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Abstract: Energy harvesters serve as continuous and long-lasting sources of energy that can be integrated into wearable and implantable sensors and biomedical devices. This review paper presents the current progress, the challenges, the advantages, the disadvantages and the future trends of energy harvesters which can harvest energy from various sources from the human body. The most used types of energy are chemical; thermal and biomechanical and each group is represented by several nanogenerators. Chemical energy can be harvested with a help of microbial and enzymatic biofuel cells, thermal energy is collected via thermal and pyroelectric nano-generators, biomechanical energy can be scavenged with piezoelectric and triboelectric materials, electromagnetic and electrostatic generators and photovoltaic effect allows scavenging of light energy. Their operating principles, power ratings, features, materials, and designs are presented. There are different ways of extracting the maximum energy and current trends and approaches in nanogenerator designs are discussed. The ever-growing interest in this field is linked to a larger role of wearable electronics in the future. Possible directions of future development are outlined; and practical biomedical applications of energy harvesters for glucose sensors, oximeters and pacemakers are presented. Based on the increasingly accumulated literature, there are continuous promising improvements which are anticipated to lead to portable and implantable devices without the requirement for batteries.

Keywords: bioelectronics; energy harvesting; wearables; implantable electronics

1. Introduction

Continuous monitoring plays a vital role in a timely medical diagnosis and prevents a large spectrum of diseases [1]. In modern medical practice this approach is implemented via wearable biosensors that register any anomalous biomarker deviations [2]. A core problem, however, is that continuous monitoring via wearable biosensors cannot be developed without a sufficient energy source. Typically, energy is provided by either a battery, by an energy harvester, or a combination of both [3,4].

Energy harvesting is a process of collecting, converting and providing ready-to-use energy for an arbitrary device. The circuitry for such a device consists of nanogenerators (NGs) and a power management unit that conditions the scavenged energy into a usable form [5]. Research into energy harvesting requires a multi-disciplinary approach which considers both electrical and biological factors to achieve optimum conversion results. Thermal, biomechanical, biochemical and solar energy (Figure 1) can be scavenged from the ambient environment or the human body [3,6–9]. In addition, the same external stimuli that are converted to energy can effectively be monitored by energy harvesters [10].

The history of energy harvesters can be traced back to 2006 when Zhong Lin Wang published a report on piezoelectric nanogenerator that was comprised of ZnO nanowire arrays [11]. This fundamental article became an instant classic among the scientific community for its breakthrough novelty at that time. The microminiaturization trend goes back to 1959 when Richard Feynman professed a famous lecture with a title "There's Plenty



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of Room at the Bottom" [12] where he discussed the possibility of manipulating atoms to severely reduce sizes of mechanical and electronic devices. The alluring capabilities of micro-sized world echoed within the research and medical communities [1,13,14] and since then a surge of interest in this area has been developed.



Figure 1. Energy conversion methods based on applied physical principles.

Batteries are quite often used in glucose biosensors, for example, because they represent a reliable and long-lasting source of energy. Typical power values of biosensing electronics are less than 10 μ W [15] but due to the sole nature of continuous monitoring, batteries become the bottleneck of the power design. For instance, glucose biosensors have a needle that penetrates the skin in order to collect data (Figure 2) and any time the battery needs to be replaced, the patient must go through a painful procedure of taking the biosensor in and out which involves puncturing the skin. Low battery capacity necessitates regular replacements, every week or two; each time the entire glucose biosensor is replaced, not just the battery. The 1.55 V coin-cell battery, which is mounted inside the Abbot's biosensor, tends to drive higher the end price of the continuous glucose monitoring. Therefore, it is desirable to identify means and methods that allow biosensors to realize continuous monitoring at full potential without the requirement to depend on batteries.



Figure 2. Abbott's continuous glucose monitoring biosensor; https://diatribe.org (accessed on 9 October 2022).

This review is aimed towards offering a basic understanding of what energy harvesters are, of the underlying physical principles, the technological challenges and the future perspectives. Apart from well-known and researched energy harvesting methods such as piezo- or triboelectricity, the review also focuses on some less known or exploited phenomena that are worthy of further investigation thus exposing a wide spectrum of energy scavenging possibilities. The review intends to offer an overview exploring modern energy harvesting techniques and materials and identifying the main trends of energy scavenging. The presentation is kept to a "high-level" style explaining core ideas providing the reader with the necessary references in case he is interested in more detailed descriptions and explanations.

2. Biofuel Cells

The first major entry in nanogenerators are biofuel cells (BFCs) which form a subgroup of fuel cells. Their modus operandi is based on biocatalysts [16–19] that cause a flow of electrons between anode and cathode thus generating energy. BFCs are represented by two main groups: microbial BFCs (Figure 3a) and enzymatic BFCs (Figure 3b). BFCs have two electrodes, anode and cathode, that are submerged in an electrolyte. The oxidation reaction of biofuel occurs at the anode, the oxidants are reduced at the cathode, and this allows electrons to flow through the circuitry. Microbial BFCs exploit microorganisms as biocatalysts forming a bioreactor while enzymatic BFCs utilize enzymes for oxidation and reduction reactions. A major advantage of microbial BFCs is that exoelectrogenic microorganisms operate in the environment that is akin to its natural biome and they have a long life span of up to five years [17,19]. The main advantage of enzymatic BFCs is their ability to effectively utilize glucose and lactate that is present in blood, sweat and tears as a fuel for chemical reactions thus proving to be extremely useful in the field of wearable and implantable electronics [16,20]. Yet, the lifespan of enzymatic BFCs is significantly shorter than of the microbial ones (7–10 days) [19].

Elasticity of BFCs plays an important role in wearable electronics related to the number of stresses and deformations they are subjected to. Electrodes of BFCs need to possess characteristics such as elasticity, electrical conductivity and biocompatibility while simultaneously not impairing the biocatalyst-bioelectrode interface [21]. Carbon-based materials, such as graphene, meet all the criteria. Carbon-based materials can be used in different forms: nanotubes, nanosheets, nanodots, etc. [19]. Combined with flexible substrates, such as elastomers, polymer films, hydrogels, they prove to demonstrate good results [21,22].

There are several materials that can be used as electrolytes. Biofluids such as sweat, urine, tears, saliva, etc. [23] are a common choice for BFCs as they have the necessary fuel to power the system. On the other hand, there are systems where the electrolyte is artificial, such as hydrogel for example [24], and the fuel is supplied from elsewhere.



