-structure Silver Nanowire based hybrid Nanogenerator	141 V & 68.2 Ω sq−1	• Monitor breath, heartbeat, swallowing and neck-tilting. . • Visualized thermometer.	• Flexible. • Biocompatibility. • Thermochromic. • Self-powering.	Sun, J.-G., et al., Nano Energy, 2018.
All-Fiber Hybrid Piezoelectric-Enhanced Triboelectric Nanogenerator	500 V & 12 μA	• Detect body motion. • Fall alert microsystem for the elderly and workers on high-risk area.	• Wearable. • Flexibility and air permeability. • Embedded in clothes.	Guo, Y., et al., Nano Energy, 2018.
Electromagnetic Shielding Hybrid Nanogenerator for Health Monitoring and Protection	Charge a capacitor up to 3 V in 200s & 20 μA	• Electromagnetic radiation shield. • Abdominal motion sensor.	• Mechanical and thermal energy harvester. • Keyboard cover. • Wearable self-powered sensor.	Zhang, Q., et al., Advanced Functional Materials, 2018.
Flexible fiber-based hybrid nanogenerator	240.1 V & 4.91 μA	• Radial artery pulse monitor. • Respiratory monitor.	• Device can be attached in different parts of the body. • Flexible. • Sensitivity.	Chen, X., et al., Nano Energy, 2017.
d-arched piezoelectric-triboelectric hybrid nanogenerator	25.8 V (Rectified) & 8.82 μA	• Self-powered vibration sensor.	• High sensitivity and good linearity. • Easily integrated into other devices. • D-arched structure.	Zhu, J., et al., Sensors and Actuators A: Physical, 2017.
One-Structure-Based (PVDF-PDMS-ITO) Hybridized Nanogenerator for Scavenging Energy	125 V & 7.58 μW	• Harvest mechanical and thermal energy.	• Highly transparent. • Flexible.	Wang, S., et al., Advanced Materials, 2016.
Hybrid Cell for High-Efficiency Energy-Harvesting and Self-Powered Sensing	1135.6 V & 146.2 mW/m^2	• Temperature sensor. • Normal force on surface sensor.	• Energy harvesting from friction.	Zi, Y., et al., Advanced Materials, 2015.
3D Fiber-Based Hybrid Nanogenerator for Energy Harvesting	2 V & 0.0255 μA	• Can harvest mechanical energy from human motions. • Self-powered strain sensor.	• Wearable. • Flexible. • Self-powered cloth.	Li, X., et al., ACS nano, 2014.

Sun et al. proposed a design of a flexible, transparent, and sensitive hybrid nanogenerator achieved through electrodes made of silver nanowires arranged like the veins on a leaf [8]. This design allowed for higher transparency than conventional nanowire films, high transmission of up to 99% with 68.2 Ω sq^{-1} sheet resistance, and low sheet resistance of 1.4 Ω sq^{-1} at 82% transmission. Polyvinylidene fluoride (PVDF) was used as the piezoelectric and pyroelectric material and PDMS was used as the triboelectric material and substrate. The device has several applications in human health monitoring. As shown in Figure 4.1 (a), a thermochromic liquid crystal (LCD) film can be integrated into the HBNG due to the HBNG transparent property, as shown in Figure 4.1 (b). The LCD film changes color depending on the temperature on its surface from black to red at lower temperatures and green to blue at higher temperatures.

Therefore, the device can be used as a visual thermometer when calibrated correctly, with the colors used to denote a fever or hypothermia. In Figure 4.1 (e), the HBNG attached to a respirator, and the magnitude of its voltage output could indicate the strength of the breath. A weak breath produced a voltage of about 25 V while a deep breath produced a voltage of 35V, with normal breathing having a value of 35 V. LCD film can be used to approximate the temperature of the breath visually. The HBNG is utilized this way to monitor or indicate the respiratory condition of a patient as the strength of the breath, respiratory rate, and breath temperature can all be derived from the device's output. The device can be especially useful for patients infected by the flu, prone to asthma, or that have other conditions that affect respiration. The device can also be used to monitor heartbeat pulses as seen in Figure 4.1 (f). Each beat could be distinguished and counted for heart rate. Additionally, as illustrated in Figure 4.1 (g-i), the device can be attached to the neck (front and side) to monitor neck tilting, coughing, and swallowing. Neck tilting may be used to predict Parkinson's disease, as noted in the paper. Information about neck tilting can also diagnose torticollis, where the range of motion in the neck is limited. Difficulty swallowing, also known as dysphagia, can be an indicator of neurological conditions such as a stroke, head injury, and multiple sclerosis. Finally, coughs are symptomatic of a multitude of diseases, and data about it, such as its frequency and intensity, can be used according to each case.

The device is composed of three basic parts: the transparent Ag nanowire electrode, PDMS, and PVDF. The process for arranging the Ag nanowires in leaf venation morphologies is described below. A leaf, from the plant *Osmanthus fragrans*, was obtained and submerged in a KOH solution at 90 °C to isolate the leaf venation skeleton, which will be used as a mold. Silver nanowires were synthesized through the galvanic displacement method. Finally, a modified try transfer printing technique was used by bringing the Ag nanowire on the cellulose acetate membrane with the venation skeleton. Two pieces of PDMS were used, one substrate layer fabricated through spinning coating functions, and the other triboelectric layer was sandpaper molded. An electrospun PVDF fiber layer was placed in the center sandwiched between two electrode layers. Finally, those electrode layers were in turn sandwiched between the PDMS films.