Figure 3. Basic operating principle of (a) microbial BFC [25] and (b) enzymatic BFC [26].

Zhang et al. [27] were able to exploit an enzymatic BFC, which was integrated into a diaper of diabetic patients, as an effective glucose concentration sensor while simultaneously powering the system. Quantitatively, they managed to approach a power density of 220 μ Wcm⁻². Zhang et al. [28] took a rather unconventional approach and designed an artificial enzyme which mimics its natural competitor with a power density of $149.2 \pm 4.0 \,\mu$ W·cm⁻². A particularly unique case of microbial BFC was studied by Jayapiriya and Goel [29] where a paper-based 3D printed microbial BFC was designed that was capable of generating as much as $11.8 \,\mu$ W·cm⁻². It is also important to add that the manufacturing method employed is important for creating a cost-effective solution for energy harvesters used in low-powered biosensors. An extraordinary power density of 703.55 mW·m⁻² was achieved by Yan et al. [30] with a nano enhancement of electrode/electrolyte interface. Overall, BFCs are prominent sources of energy for wearable and implantable bioelectronics though they have a number of drawbacks such as low power density, low power output and they are prone to have high cost and short lifetime [31].

3. Thermal Generators

Thermal energy exists in abundance in the ambient environment. Both the human body and the space around it can be seen as energy sources for thermoelectric and pyroelectric devices [32–34]. The physical principle of thermoelectric energy generation is based on the Seebeck effect that describes the generation of an electric current when n and p type conductors are electrically connected under the presence of a temperature gradient (Figure 4) i.e., charge carriers will move from the warmer to the cooler side of the formed thermocouple [34]. Advantages of thermoelectric NGs are that they supply a DC voltage, which means that they do not need to be rectified, thus making the process of energy collection easier at a price of generally having a low voltage output.



Figure 4. Physical principle of thermoelectric generator [35].

Pyroelectric materials (Figure 5a), are a subclass of piezoelectric materials that are not gradient dependent, but instead they are prone to change polarization due to temperature fluctuations [36]. Pyroelectric materials have an inherent dipole moment that adds up to the spontaneous polarization. The dipole moment remains constant unless there is a temperature fluctuation (Figure 5b). The polarization decreases when the temperature increases (Figure 5c) while a decrease in temperature normalizes the orientation of dipoles and causes the polarization to increase (Figure 5d). The main advantage of pyroelectrics is that they possess piezoelectric properties as well and their main disadvantage is that they depend on constant change of temperature.



Figure 5. Physical principle of pyroelectric generator: (**a**) ions and dipoles in pyroelectric material, (**b**) without temperature variation, there is no current, (**c**) increase in temperature tends to decrease polarization (**d**) decrease in temperature leads to increase of polarization [37].

Thermal materials can be divided into three main groups: inorganic, organic and hybrid (a combination of both). Inorganic materials consist mainly of bismuth telluride (Bi2Te3) and antimony telluride (Sb2Te3) and their respective alloys [38]. Inorganic materials possess qualities such as high electrical conductivity and they suffer from a mechanically rigid structure and toxicity [39]. Organic materials are represented by carbon-based materials and conductive polymers [38]. They are much more flexible and biocompatible in contrast with their poor electrical parameters. The combination of both types attempts to synthesize materials with the best qualities of both worlds. In practice, thermal materials sit in-between two material types. It is worth noting that usually an organic material is doped by an inorganic one to boost conductive properties of the hybrid.

The human body maintains its temperature constant at approximately 37 °C which allows thermal energy to act as a reliable source for energy harvesting. The ambient temperature and solar energy in particular [40] can be used for conversion of thermal energy. Recent advances in the field of thermoelectric harvesters, indicate that flexibility of the harvester plays one of the most important roles. Klochko et al. [41] used biodegradable polymer nanocellulose and biocompatible semiconductor copper iodide and this method resulted in a flexible design that provided a power density of up to 44 μ W·cm⁻². A different approach was followed by Bai et al. [42] who proposed a conductive quasi-solid gel for an electrical interface. Changing flexible solids for a gel had a positive effect on flexibility and proved to offer about 100 μ A in parallel and a voltage of 24 mV for 25 generator units. Rösch et al. [43] reported the design of a 3D printable thermoelectric generator with a meander structure. A highlight of this project lies in its 2D layout that was later bent into a 3D origami-like shape which could be easily scaled up. This design provided with an output of 47.8 µW·cm⁻². Ren et al. [44] described a generator that possessed self-healing capabilities, was made of recyclable material and had a modular design which was implemented via making laser cuts in polyimine substrate and inserting in an array of thermoelectric chips. Due to the bond exchange reaction of polyimine, the substate restored its original form even when it was torn apart to a certain degree. Average outputs of 45 and 83 nW·cm⁻² were achieved while a wearer was sitting and walking respectively. This approach was taken even to a greater extent when Liu et al. [45] described a thermoelectric generator filled with gel that it also had self-healing capabilities meaning it could repair self-inflicted damage to a certain degree and reached output voltage as high as 172.9 nW. The idea of self-repairing generators echoes in the article by Wu et al. [46] which reported the degenerative effect of repeated bending of flexible thermoelectric generators. Pyroelectric harvesters are usually represented by a combination of hybrid piezo- and pyro- effects that take place simultaneously [36]. Mahanty et al. [47] reported

their findings from the design of such harvesters with an energy density of $34 \,\mu\text{W}\cdot\text{cm}^{-2}$. The hybridization trend is also reported in Li et al. [40] where an energy harvester that produced 21.3 mW·m⁻² was designed via a combination of solar, thermal and pyroelectric physical interfaces. The device was integrated onto an outdoor bracelet and was reported to charge after 1 h of exposure to the environment. Moreover, hand movement of the bracelet increased pyroelectric output by more than 12.7 times. Thermoelectric and pyroelectric harvesters represent a huge potential for energy scavenging. While being capable of exploiting the highly stable and accessible energy source of the human body and the ambient temperature, this group possesses good hybridization capabilities, especially when paired with photovoltaic materials.

4. Biomechanical Energy

Biomechanical energy is one of the largest categories and one of the most utilized among all other energy sources [3,7–9,48,49]. The human body is full of flexible joints and points of concentrated pressure (Figure 6) that could be used for energy harvesting from limb movement, respiration, chest and abdomen displacement, eyelid movement, body pressure onto soil while walking, etc [50–53].



Figure 6. Biomechanical energy in the human body [54].

4.1. Piezoelectric Nanogenerators

Piezoelectric nanogenerators (PENGs) are used in many applications such as sensors and actuators [55–58], energy harvesters, micro-electromechanical systems (MEMS) [59] and microfluidics [60]. Energy generation is possible because piezoelectric materials lack central symmetry in their structure. An applied mechanical load induces spontaneous polarization in PENGs and thus electricity is generated (Figure 7). Their popularity is based on their scalability potential, high output power, simplicity of integration [57,61] and availability of "of-the-shelf" energy harvesting solutions (Würth Elektronik, Physik Instrumente, TE connectivity, etc). The downside of PENGs is that their output depends on frequency and optimum actuation values lie in a high-frequency range.

Piezoelectric materials are classified into four main groups: inorganic, organic, composites and biocomposites. Inorganic materials, such as lead zirconate titanate (PZT), barium titanate (BT) and quartz have high values for their electric parameters (piezoelectric strain constant, electromechanical coupling factor and dielectric constant) but they are rigid, brittle and require polling process to function [62]. Organic materials, represented mainly by polyvinylidene difluoride (PVDF) and its copolymer trifluoroethylene (PVDF-TrFE), are on the opposite side of the spectrum and have high elasticity, while having less electrical efficiency. Polymer composites are intended to be the best of both worlds, combining the high piezoelectric parameters of the inorganic materials while staying flexible and biocompatible like the organic materials. Mostly, this is performed by depositing ceramic element, such as BT, on a polymer matrix, such as PVDF [34,63]. Biocomposites are biological tissues that possess inherent piezoelectricity, such as hair, bone, fish bladder, etc. [63].



Figure 7. Physical principle of piezoelectric generator [9].

The most commonly used materials are ZnO, polyvinylidene difluoride (PVDF) and lead zirconate titanate (PZT) [57], all of which have inherent pyroelectric properties [36,64]. The recent advances in the field of piezoelectric energy harvesting build on developments in additive manufacturing capabilities [65]. Montero et al. [66] used inkjet printing to deposit an interdigitated electrode which is subsequently coated with PVDF film. The resulted power density was 0.5 μ W·cm⁻³ with a maximum value of 2.4 nW for the device. Potential applications are varied, for example, a backpack is a quite common form of an attire and thus it is relevant to investigate how much energy can be harvested from it. Zhang et al. [67] used force amplification via a double-bridge frame, studied effects of this method via numerical simulations and experiments and presented a backpack with the maximum output power of 4.13 μ W. This power output was reached when the harvester was integrated into a backpack and the person wearing it was jogging. Ruiz et al. [53] demonstrated a respiratory piezoelectric based sensor which, not only provided data for health monitoring, but also could act as an energy harvester. Beyaz [55] described a blood pressure sensing technique which exploits PENGs. Three piezoelectric transducers were used to exhibit and receive acoustic signals to detect geometrical changes in artery tissue. In terms of biodegradable materials, Kumar et al. [68] used reinforced polycarbonate which resulted in a flexible platform that provided high power density up to 2556 μ W·cm⁻³ at maximum. An unorthodox approach was taken by Sun et al. [69] who reported a PENG made out of a wood sponge. Balsa wood was processed to remove lignin and hemicellulose which resulted in a crystal structure that possessed a high piezoelectric coefficient. Not only does this NG used a biodegradable material, but wood is also present in an abundance thus making this PENG a prominent candidate for wearable harvesters. The scalability potential of the PENG suggests that it can be used for application for wearable electronics and for powering LED lights and LCD screens. The peak power density reached was 0.6 nW ⋅ cm⁻². Due to the way the internal electrostatic field propagates inside the piezoelectric material, it is usually synonymous with relatively low current density and thus lower power density output, especially compared to triboelectric materials. Gu et al. [70] proposed a variant of PENG with high output current density. In order to achieve this, a high piezoelectric coefficient material Sm-PMN-PT was selected, and an intercalation electrode structure was

utilized. Essentially, the way to increase piezoelectric energy lies in increasing electrode surface area. The authors of this work proposed a way to enhance PENG by integrating multiple electrodes inside the piezoelectric film and sandwiching them together resulting in a PENG which had as high as 12 units of this structure stacked together. As a result, a maximum peak short-circuit current of 320 µA was obtained by the harvester. Xu et al. [71] designed a PENG that can be attached to one of the leads of a pacemaker. The main material used was microporous P(VDF-TrFE) thin film that was deposited onto Kapton film and sandwiched between Au electrodes. From the engineering point of view, the authors decided to implement a multibeam design. The harvester had a cylindric form and its inner space was filled with piezoelectric films which play role of beams. Then, the harvester was placed onto a lead. A pacemaker lead was fixed by these films and when the lead was subject to movement, its energy was transferred to the PENG. The output energy was 6.5 μ J that was stored in a 120 uF capacitor. It can be deduced that, despite being relatively simple and long-studied subject, PENGs are in a high demand and present a very prominent foundation for energy harvesting. Yet, their cost and dependence on actuation frequency need to be taken into account during the design phase [72].

4.2. Triboelectric Nanogenerators

Triboelectric nanogenerators (TENGs) are used to power many sensors and energy harvesters of different designs [52,73,74]. TENGs harvest kinetic energy of the human body akin to PENGs and exploit the same points of mechanical pressure. The underlying physical principle is the fact that materials have different tribopolarities and when paired properly, spatial manipulation causes triboelectrification and electrostatic induction. Surface porosity plays a vital role in the process of designing TENGs [75]. There are four fundamental operational modes of TENGs as displayed in Figure 8, each utilized under different circumstances [74]. In the vertical contact separation mode (Figure 8a) which features two electrodes and a dielectric film, when the mechanical force is applied, triboelectrification charges the electrodes, and when the force is released and there is a small gap between the electrodes, electrostatic induction causes current to flow. Contact-sliding or lateral-sliding mode (Figure 8b) works similarly to the first mode, yet electrodes move to the sides. In the single-electrode mode (Figure 8c), only one grounded electrode is present which is spatially separated from a dielectric film. While approaching to and departing from the electrode, electrical field changes due to the triboelectrification. The potential difference between the materials cause electrons to flow. In the freestanding triboelectric-layer mode (Figure 8d) the dielectric layer moves, while the electrodes remain still. The major advantage of using TENGs is their low cost per Watt at low frequencies [76], their high output power and that the output voltage is independent of frequency. However, the issue of the overvoltage influences the energy conditioning circuitry and TENGs tend to have small currents.