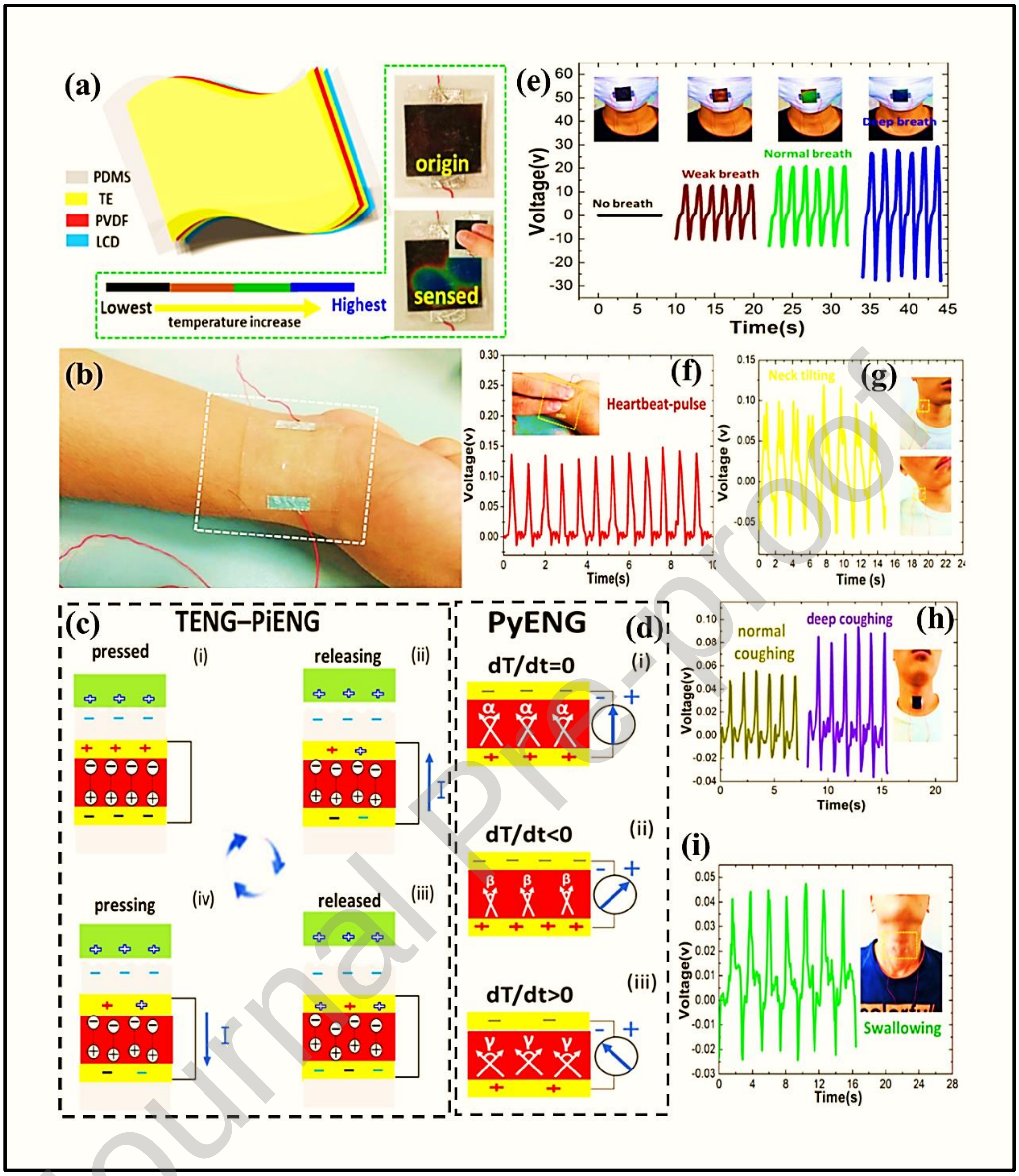


Fig 4.1: (a) A schematic diagram of the transparent HBNG with a thermochromic liquid crystal (LCD) film integrated between the transparent electrodes and PDMS. The LCD film changes color with increasing temperature, from black to blue, so that the entire device can be used as a visual thermometer. (b) A photograph showing the transparency of the HBNG attached on skin. The working mechanisms of (c) the integrated triboelectric nanogenerator and piezoelectric nanogenerator (TENG-PiENG) and (d) the pyroelectric nanogenerator. (e) When attached to a respirator, the HBNG's voltage output's magnitude corresponded with the strength of the breath. The HBNG was also attached to the wrist, the front of neck, and the side of the neck and distinct voltage outputs for (f) a heartbeat pulse, (g) neck tilting, (h) different intensity coughing, and (i) swallowing were recorded.

Another approach for HBNG in health monitoring is to power other sensors: HBNG with a sliding-mode TENG composed of aluminum foil and polytetrafluorethylene (PTFE) film and a pyroelectric-piezoelectric nanogenerator (PPENG) layer with PVDF serving as both the piezoelectric and pyroelectric material [56]. Copper electrodes sandwiched the PVDF and the bottom side of the PTFE, and a Kapton film separated the bottom TENG electrodes and top PPENG electrode, insulating electricity but allowing heat transfer. The PPENG portion of the sensor helps capture any stray thermal energy or vertically compressive forces resulting from the friction of the sliding TENG to increase the device's mechanical to electrical conversion efficiency. The HBNG produced a 10^{-5} A current and used to power an LED bulb, and immediately after it was turned off, there was still some electrical output, albeit diminished. Thus, the HBNG has a unique advantage for powering other sensors. Additionally, it was reported that the energy from the HBNG can also be stored and was used to charge a 41.9 mF capacitor. Another HBNG design that was reported to fulfill the same purpose is the Poled PVDF film with indium tin oxide (ITO) electrodes on both sides acts as the piezo-pyroelectric layer, and PDMS with PVDF nanowires make up one part of the triboelectric material alongside a flexible nylon film [14]. The device was fixed into an acrylic tube and an oscillating nylon membrane served as the other triboelectric layer. Thus, the device can harvest energy to effectively charge a 10 µF capacitor at a frequency of 0.05 Hz from vibrations. TENG-PENG produced low voltage but high current while PyENG (pyroelectric nanogenerator) exhibited low current but high voltage, compensating for each other's shortcomings. The HBNG shows potential in being able to power devices with high electric requirements.

Wearable hybrid nanogenerators also provide a unique detection for convenient health monitoring: introducing a fiber-based design focused on using nanofiber meshes [57]. As illustrated in Figure 4.2 (a), poly(vinylidenefluoride-co-trifluoroethylene) [P(VDF-TrFE)] was used as the piezoelectric material and was sandwiched between polyurethane electrodes. The PDMS was used as the triboelectric material and to separate the PENG and TENG electrodes, increasing output. The contact area was increased between the piezoelectric material and electrodes by electrospinning P(VDF-TrFE) and polyurethane into nanofiber meshes, which helped to decrease contact resistance. Examples of physiological monitoring done can be seen in the Figure 4.2.

The output of the device is characterized in Figure 4.2 (b), where the device was used to charge a 1 µF capacitor with an input of a cotton cloth flapping at 4 Hz. After 80s, PENG was able to charge the capacitor to 0.91 V, TENG to 4.35 V, and their joint output was able to charge to 4.66 V. The fiber-based design also has applications in both human health monitoring and energy harvesting. The device was attached to the abdomen, as in Figure 4.2 (c), and produced distinct outputs when the respirations were deep, shallow, fast, and slow. Therefore, the device can be used to characterize the respiration of a patient or monitor a patient with a respiratory condition. For example, dyspnea, or difficulty breathing, can be characterized by shallow and fast breaths. Additionally, respiratory rate can also be obtained as each voltage cycle represents one breath as shown in Figure 4.2 (d). For energy harvesting, the device can generate electrical energy when attached to a soft surface such as (e) the back of a chair or (f) on the human skin. On a chair, the HBNG can harvest energy when someone leans on it of up to 85V and 10.8V for TENG and

PENG respectively, and when attached to the skin, a finger touch could generate electrical energy.