Triboelectrification occurs between two materials, one of which has a higher electron affinity (acceptor), while the other material has lower electron affinity (donor). According to the results of material selection summary [77], Polytetrafluoroethylene (PTFE), polydimethyl-siloxane (PDMS), fluorinated ethylene propylene (FEP) and Kapton are widely used as electron acceptors. As electron donors, materials such as aluminum, cuprum, skin and Nylon are mostly used. In addition, triboelectric generators can be represented as four (4) layers which are the charge-generating, charge trapping, charge-collecting and charge-storage layers whereas the materials for such complex structure are described elsewhere [78].

In terms of practical application, Zhang et al. [79] presented a paper-based TENG capable of producing up to 171 mW·m⁻². A highlight of this work is that a single-electrode TENG can be produced relatively economically and fast from waste paper, which serves as a triboelectric layer. Jiang et al. [80] described a TENG with self-healing capabilities. The synthesized elastomer proved to be both extremely elastic (10000%) and could completely repair itself while reaching an output of 450 mW·m⁻². Another single-electrode mode

TENG for tactile sensors was designed by Wu et al. [81] where the surface porosity was optimized in order to provide the best results possible and a power density of $33.75 \text{ W} \cdot \text{m}^{-2}$ was achieved. Guan et al. [82] reported a TENG based on a two-electrodes contact-separate mode that had a negative Poisson-ratio fiber inserted into positive Poisson-ratio hallow cylinder. This synergistic structure could provide up to 52.36 mW \cdot m⁻². Liao et al. [83] proposed an ion-gel based TENG that could heal itself, could effectively work in a wide range of temperatures (-70 to 250 °C) and was transparent. The approach of using iongel instead of regular electrodes allows to reach outstanding stretchability parameters (1012%). The self-healing capability was tested by cutting the gel in half and sticking it back together. The demonstrated TENG reached power density of 2.17 W·m⁻². Another unusual application of gel in TENG was suggested by Sheng et al. [84] who investigated the application of highly stretchable (>10,000%) TENG as an arm training sensor or for helping patients with self-rehabilitation. This harvester reached a power density of 30 mW·m⁻². Yang et al. [85] indicated that there are still ways to improve the design layout of TENG instead of trying to improve harvesters on molecular level with a report on a honey combed TENG. The outer layer which forms a carcass of the harvester is a 3D printed TPU material, the top three honeycomb walls are coated with conductive fabric and PBAT film while the bottom three walls are coated with Al film. In this case, PBAT and Al work as triboelectric layers when being pressed against each other. Additionally, this design was very easily manufactured making it extremely useful for prototyping and massive production. This design solution reached a power output of 10.79 $W \cdot m^{-2}$ and a high voltage of 1500 V. Ryu et al. [86] described a TENG producing 4.9 μ W·cm⁻³ which is suitable for use with IMDs and pacemakers. In this work, the TENG consisted of multiple stacked units, it works in free-standing mode and harvests vertical displacement of the chest. The harvested energy was subsequently conditioned and put into a Li-ion battery. This work also featured an in vivo experiment involving an adult mongrel. Over a span of 24 h, 144 mW of power was harvested considering both periods of low and high activity. Biocompatibility was examined by the inflammation response of the animal which proved to be within limits and no signs of infections or fever were observed. Overall, TENGs are a prominent method of energy harvesting that has a considerable amount of output power that is achieved through various intricate design choices. However, the conditioning circuit plays a huge role in this type of harvesters due to the overvoltage [72].



Figure 8. Fundamental operational modes of TENG: (**a**) vertical contact-separation mode, (**b**) contactsliding mode, (**c**) single-electrode mode, (**d**) freestanding triboelectric-layer mode [9].

4.3. Electromagnetic Generators

Electromagnetic generators (EMGs) follow a variety of constructive implementations that revolve around moving a coil relative to magnets thus exploiting Faraday's law of induction [9,10] which implies that a change in magnetic flux results in an induction of electromotive force. It can be achieved through four main mechanisms: moving the magnet perpendicularly relative to the coil (Figure 9a), moving the magnet in parallel to the coil (Figure 9b), moving the magnet inside the coil (Figure 9c); and moving the coil in-between magnets (Figure 9d). The current trend in EMGs lies in the hybridization of EMGs and TENGs, which proves to have fruitful results. The main advantage of EMGs is that they have low matching resistance values [87] and can be effectively used at low frequencies [88]. On the other hand, they have inherently rigid nature and might have reliability issues [89].



Figure 9. Physical principle of electromagnetic generator: (**a**) perpendicular relative movement, (**b**) lateral or parallel relative movement, (**c**) magnet movement inside the coil, (**d**) coil relative movement in-between magnets [9].

Jiang et al. [90] presented a hybrid harvester where human body pressure from movement is transformed via transmission into radial movement of a generator. The generator consisted of rotating triboelectric blades which worked in the freestanding triboelectriclayer mode, magnets and coils that were placed in the rotor and the stator respectively. In terms of output power, the harvester provided 14.68 mJ when integrated into a shoe. Li et al. [91] developed a magnetized microscale needle array which also possessed triboelectric properties. The device used microneedles that induced triboelectrification when rubbed against the substrate, which also acted as a magnet moving up and down relatively to the coil. This combination of energy harvesting generators achieved up to 16.19 μ W·m⁻² for a load of $10^6 \Omega$. Practical application involved putting the harvester into a shoe and the values of collected voltage for walking and jogging were very different for the TENG (2.8 V and 6 V respectively), whereas the collected current for the EMG indicated less difference (4.5 µA vs. 5.3 µA). Iqbal et al. [87] described PENG mixed with EMG that could be inserted into a shoe insole. As a result, the overall output was better than using PENG or EMG separately and a power of 4.05 μ W·cm⁻³ was achieved. On the other hand, Lai et al. [92] reported on a hybrid harvester that scavenges electromagnetic energy from the ambient environment such as a mobile phone, laptop or any other electronic device. The mechanical energy was harvested via TENG that worked in the single-electrode mode. The peak power was 360 μ W·m⁻¹. Li et al. [88] designed a hybrid PENG and EMG, where PENG was connected to the EMG via a spring-loaded mechanism. In this harvester, two generators

harvested energy separately, but they were combined through the mechanical transmission. A power output of 36.21 mW·cm⁻³ was reached. Electromagnetic energy is an underutilized and unconventional source for biomechanical energy harvesting, but it may prove to be useful in combination with other NGs.

4.4. Electrostatic Nanogenerators

Electrostatic generators (ESGs) are a type of a varying capacitor and their working principle is described by electrostatic induction [8]. The capacitance of such a device changes as a result of changes in the overlap area or in the gap between two electrodes, caused by some external stimuli (Figure 10). The induced electrical charge will result in electric current. There are four main shapes of ESGs: an in-plane gap closing ESG where the electrode moves sideways (Figure 10a), an in-plane overlap ESG where the counter-electrode moves in plane thus changing the overlap (Figure 10b), out-of-plane gap closing converter where the gap between electrodes changes (Figure 10c), in-plane ESG where the overlap varies by moving across one axis (Figure 10d). The application of such varying capacitors ranges from biosensors, textile wearable electronics, biomechanical energy harvesting to solar energy storage. The main advantage of using ESGs is their simple structure and high output at high frequencies however they frequently need bias voltage to function properly and most methods of increasing frequency of a harvester (or self-oscillation feature) includes MEMS [93,94].



Figure 10. Main shapes of electrostatic generators: (**a**) in-plane gap closing converter, (**b**) in-plane overlap converter, (**c**) out-of-plane gap closing converter, (**d**) in-plane converter with variable surface [95].

Wu et al. [94] continued the trend of hybridization that is so prominent in other NGs and described a rotatory disc-based EMG and ESG. The modus operandi of the EMG followed the principles discussed in the previous section, while ESG consists of an electret film and the respective electrode. The rotatory movement of the electret film relative to the electrode causes a change in the overlap area. The maximum output density is $2.5 \text{ W} \cdot \text{m}^{-3}$ for EMG and $107.8 \text{ W} \cdot \text{m}^{-3}$ for ESG. Pourshaban et al. [96] designed an electrostatic generator which is integrated into a contact lens where a tear droplet plays the role of the electrode. The average obtained power is $0.265 \,\mu\text{W}$. Erturun et al. [97] proposed a hybrid of PENG and ESG. In this structure, a piezoelectric film is sandwiched between Au and Al electrodes. The Al electrode is coated with Teflon on the opposite side to the PENG and is isolated from the bottom Cu electrode via an air gap confined by two Styrofoam pads. When the harvester is subjected to stress, the electron flow is directed to the Al electrode and outwards, when pressure is released. The maximum attained power density was $\sim 8.8 \,\mu\text{W} \cdot \text{cm}^{-3}$. Cao et al. [98] proposed a hybrid of PENG and EMG where vibrations

of a piezoelectric cantilever were also used to harvest electrostatic energy. This is due to fluctuations of a beam that has ESG electrode on it which changes the gap distance and induces change in capacitance. Capacitive harvesters represent a stable source of energy and have been thoroughly investigated for a long period of time thus making them a very suitable choice for a hybridization.

4.5. Reverse Electrowetting on Dielectric Phenomenon (REWOD)

Recently, a lot of attention has been drawn to the reverse electrowetting on dielectric phenomenon (REWOD) [99–101]. This is a prominent subclass of ESGs which is based on the direct electrowetting on dielectric (EWOD) phenomenon. EWOD exploits the fact that the liquid-solid (droplet-electrode) interfacial energy can be manipulated by the application of an electric field. This leads to a change in the apparent contact angle between the droplet and the electrode which increases the overlap area (Figure 11). A droplet could potentially be a physiological fluid [102] thus a biomolecular absorption should be taken into account [103]. REWOD works in the opposite manner and when a bubble of conductive liquid is pressed in-between electrodes, the overlap area changes thus significantly increasing the capacitance of the system. Adhikari et al. [101] studied REWOD phenomenon via changing different parameters of the system such as dielectric thickness, electrolyte and dielectric concentrations. When two dissimilar dielectrics are introduced, the system can work without the external bias voltage. A total power density of 53.3 nW·cm⁻² was obtained. Tasneem et al. [104] proposed a wearable motion tracking sensor powered by a REWOD principle. A significant focus of the work was oriented towards the conditioning circuit. In this case, the authors used a rectifier based on a Schottky diode followed up 2. by a booster circuitry and the resulted power density of the harvester was 58 nW·cm⁻ Hsu et al. [93] described a REWOD harvester that could produce as much as $100 \text{ W} \cdot \text{m}^{-2}$ with a 4.5 V of bias voltage and it instantly became one of the most prominent works in the field. The described harvester heavily relies on multiplication of the number of REWOD units and the frequency of their oscillations. Thus, the REWOD method of harvesting biomechanical energy holds a significant potential in what it can practically be achieved.



Figure 11. EWOD and REWOD processes [93].

5. Photovoltaic Materials

Solar energy is a renewable energy source with very high potential, it is abundant [105] and can be harvested easily, under appropriate weather conditions [3,9,106,107]. Photo-voltaic materials optically collect photons emitted by a light source. The harvested solar energy is then transferred to the electrons, which makes them highly mobile, thus forming

an electric current (Figure 12). Merits of using photovoltaic materials are their stable DC output but for wearable electronics they usually need to be hybridized because of limited day-time use.



Figure 12. Solar energy harvesting [9].

Zhang et al. [105] reported a photo-thermoelectric hybrid harvester. The seamless integration with the textile fabric creates a possibility for an integration with the continuous monitoring system, while the output power under sunlight reaches 0.24 nW. Zhang et al. [108] described another unconventional application of photo-thermoelectric harvester which is conjugated with hydroelectricity. The hydroelectric effect helps to drastically increase the total output voltage from -0.092 to 1.712 mV; and, in the wet state the harvester reaches 2.45 μ W. Moreover, the evaporated body fluid also produces steam, and such a textile-based harvester can also serve as a human body humidity monitor. Yu et al. [109] proposed a gauze kerchief made from photovoltaic textile. In this case, Cu or Cu-coated polymer wires are sequentially coated with Mn substrate, ZnO nanowires, ethanol solution of N719 and CuI forming photoanodes. The synthesized generator was optimized via change of embroidery process parameters, different materials of the counter electrode and how electrodes were connected to one another. 0.79 V were obtained with a light intensity of 100 mW cm $^{-2}$. Photovoltaic devices represent efficient energy harvesters though it should be viewed as an addition to another NG that can constantly and reliably provide power.