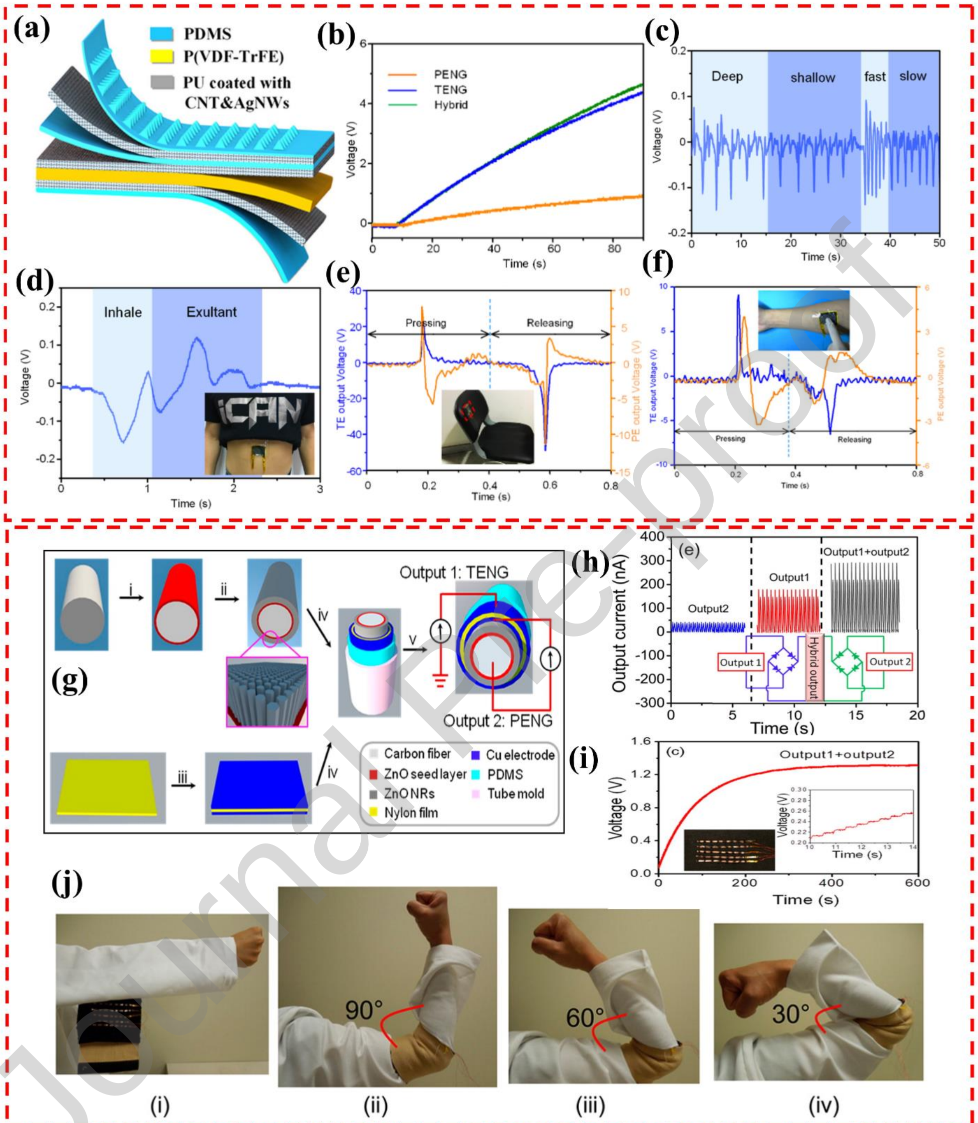


Figure 4.2: (a) A schematic diagram of fiber-based nanogenerator. (b) Voltages of the capacitor are shown for PENG, TENG, and PENG-TENG connected parallel. The device was attached to the abdomen to monitor respiration rate and (c) the output for deep, shallow, fast, and slow breaths are shown. (d) Each voltage cycle represents a single breath. (e) Attached to the back of a chair and output voltage recorded. Additionally, (f) attached to the arm and voltage recorded when pressed by a finger. (g) The fabrication process of a fiber-based hybrid nanogenerator (FBHNG). (h) The current output and (i) the voltage output of the TENG (Output 1) and PENG (Output 2) were recorded along with the hybridized output (output 3). (j) The device can be easily sewn into (i) cloth producing distinct outputs for the bending angle of arm at (ii) 90-, (iii) 60-, and (iv) 30-degree angles [57, 58] .

Referencing another fiber-based HNG in 2014, Li et al fabricated a fiber-based hybrid nanogenerator (FBHNG) that has potential both in harvesting human motion and acting as a strain sensor [58]. The researchers integrated PENG and TENG on a carbon fiber cloth acting as the substrate, which made the nanogenerator flexible and capable of being made into a wearable cloth. Zinc oxide nanorods were also utilized on the carbon fibers to increase the output. The fabrication process of the FBHNG is illustrated in Figure 4.2 (g). A 250 nm ZnO thin film was sputtered on the carbon fiber (i) so that ZnO nanorods could be grown on the layer (ii) using the hyperthermal method. The nanorods reach a length of 10 μm. On the other hand, 100 nm thin films of Ti/Cu are sputtered on a nylon thin film (iii), sandwiching it and acting as the electrodes. The coated nylon film was wrapped around the ZnO nanorod covered carbon fiber, which was in turn put in a 3 mm diameter tube mold (iv). Finally, the tube mold was submerged in a mixture of elastomer and PDMS in a 10:1 weight ratio. The solution was heated to 85°C for 1 hour and the device was obtained after the mold was peeled (v). The FHBNGs can be combined by connecting the TENGs and PENGs in parallel with other TENGs and PENGs respectively. Therefore, the output capabilities of the entire device can be easily increased by adding more units, which translates to higher sensitivity for a sensor. Indeed, Figure 4.2 (h) shows the rectified current output for the TENG (Output 1), PENG (Output 2), and TENG and PENG combined (Output 1 + Output 2) with 12 units and an effective area of 108 mm^2. The hybridized output is equal to the two individual outputs, demonstrating the device's ability to charge a capacitor or battery for energy storage. Indeed, FBNG is used to charge a 2.2 μF capacitor demonstrated in terms of a voltage vs time plot after the AC output is transformed into the same direction in Figure 4.2 (i). The device can also be weaved into cloth to be easily worn and act as a self-powered human monitoring sensor. When attached to the elbow as pictured in Figure 4.2 (j), the PENG of the device produced distinguishable outputs when the elbow was bent at 90-, 60-, and 30-degree angles. In addition, the HBNG piezoelectric output showed good linearity with the strain ratio, further cementing the device's ability to function as a wearable strain sensor. Information about a patient's motion could have applications in physical therapy, where tracking the patient's strength and range of motion is important.

Some devices have also been shown to be capable of monitoring pulse as well as human motion. For example, a HBNG that also used Ag nanowires, PVDF, and PDMS was fabricated by Yu et al [39, 59]. As seen in Figure 4.3 (a), researchers treated the Ag nanowires with HCL vapor to weld it to a PVDF substrate, which gave the device excellent optical transparency, and PDMS served as the triboelectric layer. The device was also proposed to be applicable for heart rate monitoring, with voltage peaks indicating a every heat beat in Figure 4.3 (b). Additionally, when attached the inside and outside of the elbow, the open circuit voltage output showed good linearity in regard to the bending angle as showed in Figure 4.3 (c-d).

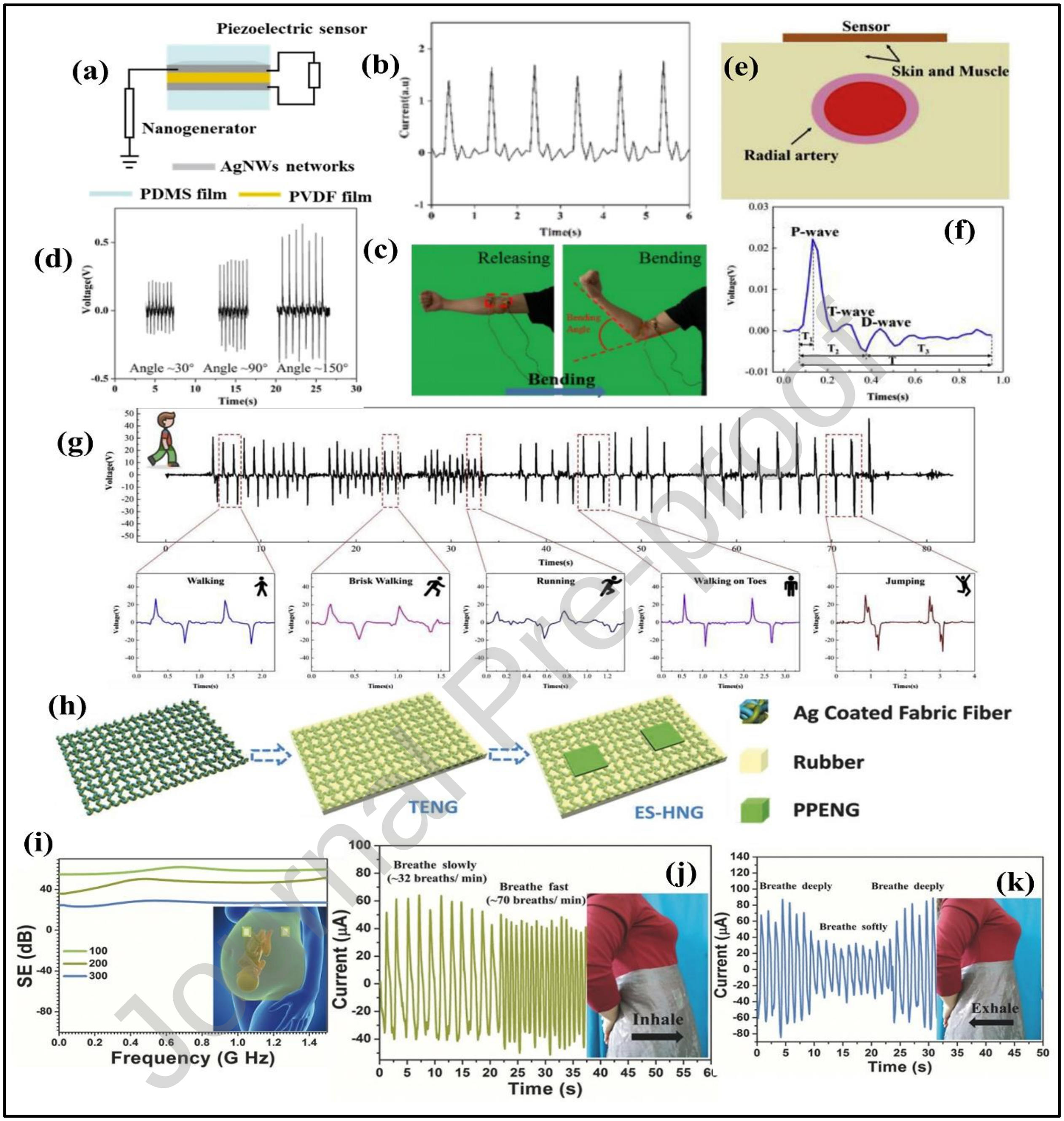


Figure 4.3: (a) A schematic diagram of a transparent, flexible hybrid nanogenerator with welded silver nanowire networks. (b) The output of the device when it was applied above the radial artery. The device was attached to the abdomen elbow in (c) to detect bending, and the results are shown in (d). (e) The skin conformal HBNG sensor applied above the radial artery to monitor pulse. Additionally, (f) attached to the arm and voltage recorded when pressed by a finger. (g) the device, when applied to heel of the feet, can produce distinct outputs for different strides (h) Schematic diagram for an electromagnetic shielding hybrid nanogenerator (ES-HNG). The ES-HNG can be used to (i) protect pregnant women from radiation, and the shielding effectiveness (SE) was measured. The device can also simultaneously monitor respiration, including (j) respiratory rate and (k) respiratory depth [18, 59, 60].

Yu et al. proposed a skin-conformal wearable HBNG sensor, with excellent sensitivity (18.96 V/kPa) and measurement range (0 kPa-1,300 kPa) [60] . A micro-frustum-arrays PZT & PDMS film was used as the triboelectric and piezoelectric layer, with a micro-frustum-arrays copper film used as the other triboelectric material. When applied above the radial artery, as seen in Figure 4.3 (e), the HBNG could indicate when the heart contracted through the voltage peaks. In fact, the HBNG sensor's output was precise enough to reflect the tidal wave (T-wave) and diastolic wave (D-wave) in addition to the percussion wave (P-wave) indicated by the voltage spikes, as seen in Figure 4.2 (f). Such detailed information about the pulse from the compact device has the potential to give insights to the wearer's cardiac output and blood pressure. The device can also be used as a gait monitor when attached on the heel. The different outputs for different styles of walking is shown in Figure 4.2 (g).

Hybrid nanogenerators can also be used to serve other functions in addition to health monitoring and energy harvesting. Zhang and coworkers created a stretchable electromagnetic wave shielding hybrid nanogenerator (ES-HNG) [18]. As seen in Figure 4.3 (h), stretchable TENG-made of an Ag coated fabric fiber weaved into a conductive anti-electromagnetic radiation fabric (AEMF) -as the base and many small PTENGs. The AEMF was also covered on both sides by rubber. The fabrication of the device is as follows. A conductive AEMF is cleaned with acetone and dried before submerged in a solution of equivalent amounts of elastomer and cross-linker to apply the rubber covering. The liquid was cured to produce a solid rubber. PPENG was made by sandwiching a polarized PVDF film with Ag thin film layers. Finally, Kapton double-sided tape was used to attach the top electrode of the PPENGs on the TENG, and the PPENG were placed in regular distance intervals from one another.

Figure 4.3 (i) shows the device being attached to the abdomen of a pregnant woman so that the generator could be dual purpose: protection from radiation and monitoring of breath depth and frequency. As calculated from the graph, AEMFs with mesh numbers 100, 200, and 300 can block 99.7911%, 99.9978%, and 99.9998% of electromagnetic waves from 0 to 1.5 GHz. Therefore, the device can effectively shield against electromagnetic radiation. This function can also be useful for people who are exposed frequently to electromagnetic radiation. For example, x-ray technicians and flight attendants can benefit. Additionally, the device can help monitor the rate of breathing, as shown in Figure 4.3 (j), and the depth of breathing, as shown in Figure 4.3 (k).

Health sensors can also be used to monitor the environment for factors that would negatively impact the patient's health. Zhu et al. proposed a D-arched hybrid nanogenerator that can effectively sense vibration with good linearity [61]. The reported device can be divided into an upper piezoelectric and the lower triboelectric layers which are separated by a space of 5 mm. The upper piezoelectric layer consisted of 200μm polarized PVDF film, aluminum electrodes, and a supporting PET film. The lower layer was formed by a silicon rubber membrane, aluminum electrodes, and a PET film. The electrodes were magnetron sputtered and the silicon rubber membrane was micropatterned with a copper mesh to increase performance. At a frequency of 10 Hz and a mechanical force of 5N, the device was capable of a peak output voltage of 25.8 V and a peak output current of 8.82 μA. Additionally, a good linear relationship between piezoelectric output and the acceleration of vibration shows that the device is a capable vibration sensor. In addition, being a finger sensor, the device can be miniaturized and be attached to the human body to monitor vibrations in the environment. It is shown that vibration can cause negatively impact the quality of life. Thus, being able to monitor these vibrations could help play a role in healthcare.