Selected types of NGs cover all the basics needed for design of the effective energy harvester however this is not the end of it. As briefly mentioned in photovoltaic materials, a new hydrovoltaic type of energy attracts a great deal of popularity [110]. Energy that comes from water evaporation can be harvested with the help of a porous conductive structures. The underlying physical principles can be explained through an electrical double layer and electrokinetic effects but the exact mechanism is yet to be described [111]. Recent survey of this topic can be found elsewhere [112].

6. Comparison of Nanogenerators

The energy harvesters that were reviewed in the previous sections and their respective features are compiled and compared in Table 1. Their main features, their electrical properties, their size and their power output are presented and compared.

NG Type	Authors	Features	Voltage, Load, Frequency	Size	Power Output
enzymatic BFC	Zhang et al. [27]	Integrated into a diaper	300 mV (OC)	$6 \times 5 \text{ cm}^2$	$220 \ \mu W \cdot cm^{-2}$
enzymatic BFC	Zhang et al. [28]	artificial enzyme	400 mV (OC)	n/a	149.2 μ W·cm ⁻²
microbial BFC	Jayapiriya and Goel [29]	3D printed, paper-based	480 mV (OC)	Coin size (~2 \times 2 cm ²)	11.8 μ W·cm ⁻²
enzymatic BFC	Yan et al. [30]	high-power, nano enhancements of materials	~0.8 V 1000 Ω	~0.3 nm ²	$703.55\ mW{\cdot}m^{-2}$
thermoelectric NG	Klochko et al. [41]	Biodegradable materials	5 V (OC)	$3 \times 2 \text{ cm}^2$	$44 \ \mu W \cdot cm^{-2}$
thermoelectric NG	Rösch et al. [43]	3D printed origami-like shape	534 mV (OC)	190 cm ²	$47.8 \ \mu W \cdot cm^{-2}$
thermoelectric NG	Ren et al. [44]	self-healing recyclable material	5 V	$6 \times 5 \text{ cm}^2$	$83 \mathrm{nW}\cdot\mathrm{cm}^{-2}$
thermoelectric NG	Liu et al. [45]	self-healing	4.15 mV 600 Ω	${\sim}4\times2cm^2$	172.9 nW
pyro- and PENG	Mahanty et al. [47]	hybrid	35 V at 3.4 M Ω	$8 imes 7\ cm^2$	$34 \ \mu W \cdot cm^{-2}$
Solar, thermal and pyroelectric NG	Li et al. [40]	hybrid	93.1 (OC)	$3 \times 9 \text{ cm}^2$	$21.3\ mW{\cdot}m^{-2}$
PENG	Montero et al. [66]	3D printed	1.1 V 60 Hz 100 MΩ	$18 imes 18 \ \mathrm{cm}^2$	$0.5 \ \mu W \cdot cm^{-3}$
PENG	Zhang et al. [67]	integrated into a backpack	~1.7 V 8 Hz 0.7 MΩ	$3.5\times3.5\times9~mm^3$	4.13 μW
PENG	Kumar et al. [68]	nano enhancements of materials	16.67 V (OC) 5 Hz	$12\times8mm^2$	$2556 \ \mu W \cdot cm^{-3}$
PENG	Sun et al. [69]	made from wood sponge	0.63 V ~1 Hz 80 MΩ	$15\times15\times14\ mm^3$	$0.6 \text{ nW} \cdot \text{cm}^{-2}$
PENG	Xu et al. [71]	multibeam structure implantable	0.3 V 1 Hz	n/a	6.5 μJ
TENG	Zhang et al. [79]	paper-based	~95 V 2 Hz 130 MΩ	$4 imes 4\mathrm{cm}^2$	$171 \text{ mW} \cdot \text{m}^{-2}$
TENG	Jiang et al. [80]	self-healing	75 V (calc) 2 Hz 5 MΩ	$2 \times 2 \text{ cm}^2$	$450 \text{ mW} \cdot \text{m}^{-2}$
TENG	Wu et al. [81]	optimized surface porosity	78.7 V (OC)	$8\times8\times0.5\ mm^3$	$33.75 \ W{\cdot}m^{-2}$
TENG	Guan et al. [82]	different Poisson-ratio materials	~25 V 10 MΩ	$20\mathrm{cm} imes$ ø $2\mathrm{mm}$	$52.36 \text{ mW} \cdot \text{m}^{-2}$
TENG	Liao et al. [83]	ion-gel self-healing	189 V (OC) 1.5 Hz	$3 \times 3 \text{ cm}^2$	$2.17~\mathrm{W}{\cdot}\mathrm{m}^{-2}$
TENG	Yang et al. [85]	3D printed honey-comb structure	1500 V (OC) 3 Hz	$68 \times 39 \text{ mm}^2 \times 5$	$10.79 \text{ W} \cdot \text{m}^{-2}$
TENG	Ryu et al. [86]	implantable stacked TENG structure	10 ΜΩ	n/a	$4.9 \ \mu W \cdot cm^{-3}$
EMG and TENG	Li et al. [91]	hybrid Microscale needles	10 V (OC) 1 Hz (TENG)	$24\times24\times3.2\ mm^3$	$16.19\ \mu\text{W}{\cdot}\text{m}^{-2}$
EMG and PENG	Iqbal et al. [87]	hybrid	7.01 V (OC)	$3.9 \times 3.9 \times 2.9 \text{ cm}^3$	$4.05 \ \mu W \cdot cm^{-3}$
EMG and TENG	Lai et al. [92]	hybrid uses ambient magnetic field	120 V/m 100 MΩ	5 cm (contact length)	$\begin{array}{c} 360 \; \mu W {\cdot} m^{-1} \text{ and} \\ 8 \; \mu W {\cdot} m^{-1} \end{array}$

Table 1. Comparison of Nanogenerators.