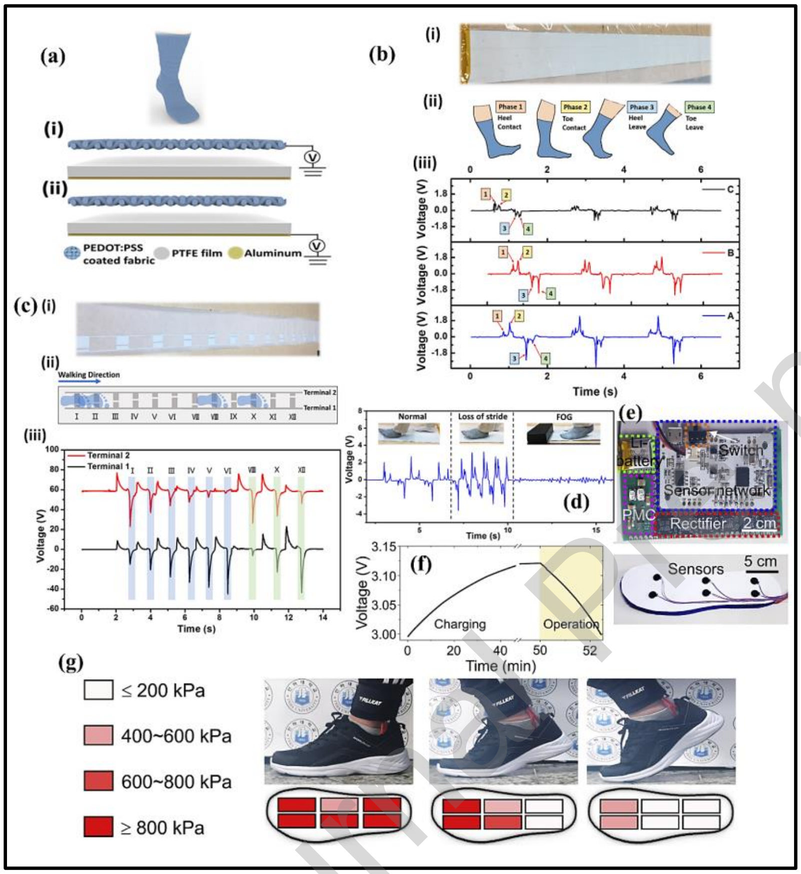


Figure 4.4: (a) A schematic diagram of the modified sock and the PTFE film with aluminum electrodes (i, ii). The device has two modes of electrical connections, the (i) sock connection and the (ii) Al/PTFE connection. (b) The device can help analyze footsteps. (i) A photograph of the PTFE laid on the floor like a carpet. The phases of a footstep (ii) can be reflected by the (iii) sock and PTFE's output. Three participants, a (A) 90 kg male, (B) 70 kg male, and (c) 60 kg male, tested the output. (c) The sock can also determine the direction and speed of walking. (i) A photograph of a PTFE modified with six pairs of designed aluminum electrodes with two electrodes. This design could determine the (ii) walking direction and the (iii) speed and distance walked. (d) The output for normal walking, loss of stride length walking (more peaks for more frequent steps), and freezing of gait, which can be used to help diagnose a Parkinson's disease patient. PVDF-based HBNG used to harvest energy from footsteps. (e) A circuit diagram of the wireless sensors system with the outputs of three rectified tribo-piezo hybrid nanogenerators (TPHG) being used to charge a Li-battery powering a wireless pressure sensor. (f) The charging and discharging process for the Li-battery is shown. (g) Through the wireless pressure sensor, the pressure on the bottom of the feet can be mapped [62, 63].

Finally, more recent studies have focused on monitoring the pressures of the foot for various uses in healthcare and sports medicine. One study by Zhu et al. integrated a hybrid nanogenerator with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)-coated fabric TENG and lead zirconate titanate (PZT) piezoelectric chips into a cotton sock [63]. As shown in Figure 4.4 (a), PDFE film was used as the second triboelectric material. As depicted in Figure 4.4 (c), the film could be laid on the floor to harness the contact-separation motion of walking (i), and the output from the device could even reflect the phases of a footstep (ii, iii). Thus, the sock and PDFE can allow for footstep analysis. Additionally, the output was unique to each participant even though they all reflected the same phases, showing that it can be used to identify patients. Additionally, by adding two terminals and using individual aluminum electrodes labeled from in roman numerals (Figure 4.4 (c)), the walking direction, speed, and distance could be obtained. Figure 4.4 (d) shows the researcher's proposed application of the device in healthcare: monitoring Parkinson's disease. As it is a difficult-to-detect disease, the device can help diagnose Parkinson's through long-term monitoring for symptoms. Namely, Parkinson's disease patients experience loss of stride length and freezing of gait (FOG) when turning or overcoming obstacles, two symptoms that the device's output can reflect. Lee et al. used a PVDF-based HBNG and embedded it underneath the insole of a shoe to power a wireless sensor system [62]. As shown in Figure 4.4 (e, f), several HBNGs were used to power a 40 mAh Li-battery, which could power the wireless sensor network for 2 minutes after a 50-minute charge time. The pressure distribution of the foot is seen in Figure 4.4 (g) and is valuable in helping patients with foot conditions.

5. Hybrid Nanogenerators in Future Health Monitoring Systems:

PENG-TENG hybrid nanogenerators for health monitoring has become more attractive in health monitoring because of their ability to work with an unlimited power supply. This hybrid nanogenerator is also highly sensitive and can be used to gather a wide range of mechanical data from the human body like vital signs, muscle contraction or relaxation, and environmental changes that affect the person wearing the nanogenerator. In table 2, some potential health conditions are presented as well as some applicable HBNG and the detectable symptoms. The sensors can alert medical professionals for the smallest changes in vital signs and physiological changes as well as to aid in medical diagnoses. [64-66]

Table 2. Applicable HBNGs for Potential Health Conditions

Condition	Potential Health Complications	Applicable HBNG/ HBNGs	HBNG Detectable Symptom	Symptom-Reflecting Output	Corresponding References
Tachycardia	•Heart failure. •Stroke or heart attack.	•Flexible one-structure silver nanowire-based hybrid nanogenerator. •Transparent and flexible hybrid nanogenerator with welded silver nanowire networks. •Hybrid piezoelectric-triboelectric sensor. •Flexible fiber-based hybrid nanogenerator.	•Rapid pulse above 100 beats per minute	•Several voltage peaks in a very small period when applied above an artery.	Sun, J.-G., et al., Nano Energy, 2018. Yu, X., et al., Smart Materials and Structures, 2020. Yu, J., et al., Nano Energy, 2019. Chen, X., et al., Nano Energy, 2017.
Bradycardia	•Fainting . •Inadequate perfusion .		•No pulse	•No/extremely diminished output even when applied above an artery.	
Cardiac Arrest	•Organ Damage. •Death .		•Slow pulse below 60 beats per minute	•Few voltage peaks even over large period when applied above an artery.	
Asthma	•Permanent narrowing of bronchial tubes. •Symptoms interfering with daily life.	•Flexible one-structure silver nanowire-based hybrid nanogenerator. •Electromagnetic shielding hybrid nanogenerator for health monitoring and protection. •Flexible fiber-based hybrid nanogenerator.	•Short breaths •Rapid respirations	•Abnormally low voltage peaks when applied to a mask or on the abdomen. •Abnormally infrequent voltage peaks.	Sun, J.-G., et al., Nano Energy, 2018. Zhang, Q., et al., Advanced Functional Materials, 2018. Chen, X., et al., Nano Energy, 2017.
Sleep Apnea	•Inadequate restorative sleep. •High blood pressure. •Liver problems.		•Periods when breathing stops during sleep, usually then followed by gasps for air.	•Periods when there is no signal when applied to a mask or abdomen. •Strong voltage peak after a period of no signal.	
Parkinson's Disease	•Cognitive Decline •Sleeping Problems Depression	•Flexible one-structure silver nanowire-based hybrid nanogenerator. •Self-Powered cotton sock hybrid nanogenerator.	•Difficulty or slowed swallowing. •Freezing of gait when walking. •Loss of stride length.	•Abnormally prolonged/ widened voltage peaks during mealtime when applied to the front of the neck. •Spontaneous periods of no voltage output using the sock-PDFE system. •Abnormally increased amounts of voltage peaks (more steps) when using the sock-PDFE system.	Sun, J.-G., et al., Nano Energy, 2018. Zhu, M., et al., ACS nano, 2019. 13(2): p. 1940-1952.

One use of hybrid nanogenerators in future health monitoring is in detecting potentially life-threatening impacts. Currently, scientists have explored fiber-based PENG-TENG hybrid nanogenerator, which can be integrated into clothing [57, 58, 67]. One study has explored using fiber HBNGs to detect falls in the elderly, which is one of the leading causes of death in the 65 years old and above demographic. In Guo et al.'s study, their wearable piezoelectric-enhanced triboelectric nanogenerator demonstrated the ability to detect a real-time fall and respond with an emergency alert [67]. The flexible and easily tailored nanogenerator was and can be sewn onto gloves, pants near the knees, sleeves near the elbow, and wherever an impact from a fall can be detected. As shown in Figure 5.1 (a), a micro-cantilever sends out a prewritten emergency message through the internet if the output voltage of the HBNG reaches the voltage threshold, and a remote terminal then receives the emergency message. Such an automated response to a fall can lead to a shorter response time for emergency medical personnel, which can improve outcomes and save many lives. Other potential applications for impact-detecting HBNGs would be for detecting car-crash accidents, motorcycle accidents, sports injuries, and violence. Additionally, several professions where physical accidents are more likely to occur could benefit from the technology. These careers could include agricultural workers, truck drivers, roofers, and construction workers.

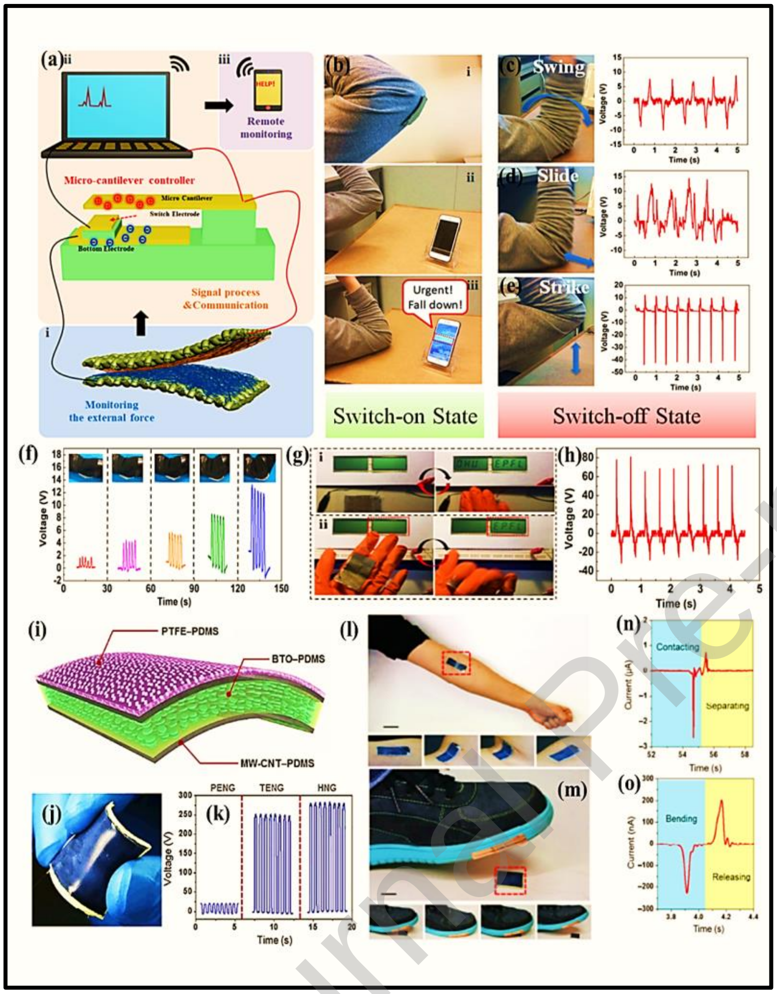


Figure 5.1: (a) An illustration of a fall alert system by fiber based HBNG. The device was tested attached to the elbow (b), and a simulated fall by dropping the elbow against the table (b ii) resulted in an emergency message (iii). Additionally, the device can also be used in energy harvesting while the electrical output does not reach the threshold, and the outputs of common motions like a swing (c), slide (d), and strike (e) are shown. (f) Different voltage outputs for different bending angles from 101° to 146° for the HBNG when attached to the elbow. The device was used to power LCDs with tapping (g i) and with folding (g ii). The voltage output with ~ 2 Hz frequency hand tapping reached 78 V (h). (i) A schematic diagram of a HBNG fabricated using multilayered nanocomposite materials with a PTFE nanoparticle and PDMS matrix top layer. The device is flexible and can be bent (j). The output was recorded (k), and the hybrid nanogenerator output (HNG) exceeded both the TENG and PENG outputs. (l) The hybrid nanogenerator used to harvest energy from the flexion and extension of the elbow joint and the output was recorded (o). The HBNG could also harvest energy from footsteps as shown in (m), and (n) shows the output. [27, 67]

Moreover, hybrid nanogenerators can be used in sports medicine, physical therapy, and even performance monitoring. In a study done by Chen et al., hybrid nanogenerators were attached to various parts of athletes' bodies to monitor respiratory rates and depth [57]. The flexibility of the hybrid nanogenerator allowed them to be easily attached to the athletes' skin, and it was able to monitor the vital signs without being invasive. When attached to the abdomen, the device was able to detect respiratory rate as the output could show every inhalation and exhalation as discussed earlier. In this study, it was also shown that the hybrid nanogenerator was able to produce a reading of heart pulses. The nanogenerator attached to the wrist was able to read the athlete's heart's electrical signals of every pulse. Pulse and respiratory rate are important measurements in sports medicine as they can be a measure of the performance of an athlete. The non-restrictive nature of this HBNG also offers an important aspect of convenience. Beyond these two psychological signals, the ability of HBNGs to detect physical motion and strain [58], can also be used to detect the impact on joints for athletes. Injuries to a knee or an elbow can be disastrous for an athlete. By using wearable HBNGs, the impact on these critical areas can be carefully monitored to prevent these injuries before they occur. Strain sensing can also help a physical therapist better understand the range of motion of a patient and monitor improvements.

As an additional feature, when placed on the neck instead of the joint, many useful measurements can be obtained. For example, the device can be placed on the throat to track swallowing. Difficulty in swallowing can be indicative of an underlying neurological condition such as a head injury and stroke. Placed on the neck, the device can be used to predict Parkinson's disease from data about neck tilting [8]. Finally, tracking coughs can be useful in many respiratory conditions.

HBNGs can also play a crucial work in cardiovascular monitoring in the future. Heart disease is one of the leading causes of death worldwide, but many conditions can be detected and prevented beforehand with careful monitoring. Implantable TENG designs have already been created, and their ability to detect physiological signs has been demonstrated [36, 37]. Some of these physiological signs include heart rate, blood pressure, blood volume speed, endocardial pressure, respiratory rate, and heart rhythm. Innovations upon these designs by integrating piezoelectricity can potentially lead to precise and accurate 24-hour heart monitoring sensors in the future.