NG Type	Authors	Features	Voltage, Load, Frequency	Size	Power Output
EMG and PENG	Li et al. [88]	hybrid MEMS	18 V (OC) PENG 22 V (OC) EMG	$4 \times 2.5 \times 5.8$	$36.21 \text{ mW} \cdot \text{cm}^{-3}$
ESG and EMG	Wu et al. [94]	hybrid	~40 V (OC) EMG ~0.1 V (OC) ESG 50 rpm	ø 50 mm	2.5 W·m ^{−3} and 107.8 W·m ^{−3}
ESG	Pourshaban et al. [96]	contact lens	450 mV 100 kΩ	$2 \times 10 \text{ mm}^2$	0.265 μW
ESG and PENG	Erturun et al. [97]	hybrid	4.2 V 1 MΩ—PENG 17 V 10 MΩ—ESG 20 Hz	ø 3 × 0.65 cm	$8.8 \ \mu W \cdot cm^{-3}$
REWOD NG	Adhikari et al. [101]	no bias voltage	0.103 V 0.15 MΩ 3 Hz	ø 50.5 mm	$53.3 \mathrm{nW}\cdot\mathrm{cm}^{-2}$
REWOD NG	Tasneem et al. [104]	conditioning circuit	943 mV pp 1.6 MΩ 10 Hz	4 mm gap between electrodes	$58 \mathrm{nW}\cdot\mathrm{cm}^{-2}$
REWOD NG	Hsu et al. [93]	self-oscillation	bias voltage used 0.877 MΩ	$\begin{array}{c} 40\times40~\mathrm{mm^2}\\ (628~\mathrm{mm^2}) \end{array}$	$100 \text{ W} \cdot \text{m}^{-2}$
photo- thermoelectric NG	Zhang et al. [105]	hybrid	0.56 mV 1.32 kΩ	$4\times 0.3\text{cm}^2$	0.24 nW
photo-, thermo-, hydroelectric NG	Zhang et al. [108]	hybrid hydroelectricity	12.5 mV 15.93 Ω	$1.5 \times 1.5 \mathrm{cm}^2$	2.45 μW
photovoltaic NG	Yu et al. [109]	photovoltaic textile	0.79 V	4.5 mm pitch	$\sim 134 \ \mu W$

 Table 1. Cont.

A summary of the advantages and disadvantages of the main classes of NGs is presented in Table 2.

 Table 2. Advantages and disadvantages of various types of Nanogenerators.

Energy Ha	rvester Type	Advantages	Disadvantages	Voltage Output	Current Density	Power Density
Microbial BFCs Enzymatic	No enzymes Long life span (5 years) DC output voltage	Need special mediators Low power density	100–500 mV	10–100 μA×cm ⁻²	1–10 μ W \times cm ⁻²	
	Enzymatic	Effective use of body liquids (sweat, tears, etc) as fuel DC output voltage	Short life span	0.1–1 V	100–500 μA×cm ⁻²	10–100 μ W \times cm ⁻²
	Thermoelectric	DC output voltage	Low voltage	0.1–1 V	0.1–10 μ A \times cm ⁻²	0.1–10 μ W \times cm ⁻²
Thermal	Pyroelectric	Are a sub-class of piezoelectric materials	Require tempera- ture fluctuations	0.1–10 V	0.01–10 μA×cm ⁻²	0.1–1 μ W×cm ⁻²
Piezo	electric	Availability "of-the-shelf" Can possess pyroelectric properties	Frequency dependent output	0.1–10 V	0.01–10 μA×cm ⁻²	1–100 μ W \times cm ⁻²
Tribo	electric	High output High elasticity Low cost	Overvoltage Small current	10–1000 V	1–10 μ A \times cm ⁻²	$1-100 \text{ mW} \times \text{m}^{-2}$
Electro	magnetic	Hybridization with TENGs and ESGs Low impedance	MEMS (low reliability) Rigid, non-flexible nature	0.1–10 V	$1–10 \ \mu\text{A} \times \text{cm}^{-2}$	10 μW×cm ⁻² (mostly used as a hybrid with TENGs)
Elect	rostatic	Simple structure	Practical applications involve MEMS	0.1–1 V	1–10 µA×cm ⁻²	0.1–10 μ W \times cm ⁻²

Energy Harvester Type	Advantages	Disadvantages	Voltage Output	Current Density	Power Density
REWOD	High output voltage at high frequencies	Needs bias voltage for high output Frequency dependent	10–100 mV	10–100 nA×cm ⁻²	0.01–0.1 μ W×cm ⁻²
Photovoltaic	DC current	Needs hybridization for constant energy	1–100 mV	1–100 μ A \times cm ⁻²	0.1–10 μ W \times cm ⁻²

Table 2. Cont.

7. Biomedical Application of Energy Harvesters

In addition to the aforementioned glucose biosensor, another example of a commonly used biosensor is a pulse oximeter (Figure 13) biosensor that had seen an extensive use throughout the COVID-19 pandemic [113–115]. A pulse oximeter is used to measure the blood oxygen saturation level and the heart rate. Its working principle is based on hemoglobin light absorption [116]. Near infrared and red LEDs are mounted on one side of the device and the opposing side is equipped with photodiodes. Detection of oxygenated and deoxygenated hemoglobin appears at the red-light wavelength while near infrared is used as a reference. Because the heart pumps blood at certain frequency, this pulsative nature or pulse can be monitored with the same method thus making a combined biosensor. Batteries for pulse oxygen biosensors are replaceable and can last for 30 h and more. Biosensors consume approximately 40 mW of total energy during continuous work [117]. Introduction of an energy harvesting module would allow pulse oximeters to continuously monitor hemoglobin without the need to constantly replace or recharge batteries making it fully autonomous.



Figure 13. An example of a pulse oximeter from Kinetik wellbeing; https://www.kinetikwellbeing. com/ (accessed on 19 August 2022).

A different application for energy harvesting can be found within cardiovascular implantable medical devices (IMDs) such as implantable cardioverter-defibrillators (ICDs) and pacemakers (Figure 14). ICD represents a combination of a continuous monitoring system and actuator for administration of an electric stimuli if heart rate is higher than a designated threshold (tachycardia) [118]. Pacemakers, depending on their type, can sense intracardiac signal and stimulate the according chambers or ventricles thus pacing heart [119]. Both devices follow a similar design and quite frequently they are combined into one device. A pacemaker, for example, consists of a pulse generator module with leads which are placed into hears chamber or ventricles. The electric stimuli are delivered from the pulse generator to the heart. Typical power consumption values for pacemakers are less than 100 μ W while ICDs may reach more than 200 μ W [120]. Depending on the frequency of its use, a pacemaker may last up to 12 years [121] but an implantable cardioverter-defibrillator lasts for 9 years [122]. However, when the battery runs out or it depletes prematurely, which happens to 8% of IMDs [123], a new surgery needs to be performed to replace an IMD thus involving health risks and financial implications [86].