Finally, hybrid generators can power other sensors instead of directly being used as one. Flexible hybrid nanogenerator designs have made them increasingly suitable for harvesting energy from human motion [8, 57, 58, 68]. Additionally, their high mechanical to electrical energy conversion efficiency gives them an advantage in this niche compared to other types of nanogenerators. Studies have already investigated HBNGs as an energy source in powering smaller devices [27, 56, 69-71]. HBNG attached to the elbow joint to harvest the mechanical energy from flexion and extension movements has also been reported. Since the elbow is a frequently bent joint, energy can be potentially harvested a multitude of times throughout one day, though a battery or storage system would be needed if the energy were to be stored. Systems can be developed in the future with HBNGs being the power source, replacing batteries or wires, for a variety of other monitoring and health devices. [27]

5.1 Enhancement in Hybrid Nano-Generator for better output and efficiency:

The presence of nanogenerators in the healthcare field can positively ease diagnoses, monitor vital and physiological signs of people, help detect pre-conditions, and power important medical devices. Additionally, hybrid piezoelectric-triboelectric nanogenerators can provide a greener alternative to other monitoring devices due to the general nature of their materials. These hybrid nanogenerators can be easily integrated, with possibilities ranging from being sewn into cloth, attached to the skin, worn, or even implanted. More importantly, they have the potential to provide constant and accurate health monitoring.

Innovations to nanogenerators, in general, can increase the feasibility and usefulness of HBNGs as health monitoring sensors. Methods that increase output power density, voltage, and current or conversion efficiency could translate to a more sensitive and reliable health sensor. Thus, this section will summarize progress made to nanogenerators in general that can be potentially applied to a nanogenerator sensor, and in this regard, both piezoelectric and triboelectric innovations can be applied to a hybrid nanogenerator.

One way to enhance piezoelectricity is by mitigating the screening effect, which occurs when free carriers in the nanowires of a piezoelectric nanogenerator partially cancel out the piezo potential generated from compression [72]. Researchers used Au nanoparticles on the surface of ZnO (Figure 5.2 (a-d)) to decrease this effect and increase output. For a ZnO nanoarray-based (NA-based) PENG with Au had an output of 2V and 1 $\mu A/cm^2$, ~10 times compared to that without an Au, as shown in Figure 5.2 (b, d). As supported by Figure 5.2 (e), the average surface potential for ZnO with Au was lower, showing that free carriers were indeed reduced.

Abolhasani et al discovered by adding graphene in ideal amounts to PVDF/MF solutions (20 wt. %) that were then electrospun into nanofibers, the open-circuit output voltage of the resulting piezoelectric nanogenerator could be nearly doubled [73]. As shown in Figure 5.2 (f), adding 0.1 wt% graphene could increase the open circuit output voltage from 3.8 V to 7.9 V. However, increasing the amount beyond that resulted in lower outputs (Figure 5.2 (g)). Additionally, Figure 5.2 (h), FTIR spectra for polymorphic analysis with different, wt% graphene, showed that F(β) increased significantly for only the sample with 0.1 wt%. Another approach used multi-walled carbon nanotubes (MWCNTs) to increase β-phase content and surface charge density of PVDF [74]. Without any MWCTs, the PVDF generated an open circuit output voltage of about 2V. The output voltage generated peaked at 5 wt% at 6V but decreased with higher wt% values measured afterwards[73].

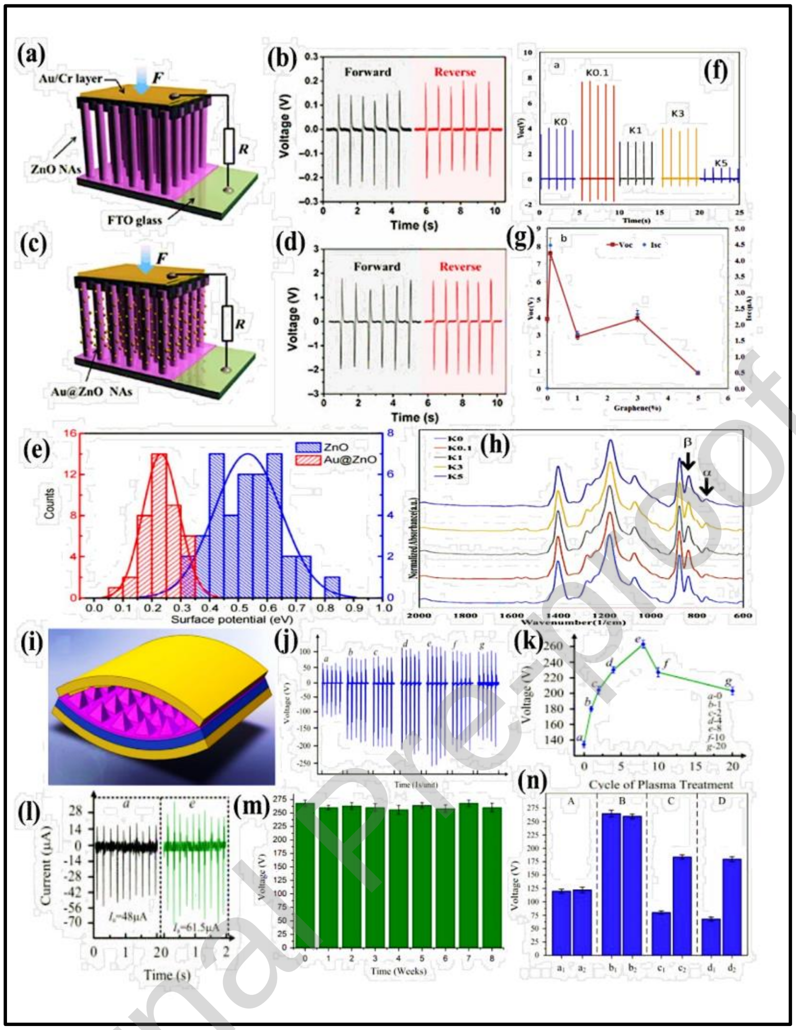


Figure 5.2: A schematic diagram of (a) ZnO NA-based PENG without Au, (b) along with its output voltage, and (c) ZnO NA-based PENG with Au, (d) along with a significantly higher voltage. The distribution of surface potential for the device with and without gold, (e) shows average surface potential for ZnO with Au. (f) Open circuit voltage (Voc) for a nanofiber sample with no graphene (KO), 0.1 wt% graphene (K0.1), 1 wt% graphene (K1), 3 wt% graphene (K3), and 5 wt% graphene (K5). (g) The Voc and short circuit current Isc vs graphene wt% was also graphed, showing a peak at 0.1 wt% graphene. (h) FTIR spectrum of the electrospun nanofibers with graphene and α and β characteristic peaks were found at 763 cm^{-1} and 840 cm^{-1}, respectively. (i) A schematic diagram of an arched shaped TENG with a fluorocarbon polymer layer (pink). The (j) output voltage waveform for different cycles and the (k) change in output voltage as the cycles increase (a-0 cycle, b-1 cycle, c-2 cycles, d-4 cycles, e-8 cycles, f-10 cycles, g-20 cycles). (l) The output current waveform for a (0 cycles) and c (2 cycles). The output of TENG for many weeks after the polymer treatment was recorded to test for consistency (m). (n) shows the output before (1) and after (2) different treatments, including with (A) Ar plasma treatment, (B) DRIE and RIE process, (C) with flat PET substrate, and (D), with flat Kapton. [72, 73, 75]

Several TENG modifications have also been created that can potentially be used in a hybrid nanogenerator. One study by Zhang et al used fluorocarbon plasma treatment in enhancing performance [75]. The fluorocarbon polymer layer is seen in pink in Figure 5.2 (i). The most output-changing factor was the reaction time (plasma treatment cycles), and the outputs of the different number of cycles of treatment were recorded in Figure 5.2 (j-l). The output reaches a maximum with 8 cycles at 265 V(k). A treated device showed good consistency and durability as the voltage output remained relatively constant for 8 weeks after the treatment (Figure 5.2 (m)). As demonstrated in Figure 5.2 (n), the increase in output can be attributed to the fluorocarbon plasma treatment and not any extraneous factors. Firstly, another method, (A) Ar plasma treatment, was tested and did not affect the output. Next, (B) reactive ion etching (RIE) and deep reactive ion etching (DRIE) processes showed similar outputs. Finally, the fluorocarbon plasma treatment was also applied to other materials, includuing (C) PET and (D) Kapton, and similar increases in output occurred. Triboelectricity was able to be enhanced through a composite sponge PDMS film TENG (CS-TENG), which has pores and $SrTiO_3$ nanoparticles [76]. The TENG is improved by increasing permittivity and porosity. At 10% SrTiO3 nanoparticles (NPs) of a PDMS film and 15% pores of the total volume, the performance increased up to 338 V for open-circuit output.

This section presented the progress made to nanogenerators in general that can potentially be applied to a hybrid nanogenerator sensor. Methods that boost output power density, voltage, and current or conversion efficiency could translate to a more sensitive and reliable health sensor. Piezoelectric and triboelectric innovations can be applied to a hybrid nanogenerator and can increase the feasibility and usefulness as health monitoring sensors.

6. Challenges of Hybrid Nanogenerators as health monitoring sensors

Despite the promise of tribo-piezo dual effect hybrid nanogenerators for health monitoring, several challenges still need to be addressed if they are to be used widespread. Some of these challenges will be listed so that they can be identified and overcome in future research.

6.1 Sensitivity and accuracy

Although combining PENG and TENG offers a significant improvement in mechanical to electrical energy conversion efficiency and power output [17], sensitivity and accuracy are still aspects of nanogenerators that need constant improvement. More specifically, in the healthcare field, the measurement of a patient's physiological signs must be precise and accurate, as a slight discrepancy of these values might lead to misdiagnoses or misinformation. In addition, the use of HBNGs as human health sensors has mostly focused on respiratory rate, heart rate, and joint motion [8, 57, 58]. Higher sensitivities could allow for more minute physiological signs to be sensed (i.e. strengths of heartbeats, intestinal movement, etc.) and allow for broader potential integration of HBNGs in the healthcare field.

6.2 Stability

Ideally, sensors should also be extremely consistent regardless of any extraneous factors. If temperature or humidity affected the performance of the sensor, its functionality would be compromised outside of a controlled environment, and the device's potential utilization outside of a hospital setting would be severely limited. So far, many studies have not explored this area with their HBNGs [8, 58]. Being able to maintain its functionality while exposed to the elements would be a big step towards convenient 24-hour monitoring.

6.3 Mass Production

The ability to be mass-produced is crucial to the practicality of hybrid nanogenerator's commercial use. The sensor should be able to be efficiently and cheaply produced in large quantities. Otherwise, even if they show immense functionality, their use will be limited. In this regard, HBNGs may face more challenges than either triboelectric or piezoelectric nanogenerators as they need to incorporate materials from both types of nanogenerators. However, progress has been made upon the cost and production ease of triboelectric nanogenerators [77-79] and hybrid nan generators [80]. Still, several studies of HBNG sensors do not indicate the mass production capabilities of their sensors or require several steps in the fabrication process [57, 61, 68].

6.4 Durability

Hybrid nanogenerators typically require some degree of contact-separation or rubbing motion in order for the triboelectric effect to take place [17]. Therefore, they potentially face the same issue as TENG and can be damaged through repeated use. Critically low durability would affect the hybrid nanogenerator's practicality in the healthcare field and its use for long term monitoring. Durability is a concern, especially in implantable designs, where repeated surgery should be avoided as much as possible.

6.5 Sensing Capabilities

The hybrid nanogenerator's ability to sense motion, pressure, and temperature if the pyroelectric effect is integrated allows us to monitor respiration, pulse, body temperature, among others [8, 57, 58, 61, 68]. Increasing the number of measurements, a hybrid nanogenerator can sense will substantially broaden its applications in healthcare. Additionally, linearity is another aspect of hybrid nanogenerators that could use be researched and improved. Currently, the output from nanogenerators with poor linearity can provide a little more than binary information (i.e. is there an external force or is there not a force). An HBNG with excellent linearity would possibly be able to identify the exact amount of force applied on it, which could be useful in sports medicine, and more information, in general, will be able to be extracted from its output.

7. Conclusion

The use and development of nanogenerators as renewable energy sources have become very attractive in recent years to preserve the health of our environment. Furthermore, the energy harvesting capability and mobility of these nanogenerators can be applied in other areas, such as health sensors. In this review, we discussed the fabrication and application of piezoelectric and triboelectric nanogenerators and their hybrids as human health monitors as well as the challenges of these.

Piezoelectric sensory applications are numerous and adhere to the unifying principles of noninvasive biotechnology in human health monitoring. Piezoelectric elements provide an alternative means of providing electrical input without an external source. The piezoelectric materials could be utilized in 24-hour full-body monitoring or in wearable fabrics. The technology allows for a wider range of mobility and flexibility for the user. Various factors beyond that of general temperature monitoring may be utilizing piezoelectric materials, such as humidity. Combine this with wireless data transmission, piezoelectric technology is extremely convenient and provides a seamless means of capturing and relaying information.

TENGs have a higher voltage output than PENGs and are more proficient. TENG also exhibited the potential to detect CO_2 in the blood and can even be used to measure pulse, respiration, and joint motion when attached to the surface of the skin. Additionally, TENGs can be used as heart implants to measure heartbeat, which can aid in the detection of cardiac illnesses. Nanogenerators utilizing the triboelectric effect in addition to piezoelectric elements provide a high voltage output as health monitoring sensors. Nanoparticles, nanowires, and potentially chemical means may be utilized to affect the triboelectric surface with micro-geometry.

Combining TENG and PENG, Hybrid nanogenerators have great potential for health monitoring applications because of their high sensitivity and the capability to distinguish different vital signs as well as detecting muscle contraction or relaxation, and even abnormal changes in the environment such as a fall. Modifications can be done on the triboelectric and piezoelectric parts to enhance the hybrid output as well as to increase the strength of the devices. Challenges of NGs as health monitoring sensors that can be improved are sensitivity and accuracy, stability in the face of various external factors, the ability of high-volume manufacturing, and increasing durability. Therefore, the presence of NGs can positively impact the quality of healthcare if the challenges are overcome.

Declaration of Competing Interest

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

Acknowledgements

This research was supported by the College of Sciences, University of Texas Rio Grande Valley through Presidential Graduate Research Assistantships to Sk Md Ali Zaker Shawon and Valeria Suarez Vega. The Department of Chemistry is grateful for the generous support provided by the Departmental Grant from the Robert A. Welch Foundation, and the J. Elliott Research Assistantship.

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Declaration of interests

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

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Piezo-Tribo dual effect Hybrid Nanogenerators (HNGs) as health monitoring sensors.
- HNGs as sensors to measure the different movements and changes in the body such as blood circulation, respiration, and muscle contractions.
- Application of Piezo-Tribo dual effect HNGs within various healthcare settings as a means of powering noninvasive sensors, capable of constant patient monitoring without interfering with the range of motion or comfort of the user.
- This review discusses the improvements that contribute significantly in terms of the electrical output of the HNGs and can enhance their prospects of applications in the field of health monitoring, as well as various in vitro/in vivo biomedical applications.
- While a promising option, improved HNGs are still lacking. This review also discusses the technical issue which have prevented so far, the real use of the HNGs as sensors.