Clinical application of biosensors and sensors alike is vast. Apart from glucose and pulse oximeter biosensors, human respiration efficacy, temperature, sweat content, interstitial fluid and heart electrical signal. Such types of sensors and biosensors can be integrated into clothing, wristbands, contact lenses, skin or be implanted into the human body [8,124].

Overall, almost all sensors for monitoring human biomarkers rely on batteries to a certain degree which creates a gap in continuous monitoring and necessitates additional actions to be performed by a patient. Energy harvesting offers a solution which can reduce the size of batteries or get rid of them completely offering more stable and comfortable monitoring platform.



Figure 14. A pacemaker implanted into the human body; https://www.stanfordchildrens.org/ (accessed on 19 August 2022).

8. Discussion on Current Trends

This brief review of energy harvesting identifies two main current trends: hybridization of several NGs and manipulation of material structure. In addition, the overall application of the harvester is of paramount importance because it largely influences the design of harvester. Extensive presence of TENGs and PENGs indicates that biomechanical energy is one of the most used and effective sources for scavenging. Since TENGs and PENGs already represent an established field, prototyping and manufacturing of these devices is lower compared to other NGs. However, the choice between the two is not the simplest decision to make because, as previously mentioned, PENG has lower output than TENG and its impedance is dependent on actuation frequency while TENG have a necessity to come with complex energy conditioning circuitry to combat overvoltage. ESGs and EMGs are essentially MEMS meaning that their mechanical reliability is going to be a prime issue during the design stage [89].

Judging from the comparison presented in Table 1, it can be observed that PENGs and TENGs dominate the area by analyzing how many research publications deal with these types of harvesters and their hybrid derivatives. Moreover, both harvesters seem to be equally frequently chosen for hybridization purposes.

From the same table, it can be discerned that EMGs and ESGs that are based of MEMS are slowly being replaced by solid state NGs such as TENGs and PENGs because of the reliability issues and rigidity. EMGs and ESGs are quite often found in hybrid harvesters as an auxiliary unit while their use as a single harvester is less frequent. This can be expanded as a forecast that MEMS are going to be driven out of this field and solid-state single and hybrid harvesters are going to take their place. This does not mean that EMGs and ESGs are going to cease to exist, they will become more flexible, less dependent on actual MEMS structures and the energy generation is going to take place at nano-scale level, like using magnetized microneedles [91]. Thermoelectric and pyroelectric NGs tend to be hybridized with other NGs more frequently than any other NGs due to nature of the energy source and low power density they exhibit. BFCs are a good choice for specific biosensors, where chemical reactions may be chained in order to harvest energy, but this comes with the cost of manufacturing combined with short life span and low power density.

Looking at the various types of NGs, it is apparent that flexibility plays a major role during the design stage regardless of the chosen type. Due to inherent flexibility of the human body (skin, muscles, joint movements) and unique body structure of every individual, it is imperative to look at flexible materials such as elastomers, polymers, gels. A good description of the challenges of flexible and conductive materials was analyzed in recent works [125–127], where bioinspired by cuit cocoon structure significantly increased foldability of electrodes. In particular, foldability of electrodes was significantly increased by utilizing two principles: firstly, a rigid web structure of a raw cocoon is tough but reeling process forms fibers that can slide one against the other and the layers become separable in a cuit cocoon. Secondly while folding, the cuit cocoon bends into an ε -shape at the crease. These features of the cuit cocoon can be combined with other biological structures, such as leaves. For example, a cockscomb petal has a spring-like structure which allows it to be flexible in terms of compression and tensile and it can be also viewed as a membrane for attachment of substrates, [127]. Combined biological structures of the cuit cocoon and the cockscomb petal were used to design a super-foldable C/NiS nanofiber electrode. In another case [126], a Mimosa leaf structure was used to ensure scatheless foldability of electrodes by addition of cone-like arrays (bottom diameter was ~100 nm and top diameter was ~20 nm) on top of the C-fiber/FeOOH electrode.

A more general trend is emerging when the overall use of electronic sensors and electronics in general is expected to increase in the following years [128]. The same trend also correlates with the rising interest in the field of biosensors as a whole [129]. This in turn will increase the total energy consumption which can be balanced out with the use of energy harvesters. Therefore, the multi-disciplinary field of energy harvesting will highly likely experience even bigger influx of research articles and industry interest in the following years.

9. Conclusions

Continuous monitoring of biomarkers and reliable supply of energy to implantable bioelectronics are topics that are closely interrelated with energy harvesting. As this review indicated, there are numerous biosensors that are used in medical practice today that can be improved by integrating them with efficient energy harvesters.

The human body produces several types of energy such as biochemical, thermal and mechanical. Biomechanical energy is the largest and most well-refined energy type that is currently used for harvesting. The most prominent type of harvesters employed here are piezoelectric and triboelectric harvesters. Photovoltaic materials had also seen an increase in popularity in a form of wearable energy scavengers.

The main problem of energy harvesters is their low power density and there are two main design philosophies that try to solve this issue. It is possible to alternate material structure in nanoscale employing different manufacturing processes. This usually increases complexity of the material while improving its output parameters. Another way of maximizing the power output is through the hybridization of different harvesters in one compact structure. A resulting harvester offers a better output power at the cost of more complex external conditioning circuitry. Flexibility and foldability are important material properties and increasing research accumulates in order to accomplish this requirement.

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Abbreviations

BFC	Biofuel cell
EMG	Electromagnetic generators
ESG	Electrostatic generators
EWOD	Electrowetting on dielectric
ICD	Implantable cardioverter-defibrillators
IMD	Implantable medical devices
MEMS	Micro-electromechanical system
NG	Nanogenerator
OC	Open-circuit
PENG	Piezoelectric nanogenerator
PVDF	Polyvinylidene fluoride
PZT	Lead zirconate titanate
REWOD	Reverse electrowetting on dielectric
TENG	Triboelectric nanogenerator

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